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PHOTOGRAPHIC IMAGE TRANSFER SYSTEMS UTILIZING PROCESSING COMPOSITIONS CONTAINING HIGH VISCOSITY HYDROXYETHYL CELLULOSE

Filed April 22, 1964

Fig. 1

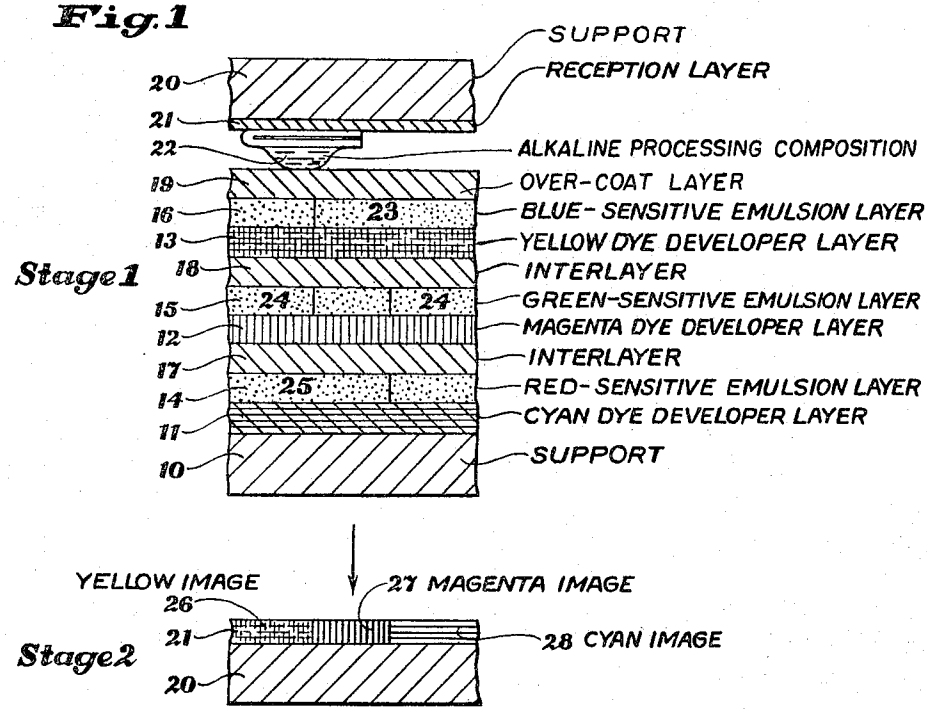
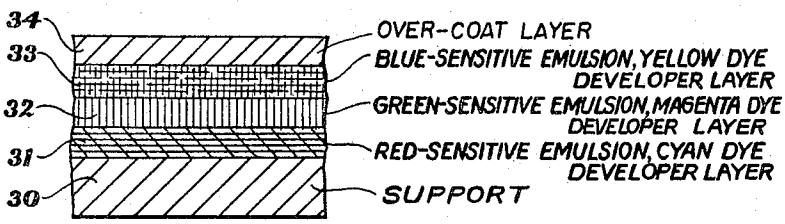


Fig. 2



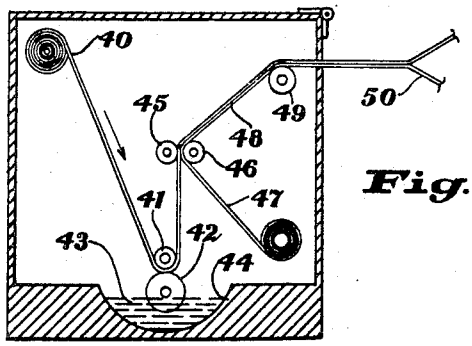


Fig. 3

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PHOTOGRAPHIC IMAGE TRANSFER SYSTEMS UTILIZING PROCESSING COMPOSITIONS CONTAINING HIGH VISCOSITY HYDROXYETHYL CELLULOSE

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This application is a continuation-in-part application of our application, Serial No. 77,666 filed December 22, 1960, now abandoned, which in turn is a continuation-in-part application of our application, Serial No. 50,962 filed August 20, 1960, now abandoned.

The present invention relates to the art of photography, and more particularly, to image transfer systems including systems 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 2,559,643, 2,647,049, 2,698,798, 2,774,668, 2,983,606, and British Patent 804,971, as well as elsewhere in the literature.

In the above described 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. It is thus possible to more easily control and uniformly spread the processing composition between the two surfaces in a predetermined area so that excess processing composition is not deposited to any great extent outside of the image area or on the processing equipment. A viscous processing composition permits an appreciable volume of the solution to be spread between the surfaces and this composition can contain the liquid and reagents required to bring about the chemical reaction and the diffusion of the dye developer images to the receiving layer. Also, the thickening agent serves to temporarily adhere

the emulsion surface to the surface of the receiving layer so that the two surfaces do not become displaced during the diffusion of the dye developer images to the receivng layer. However, the processing composition should not stick to the image receiving layer in sizable amounts after the receiving layer and the negative element are stripped apart. The thickening agent can also serve to delay the diffusion of the dye developers from the film until the alkali has diffused to the silver halide emulsions, development has been completed and the dye developers have been immobilized in the developed areas.

Such thickening agents as carboxymethyl cellulose and low or medium viscosity hydroxyethyl cellulose have not proven to be satisfactory in processing compositions for dye developer diffusion transfer processes. For example, when such thickening agents are used in sufficient concentrations to produce processing compositions of a desired viscosity that can be uniformly spread or coated, resulting dye transfer images were found to be of undesirably low density, and the processing composition was found to adhere to an undesirable degree to the dye image receiving elements.

It is accordingly an object of this invention to provide a novel viscous alkaline processing composition particularly adapted for use in photographic image transfer systems.

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

It is another object of this invention to provide a novel multicolor photographic dye developer diffusion transfer system particularly adapted for in-camera processing wherein alkaline processing composition is utilized in a rupturable container or pod.

It is likewise an object of this invention to provide a new photographic process for preparing dye developer transfer positive prints having high dye image density.

It is also an object of this invention to provide a new photographic dye developer diffusion transfer process utilizing a light-sensitive negative element, a superposed dye developer receiving sheet and an alkaline processing composition interposed between the negative element and the receiving sheet, the alkaline processing composition being a novel viscous composition that can be readily uniformly spread, which does not adhere in undesirable amounts to the receiving sheet when the receiving sheet is stripped apart from the negative element after the transfer of a positive dye developer image to the receiving sheet, and which does not adversely interfere with the image formation and transfer chemistry.

These and other objects of the invention are accomplished with alkaline processing compositions containing high viscosity hydroxyethyl cellulose. We have discovered that such viscous alkaline processing compositons have particular utility in activating or processing photographic elements containing at least one silver halide emulsion layer having a dye developer contiguous to the silver halide.

The hydroxyethyl cellulose utilized in the invention has a viscosity of more than about 10,000 cps., and more generally more than about 10,000 cps., to about 25,000 cps., in 2% solution in water at 25° C. Typical suitable hydroxyethyl cellulose materials are those prepared by hydroxyethylating a substantial portion of, and more generally more than one-half of, the hydroxyl groups of the cellulose molecule, the remaining hydroxyl groups of the

cellulose molecule being preferably substantially free or unsubstituted although minor proportions of other groups such as hydroxypropyl or the like can be present.

The processing compositions or activators of the invention are strongly alkaline. Such processing compositions are generally aqueous compositions having a pH of at least 12 or contain at least .01 N hydroxyl ion. Alkali metal hydroxides and carbonates such as sodium hydroxide and sodium carbonate are advantageously used in the processing compositions 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 transfer prints to leave no residue of alkali. Sufficient high viscosity hydroxyethyl cellulose is used in the processing composition to impart thereto a viscosity of at least about 5,000 cps. to greater than 100,000 cps., but more generally to about 200,000 cps. Concentrations of the hydroxyethyl cellulose of about 2% to 5% by weight based on the weight of the processing composition are more generally used. Also, the processing compositions can contain onium compounds, and which onium compounds cooperate with the hydroxyethyl cellulose to produce improved transfer images in dye developer diffusion transfer systems. Likewise, silver halide solvents and antifoggants can be used in the processing compositions.

Solution viscosities referred to herein are in Brookfield centipoise units determined at 25° C.

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, arylamido, 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, alkoxyl or halogen groups.

A useful class of dye developers is disclosed in Australian Patent 220,276 and German Patent 1,036,640, typical members of the class being listed below.

4-[p-(2′,5′-dihydroxyphenyl)-phenylazo] - 5 - acetamido-1-naphthol
4-[p-(2′,5′-dihydroxyphenethyl)-phenylazo] - 5 - benzamido-1-naphthol
1-phenyl-3-methyl-4 - [p - (2′,5′ - dihydroxyphenethyl)-phenylazo]-5-pyrazolone
2-[p-(2′,5′-dihydroxyphenethyl)-phenylazo]-4 - acetamido-1-naphthol
2-[p-(2′,5′-dihydroxyphenethyl)-phenylazo] - 4 - amino-1-naphthol
2-[p-(2′,5′-dihydroxyphenethyl)-phenylazo]-4 - methoxy-1-naphthol
2-[p-(2′,5′-dihydroxyphenethyl)-phenylazo] - 4 - ethoxy-1-naphthol
2-[p-(2′,5′-dihydroxyphenethyl)-phenylazo]-4 - n - propoxy-1-naphthol
1-phenyl-3-N-n-butyl-carboxamido-4-[p-(2′,5′ - dihydroxyphenethyl)-phenylazo]-5-pyrazolone
1-phenyl-3-N-n-hexylcarboxamido-4-[p-(2′,5′ - dihydroxyphenethyl)-phenylazo]-5-pyrazolone
1-phenyl-3-carbethoxy-4-[p-(2′,5′ - dihydroxyphenethyl)-phenylazo]-5-pyrazolone
2-[p-(2′,5′-dihydroxyphenethyl)-phenylazo] - 4 - isopropoxy-1-naphthol
1-phenyl-3-N-cyclohexylcarboxamido-4-[p - (2′,5′ - dihydroxyphenethyl)-phenylazo]-5-pyrazolone
1-phenyl-3-phenyl - 4 - [p - (2′,5′ - dihydroxyphenethyl)-phenylazo]-5-pyrazolone
2-4′-[p-(2″,5″ - dihydroxyphenethyl) - phenylazo] - α-naphthylazo-4-methoxy-1-naphthol
1-phenyl-3-amino-4-(4′-[p-(2″,5″ - dihydroxyphenethyl)-phenylazo]-2′,5′-diethoxyphenylazo)-5-pyrazolone
1-acetoxy-2-[p-(β-hydroquinonylethyl) - phenylazo] - 4-methoxy naphthalene
4-isobutoxy-2-[p-(β-hydroquinonylethyl)-phenylazo] - 1-naphthol
1-acetoxy-2-[p-(β-hydroquinonylethyl) - phenylazo] - 4-propoxy naphthalene
2-[p-(2′,5′-dihydroxy-4′-methylphenethyl) - phenylazo]-4-propoxy-1-naphthol
1-phenyl-3-[N-(β-ethylhexyl)-carboxamido]-4-[p-(β′-hydroquinonylethyl)-phenylazo]-5-pyrazolone
1-phenyl-3-(N-n-heptyl)-carboxamido-4-[p-(β-hydroquinonylethyl)-phenylazo]-5-pyrazolone
1-(o-carboxyphenyl)-3-phenyl-4-[p-(2,5-trifluoro acetoxy-β-phenylethyl)-phenylazo]-5-hydroxy pyrazole lactone
1-(o-carboxyphenyl)-3-N-phenylcarboxamido-4-[p-(β′-hydroquinonylethyl)-phenylazo]-5-hydroxypyrazole lactone

Another useful class of dye developers is disclosed by British Patent 804,971 and British Patent 804,973, several being listed below.

1,4-bis(2′,5′-dihydroxyanilino)-anthraquinone
1,5-bis(2′,5′-dihydroxyanilino)-4,8-dihydroxy-anthraquinone
1,4-bis[β-(3′,4′-dihydroxyphenyl)-ethylamino]-anthraquinone
1,4-bis[β-(2′,5′-dihydroxyphenyl)-isopropylamino]-anthraquinone
1,4-bis[β-(2′,5′-dihydroxyphenyl)-ethylamino]-anthraquinone
1-chloro-4-[β-(2′,5′-dihydroxyphenyl)-ethylamino]-anthraquinone
N-monobenzoyl-1,4-bis[β-(3′,4′-dihydroxyphenyl)-ethylamino]-anthraquinone
N-monobenzoyl-1,4-bis[β-(2′,5′-dihydroxyphenyl)-ethylamino]-anthraquinone
5,8-dihydroxy-1,4-bis[(β-hydroquinonyl-α-methyl)-ethylamino]-anthraquinone (Compound I)
1,4-bis[(β-hydroquinonyl-α-ethyl)-ethylamino]-anthraquinone
5-hydroxy-1,4-bis[(β-hydroquinonyl-α-methyl)-ethylamino]-anthraquinone
1-(β-hydroxy-α-ethyl-ethylamino)-4-(β-hydroquinonyl-α-methyl)-ethylamino-anthraquinone
1-(butanol-2′-amino)-5,8-dihydroxy-4-hydroquinonyl-isopropylamino-anthraquinone

Also useful are the following dye developers. Cyanurated dye developers such as 2-hydroquinoneamino-4-(p-phenylazo)-anilino-6-hydroxy-4-triazine described in Canadian Patent 579,038. Anthraquinone dye developers such as 1,4-bis(2′,5′-dihydroxyanilino)-anthraquinone and

1,4-diamino - N - (β - 2',5' - dihydroxyphenyl - α - methylethyl)-2,3-anthraquinone - dicarboximide. Amino-substituted anthraquinone dye developers such as prepared by reaction of 1-amino-4-(p-aminoanilino)-anthraquinone-2-sodium sulfonate with chloroacetamido hydroquinone monobenzoate. Dye developers obtained by reaction of 1-phenyl-3-amino-4-phenylazo-5-pyrazolone or 1,4-bis(β-aminoethylamino)-anthraquinone with homogentisic acid lactone or acid chloride, or gentisic acid chloride, e.g., 1-phenyl - 3 - (2',5' - dihydroxyphenylacetamido)-4-phenylazo-5-pyrazolone described in Canadian Patent 577,021. Naphthamide dye developer such as 1-(2,5-dimethoxyphenylazo) - 2 - hydroxy - N - (2',5'-dihydroxyphenyl)-3-naphthamide described in French Patent 1,168,292. Diazo dye developers such as 2-[p-(1-hydroxy-3,6-disulfo-8-amino - 2 - naphthylazo) - 3,3' - dimethoxybisphenyleneazo]-hydroquinone and 2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-phenylazo) - 1,8 - naphthalene diol-3,6-disulfonic acid. Arylazonaphthol dye developers, e.g., 1-amino-4-phenylazo-2-naphthol. Anthrapyridone dye developers, e.g., 1-acetyl-3-β-(2',5'-dihydroxyphenyl)-ethyl - 6 - β - (2',5'-dihydroxyphenyl)-ethylaminoanthrapyridone. Thiohydroquinolyl dye developers, e.g., 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-5-pyrazolone described in Belgian Patent 568,344. Ortho-coupled dye developers exhibiting limited sensitivity to changes of pH, e.g., 2-[p-(2'',5'' - dihydroxyphenoxy) - phenylazo] - 4 - methoxy-1-naphthol and 1-phenyl-3-methyl-4-[p-hydroquinolyl-sulfonyl)-phenylazo]-5-pyrazolone. Oxalyl ester dye developers, e.g., 1-phenyl-3-amino-4-[p-(2',5'-bis-ethoxalyloxyphenethyl)-phenylazo] - 5 - pyrazolone. Leuco compounds can also be used similarly, e.g., 1-phenyl-3-methyl-4-(2'-methyl - 4' - diethylamino)-anilino - 5 - pyrazolone, which do not exert a filtering action on underlying emulsion layers and which are immobilized in the developed regions, diffuse imagewise from undeveloped areas to the reception layer and are oxidized to colored images therein. Additional suitable dye developers are disclosed in Belgian Patent 554,935, British Patents 804,971, 804,974–5 and French Patent 1,168,292.

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. In preparing such dispersions of dye developers, high-boiling or substantially water-immiscible organic liquids having boiling points above about 175° C. are utilized. The high-boiling solvent can be used alone in dissolving the dye developer and in forming the dispersion or it can be mixed with a low-boiling organic solvent (e.g., boiling at least 25° C. below the boiling point of the higher boiling solvent), or a water-soluble organic solvent, as an auxiliary solvent to facilitate solution of the dye developer. A preferred range of proportions of high-boiling solvent to auxiliary is 1/0 to 1/10 on a weight basis. Such auxiliary solvents can be readily removed from the colloidal vehicle by air-drying a chilled, noodled dispersion or by continuous water washing. 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.

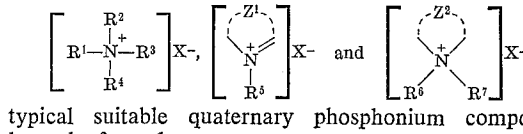
The dye developers are utilized contiguous to the silver halide of the photographic silver halide emulsion layers of the present photographic elements. Such dye developers can be incorporated directly in the silver halide emulsions or preferably positioned in a sublayer contiguous to each silver halide 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 below.

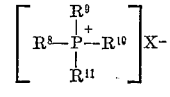
Phenylhydroquinone
2'-hydroxyphenylhydroquinone
Phenoxyhydroquinone
4'-methylphenylhydroquinone
1,4-dihydroxynaphthalene
2-(4-aminophenethyl)-5-bromohydroquinone
2-(4-aminophenethyl)-5-methylhydroquinone
4'-aminophenethylhydroquinone
2,5-dimethoxyhydroquinone
2,5-dibutoxyhydroquinone
m-Xylohydroquinone
Bromohydroquinone
3,6-dichlorohydroquinone
2-dimethylaminomethyltoluhydroquinone
2-cyclohexylhydroquinone
Sec. butylhydroquinone
2,5-dichlorohydroquinone
2,5-diisopropylhydroquinone
2,5-diiodohydroquinone
3-chlorotoluhydroquinone
Tetrachlorohydroquinone
2,5-diphenylhydroquinone
2,5-diresorcylhydroquinone
2,5-dioctylhydroquinone
Dodecylhydroquinone

In dye developer diffusion transfer systems, the hydroquinone derivative can be present in any of the layers of the light-sensitive or negative element such as in an overcoating layer, in a silver halide emulsion layer, in a dye developer layer, in an interlayer, or in the dye developer image reception sheet. The hydroquinone derivatives are preferably used in one or more layers of the light-sensitive element in quantities of the order of about 10 to 100 mg. or more per square foot. However, the quantity used can be widely varied and depends in part on the amount of silver halide in the emulsion layers.

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. The onium compounds can be used as hydroxides or as other types of salts. Typical suitable quaternary ammonium compounds have the formulas



typical suitable quaternary phosphonium compounds have the formula

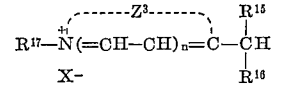


and typical suitable tertiary sulfonium compounds have the formula



In the above formulas: R^1 to R^{14} are each organic radicals such as alkyl radicals, aryl radicals, aralkyl radicals of the benzene series, and including substituted alkyl, aryl or aralkyl radicals, the alkyl chains generally being 1 to 18, and preferably 1 to 4, carbon atoms, and the aryl radicals preferably being phenyl; X is an anion including hydroxyl or an anion derived from an acid such as bromide, chloride, p-toluene sulfonate, perchlorate or the like; and Z^1 and Z^2 each represent the nonmetallic atoms necessary to complete a heterocyclic ring generally having 5 to 10, and preferably 5 or 6 atoms in the heterocyclic nucleus such as carbon, nitrogen, oxygen, selenium and sulfur atoms to form such heterocyclic rings as pyridine, quinoline, benzoquinoline, benzoxazole, benzoselenazole, thiazole, benzothiazole, piperidine, naphthothiazole, benzimidazole, naphthimidazole, naphthoxazole, naphthoselenazole, isoquinoline, pyrrole, pyrrolidine and the like, such heterocyclic rings being suitably substituted with such substituents as halogens, lower alkyl radicals and halo lower alkyl radicals.

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 quaternary ammonium compounds can be illustrated by the formula



wherein: X is an anion as described above, *n* is an integrer of 0 or 1, Z^3 represents the nonmetallic atoms necessary to complete a heterocyclic ring as described above for Z^1 and Z^2 but is preferably a pyridine ring, R^{15} and R^{16} are either hydrogen atoms or lower alkyl radicals having 1 to 4 carbon atoms, and R^{17} is an organic radical as described above for R^1 to R^{14}.

Typical onium compounds that can be utilized in the present invention are listed below.

1-benzyl-2-picolinium bromide
1-(3-bromopropyl)-2-picolinium-p-toluenesulfonate
1-phenethyl-2-picolinium bromide
1-γ-phenylpropyl-2-picolinium bromide
2,4-dimethyl-1-phenethylpyridinium bromide
2,6-dimethyl-1-phenethylpyridinium bromide
5-ethyl-2-methyl-1-phenethylpyridinium bromide
α-Picoline-β-naphthoylmethylbromide
1-β-phenylcarbamoyloxyethyl-2-picolinium bromide
Anhydro-1-(4-sulfobutyl)-2-picolinium hydroxide
2-ethyl-1-phenethylpyridinium bromide
1-[3-(N-pyridinium bromide)propyl]-2-picolinium-p-toluenesulfonate
1-methyl-2-picolinium-p-toluenesulfonate
1-phenethyl-2,4,6-trimethylpyridinium bromide
1-phenethyl-4-n-propylpyridinium bromide
4-γ-hydroxypropyl-1-phenethylpyridinium bromide
1-n-heptyl-2-picolinium bromide
2-isopropyl-1-phenethylpyridinium bromide
Tetraphenylammonium bromide
Tetraethylammonium bromide
N-ethylpyridinium bromide
N,N-diethylpiperidinium bromide
Ethylene-bis-pyridinium bromide
1-phenethyl-3-picolinium bromide
Cetyltrimethylammonium bromide
Polyethylene oxide bis-pyridinium perchlorate
3-methyl-2-ethylisoquinolium bromide
3-methylisoquinolinium methyl-p-toluenesulfonate
1-ethyl-2-methyl-3-phenethylbenzimidazolium bromide
5,6-dichloro-1-ethyl-2-methyl-3-(3-sulfobutyl)-benzimidazolium betaine
Lauryldimethylsulfonium-p-toluenesulfonate
Nonyldimethylsulfonium-p-toluenesulfonate
Octadimethylsulfonium-p-toluenesulfonate
Butyldimethylsulfonium bromide
Triethylsulfonium bromide
Dodecyldimethylsulfonium-p-toluenesulfonate
Decyldimethylsulfonium-p-toluenesulfonate
Phenyldimethylsulfonium bromide
Phenethyldimethylsulfonium bromide
Tetraethylphosphonium bromide
Ethylene-bis-oxymethyltriethylphosphonium bromide
Tetraphenylphosphonium bromide
Phenethyltrimethylphosphonium bromide

In dye developer diffusion transfer systems, the onium compounds are preferably utilized in the subject viscous 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.

The onium compounds can be used in a wide range of concentrations in dye developer diffusion transfer systems, optimum amounts varying with the particular onium compound. Typical useful amounts of the onium compounds in the alkaline processing compositions range from about 2% to 11% by weight of onium compound based on the weight of the processing composition.

When water-soluble silver halide solvents are employed in processing compositions used in dye developer transfer systems, particularly in conjunction with onium compounds and colorless hydroquinone derivatives as described above, further improvement in color quality results. Preferred silver halide solvents are thiosulfates such as sodium, potassium and ammonium thiosulfate. Other suitable silver halide solvents include thiocyanates, N,N - diethyl - 1,3 - propanediamine, triethanol amine, aminoethanol, ammonium hydroxide, and the like. Such silver halide solvents are preferably incorporated in the alkaline processing composition in amounts of about .8 to 2% by weight, although they can also be positioned in the reception layer for the dye images. Substantially no silver halide is transferred to the reception layers, and thus, the present process is to be distinguished from silver halide diffusion transfer processes.

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 bromoiodide, silver chloroiodide, silver chlorobromoiodide 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 systems, 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, immidized 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, 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.

Camera apparatus of the type useful for exposing and processing image diffusion transfer systems have been described, for example, in U.S. Patent 2,435,717. Such cameras permit successive exposure of individual frames of the photosensitive element as well as processing of exposed frames. With such cameras, the exposed portion of the photosensitive element is brought in superposed relation with a portion of an integral print receiving element with a container for alkaline processing material therebetween, the alkaline processing material containing high viscosity hydroxyethyl cellulose as described above. The film assembly is then drawn between a pair of pressure rollers which rupture the processing composition container and spread the alkaline processing composition between and in contact with the photosensitive element and the corresponding registered area of the print receiving element. The photosensitive element and print receiving element during the spreading of the container contents become formed into a combination wherein the photosensitive element and print receiving element are so superposed with respect to each other that the spread alkaline processing composition has access to both of the elements. This superposed relationship between the photosensitive and print receiving elements is maintained until the elements are stripped apart following the deposit on the print receiving element of the dye developer forming the final positive color image.

The processing of photographic elements in the present diffusion transfer process can also be effected in accordance with the invention outside of camera apparatus. A typical suitable processing means is illustrated by FIG. 3 of the drawing described hereinbelow.

In the accompanying drawing are shown in enlarged cross-sectional view representative elements and processing means 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 a 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 viscous alkaline processing composition **22** containing high viscosity hydroxyethyl cellulose and typically onium compounds 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 viscous 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 are also contemplated. 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-impervious 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** containing high viscosity hydroxyethyl cellulose as described above. 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 examples will serve to further illustrate the present invention.

EXAMPLE I

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-methyl)ethylamino]-anthraquinone, dissolved in N-n-butylactanilide, 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 diisopropylnaphthalene 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 bromoiodide (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'-dihydroxyphenethyl) - 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-butylactanilide. 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 diisopropylnaphthalene 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 bromoiodide (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 diisopropylnaphthalene 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 bromoiodide (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. The dispersion was prepared as follows:

Hydroquinone derivative dispersion D–1

PART A

4'-methylphenylhydroquinone	g	136
Methyl alcohol	ml	136
Di-n-butylphthalate	ml	272

Heat at 70° C. to dissolve, then cool to 40° C.

PART B

10% gelatin solution	g	1360
Water	ml	1360
Mucochloric acid (2.7% aqueous solution)	ml	136

Heat to 40° C.

Part A was slowly added to Part B with the aid of mechanical agitation. The solution obtained was then passed through a colloid mill five times. The colloid mill was then rinsed and the dispersion was adjusted to a weight of 3775 g., chill set and stored in a refrigerator. The coating composition for the overcoat layer (e.g., layer 19 of FIG. 1) was prepared as follows:

PART I

Dispersion D–1	g	3,775
Water	ml	2,225

Heat to 40° C.

PART II

10% gelatin solution	g	3,180
Water	ml	12,000
Mucochloric acid (2.7% aqueous solution)	ml	515

Heat to 40° C., adjust pH to 5.5.

Parts I and II were then combined and diluted with water to 22,700 ml. This solution was then coated.

Samples of the resultant element were exposed in an intensity scale sensitometer and wetted with various activators as described below in contact with Receiving Sheet A described below composed of a support and a reception layer. As a result, 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 colored positive image composed of dye images (e.g., images 26, 26 and 28 as shown in FIG. 1, Stage 2 of the drawing). The processing and transfer time was about 2 minutes at 70° F. The $D_{min.}$ and $D_{max.}$ values of the neutral scale were recorded using red, green and blue filters in the usual manner. These data are tabulated in Table I below as Tests 1 to 8. By comparing Tests 1, 3, 5 and 7 with Tests 2, 4, 6 and 8 respectively, it can be seen that high viscosity hydroxyethyl cellulose in the activators produces appreciably higher $D_{max.}$ in the green and blue scales than the common thickening agent, carboxymethyl cellulose.

TABLE I

Test	Activator	Receiving Sheet	Neutral Scale					
			D_{min}			D_{max}		
			Red	Green	Blue	Red	Green	Blue
1	XI	A	.16	.17	.23	1.83	1.12	1.37
2	II	A	.17	.20	.27	1.82	1.48	1.83
3	XIII	A	.14	.17	.29	1.68	1.02	1.33
4	VIII	A	.16	.20	.36	1.54	1.35	1.90
5	XIV	A	.16	.18	.33	1.73	1.02	1.31
6	IX	A	.16	.21	.41	1.65	1.40	1.95
7	XII	A	.17	.21	.43	1.51	0.89	1.29
8	X	A	.16	.21	.51	1.39	1.15	1.83

The activators referred to in the examples are aqueous compositions containing the following components on a weight basis:

Activator I—3.5% HEC [1]; 4.5% NaOH; 2.0% benzotriazole

Activator II—Activator I+2.0% 1-phenethyl-2-picolinium bromide

Activator III—Activator I+2.0% 1-benzyl-2-picolinium bromide

Activator IV—Activator III+1.0% sodium thiosulfate

Activator V—Activator II+1.0% 4'-methylphenylhydroquinone (MPHQ)

Activator VI—Activator I+1.0% sodium thiosulfate

Activator VII—3.5% HEC [1]; 4.5% NaOH; 2.0% 1-phenethyl-2-picolinium bromide

Activator VIII—Activator VII+0.2% 5-nitrobenzimidazole

Activator IX—Activator VII+0.2% benzimidazole

Activator X—Activator VII+0.2% imidazole

Activator XI—3.5% CMC [2]; 4.5% NaOH; 2.0% benzotriazole; 2.0% 1-phenethyl-2-picolinium bromide

Activator XII—Activator XI, but with 0.2% imidazole in place of the benzotriazole

Activator XIII—Activator XI but with 0.2% 5-nitrobenzimidazole in place of the benzotriazole

Activator XIV—Activator XI but with 0.2% benzimidazole in place of the benzotriazole

The receiving sheets referred to in the examples are of the following composition:

RECEIVING SHEET A

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).

[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.

[2] Carboxymethyl cellulose sold by Hercules Powder Co. as Type 70 and contains about 0.4 to 0.6 carboxymethyl cellulose groups per anhydroglucose unit of the cellulose.

RECEIVING SHEET B

A paper support carrying a gelatin (300 mg. per square foot) layer containing a mixture of poly-4-vinylpyridine (300 mg. per square foot), 1-phenyl-5-mercaptotetrazole (15 mg. per square foot) and 1-phenethyl-2-picolinium bromide (100 mg. per square foot).

EXAMPLE II

Samples of films were prepared in the manner as described in Example I and designated "Film A." Other films were prepared in the same manner except omitting the MPHQ from the over-coat layer and designated "Film B." Each of the films were then given filtered step tablet exposures in an intensity scale sensitometer and processed with Activators I, II and III using Receiving Sheets A or B as shown in Tests 9 to 16 of Table II below. From the D_{min} values of Tests 9 to 12 it can be seen that when the quaternary salt was in the activators or receiving sheet the minimum densities of the prints were reduced even in absence of MPHQ. From tests 13 to 16 it can be seen that MPHQ reduces the D_{min} but more so in the presence of the quaternary salt (Tests 14 to 16). Moreover, by visual examination of the color scales of Tests 13 to 16 it is clearly seen that less color contamination and more saturated colors were present in Tests 14 to 16.

TABLE II

Test	Film	Activator	Receiving Sheet	Neutral Scale					
				D_{min}			D_{max}		
				Red	Green	Blue	Red	Green	Blue
9	B	I	A	.69	1.15	1.72	1.61	1.91	2.11
10	B	II	A	.45	.55	1.76	1.61	1.58	1.78
11	B	III	A	.53	.68	2.00	1.79	1.90	2.29
12	B	I	B	.53	.89	2.32	1.76	1.97	2.36
13	A	I	A	.55	.69	.95	1.42	1.81	1.69
14	A	II	A	.32	.25	.26	1.71	1.79	2.05
15	A	III	A	.31	.28	.41	1.63	1.81	2.20
16	A	I	B	.20	.25	.53	1.68	1.99	2.49

EXAMPLE III

A. Effect of antifoggant in activator solution

The film of the type described in Example I and designated "Film C" was processed as described in Example I using Activators II and VII, the former containing HEC, 1-phenethyl-2-picolinium bromide and benzotriazole; the latter containing no benzotriazole. The results are shown in Table III, Tests 17 and 18. It is apparent from the D_{max} values that the antifoggant is instrumental in producing much greater maximum density. Moreover, the colors of the prints of Test 18 had much less color contamination and much less drop off (more saturation).

B. *Effect of hydroquinone derivative in film or activator*

Samples of films with and without the MPHQ in the over-coat layer and designated "Film A" and "Film B" as described in Example II were processed as described in Example I with Activators V and II giving the results shown in Tests 19 and 20 of Table III the D_{min} values of which show the improvement in minimum density when the film contains MPHQ. Inspection of the prints showed that Test 20 also had less color contamination and color drop off.

C. *Effect of silver halide solvent*

Samples of Film A and Film B described above were processed as described in Example I with Activators I, III, IV and VI and Receiving Sheets A and B with results shown in Tests 21 to 28 of Table III. In Tests 22 to 24, 26 to 28 the minimum densities were reduced since 1-benzyl-2-picolinium bromide and the thiosulfate were present. The prints also visually showed less color contamination and drop off. The prints of Tests 26 to 28, in particular, show much less color contamination and drop off since MPHQ was in the film.

In a similar manner the other hydroquinones can be utilized in the film, e.g., 4'-chlorophenyl hydroquinone, about 44 mg. per square foot; phenyl hydroquinone, about 28 mg. per square foot; phenoxy hydroquinone, about 40 mg. per square foot; 2,5-dioctyl hydroquinone, about 50 mg. per square foot.

As can be observed, high viscosity hydroxyethyl cellulose in alkaline processing compositions or activators cooperates with a wide variety of activator and film addenda utilized in diffusion transfer systems.

TABLE III

Test	Film	Activator	Receiving Sheet	Neutral Scale					
				D_{min}			D_{max}		
				Red	Green	Blue	Red	Green	Blue
17	C	VII	A	.19	.20	.41	1.58	1.13	1.55
18	C	II	A	.19	.20	.25	1.97	1.60	1.93
19	B	V	A	.59	.71	.86	1.60	1.94	2.19
20	A	II	A	.32	.25	.26	1.71	1.79	2.05
21	B	I	A	.69	1.15	1.72	1.61	1.91	2.11
22	B	III	A	.53	.68	2.00	1.79	1.90	2.29
23	B	IV	A	.51	.71	1.72	1.66	1.75	2.14
24	B	VI	B	.40	.67	1.51	1.547	1.85	2.42
25	A	I	A	.55	.69	.95	1.42	1.81	1.99
26	A	III	A	.31	.28	.41	1.63	1.81	2.20
27	A	IV	A	.27	.27	.35	1.59	1.74	2.09
28	A	VI	B	.19	.24	.42	1.53	1.83	2.31

EXAMPLE IV.—EFFECT OF VISCOSITY OF THE HYDROXYETHYL CELLULOSE

A film prepared as in Example I was processed using Receiving Sheet A as described in Example I utilizing aqueous Activators A to F, each activator containing 4.5% sodium hydroxide, 2% benzotriazole; 2.0% 1-benzyl-2-picolinium bromide and 0.8% sodium thiosulfate, by weight. In addition:

Activator A contained 4.5% high viscosity hydroxyethyl cellulose [1]

Activator B contained 3.5% high viscosity hydroxyethyl cellulose [1]

Activator C contained 2.5% high viscosity hydroxyethyl cellulose [1]

Activator D contained 10.0% medium viscosity hydroxyethyl cellulose [2]

Activator E contained 7.0% medium viscosity hydroxyethyl cellulose [2]

Activator F contained 4.5% medium viscosity hydroxyethyl cellulose [2]

[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 a 2% aqueous solution.

[2] Medium viscosity hydroxyethyl cellulose sold by Hercules Powder Co. as Natrosol 250 Type M having a viscosity of about 2,500 to 5,500 cps. at 25° C. as a 2% aqueous solution.

The relative viscosities of the above activators appeared to be in the following order:

$$A>D>B>E>C>F$$

Listed below are the neutral scale D_{min} and D_{max} values obtained from the prints processed through Activators A to F.

	D_{min}			D_{max}		
	Red	Green	Blue	Red	Green	Blue
Activator A	.18	.19	.25	1.71	1.61	2.05
Activator B	.19	.20	.25	1.97	1.86	2.30
Activator C	.21	.21	.26	2.29	2.00	2.49
Activator D	.17	.18	.21	.71	.84	1.25
Activator E	.18	.19	.23	1.30	1.22	1.72
Activator F	.21	.21	.25	1.86	1.59	2.15

Upon examination of these data it can be seen that when the same concentrations (4.5%) were used (*A* v. *F*), the densities obtained were similar; however, the minimal viscosity of Activator F allowed portions of the activator to disadvantageously adhere to the receiving sheet rather than producing a clean separation of the entire activator from the color-image bearing receiving sheet. These adhering portions of the activator when removed by wiping of the print produced areas of lowered densities or, when removed by swabbing the print under running water, areas of raised densities. The overall effect being that of a poor print exhibiting non-uniform density. When the results of using activators having comparable viscosities are compared, e.g., Activator D (10% medium viscosity hydroxyethyl cellulose) versus Activator B (3.5% high viscosity hydroxyethyl cellulose), the use of Activator D produced disadvantageously low maximum densities, i.e., 0.71, 0.84 and 1.25 compared to 1.97, 1.86, and 2.30 for Activator B. These data show therefore, in part, the reason for preference for use of high viscosity hydroxyethyl cellulose in alkaline processing compositions. Similarly, particularly high density diffusion or chemical transfer silver images can be prepared by methods of the type described by Rott in U.S. Patent No. 2,352,014 and utilizing alkaline processing compositions thickened with the high viscosity hydroxyethyl cellulose addenda described herein, medium viscosity hydroxyethyl cellulose addenda being substantially less effective.

EXAMPLE V

A single color photographic element was prepared by coating successively the following layers on a subbed cellulose acetate film support:

(1) *Magenta dye developer layer.*—A coating of the magenta dye developer, 2-[p-(2',5'-dihydroxyphenethyl)-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 diisopropylnaphthalene sulfonate. The resulting mixture was passed through a colloid mill several times, chill set, washed to remove the cyclohexanone, melted and thereafter coated.

(2) *Green-sensitive emulsion layer.*—A coating of a developing-out negative gelatino-silver bromoiodide (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.

(3) *Over-coat layer.*—A gelatin coating containing dispersed therein the colorless auxiliary developer, 4'-methylphenylhydroquinone, dissolved in di-n-butylphthalate at a coverage of 120 mg. of gelatin per square foot and 40 mg. of the 4'-methylphenylhydroquinone per square foot as described in Example I.

A series of samples of the resulting prepared film was exposed and processed with an aqueous alkaline processing composition and a receiving sheet as described in Example I except that the aqueous alkaline processing compositions or activators described below and referred to in Table IV were utilized. The various activators were aqueous solutions containing the following components as indicated, on a weight basis. The high and medium viscosity hydroxyethyl cellulose ("HEC") addenda utilized in the activators were those described in Example IV.

Activator G—4.5% high viscosity HEC, 4.5% NaOH, 2% benzotriazole, 0.8% sodium thiosulfate

Activator H—like Activator G except 3.5% high viscosity HEC used

Activator I—like Activator G except 2% high viscosity HEC used

Activator J—10% medium viscosity HEC, 4.5% NaOH, 2% benzotriazole, 0.8% sodium thiosulfate

Activator K—like Activator J except 4.5% medium viscosity HEC used

Activator L—like Activator J except 2% medium viscosity HEC used

Activator M—4.5% high viscosity HEC, 4.5% NaOH, 2% benzotriazole, 0.8% sodium thiosulfate, 2% 1-benzyl-2-picolinium bromide

Activator N—like Activator M except 3.5% high viscosity HEC used

Activator O—10% medium viscosity HEC, 4.5% NaOH, 2% benzotriazole, 0.8% sodium thiosulfate, 2% 1-benzyl-2-picolinium bromide

Activator P—like Activator O except 4.5% medium viscosity HEC used

The results of the tests with the various activators are summarized in Table IV below.

TABLE IV

Activator	Percent HEC	Type of HEC	Activator Viscosity, cps.	D_{max}
G	4.5	High viscosity	>100,000	1.88
H	3.5	do	>100,000	2.06
I	2.0	do	5,500	2.21
J	10.0	Medium viscosity	>100,000	1.04
K	4.5	do	5,000	[1] 2.02
L	2.0	do	105	[1] 2.30
M	4.5	High viscosity	>100,000	1.33
N	3.5	do	>100,000	1.56
O	10.0	Medium viscosity	>100,000	.84
P	4.5	do	5,000	[1] 1.65

[1] Activator non-uniformly spread and/or stuck to receiving sheet.

All of the activators utilizing the high viscosity hydroxyethyl cellulose (Activators G, H, I, M and N) readily uniformly spread between the negative elements or films and the receiving sheets, did not stick to the receiving sheets, and resulted in transfer prints having high magenta dye developer image D_{max} values. All of the activators utilizing the medium viscosity hydroxyethyl cellulose (Activators J, K, L, O and P) either non-uniformly spread between the negative elements or films and the receiving sheets during processing, stuck to the receiving sheet or resulted in transfer prints having low magenta dye developer image D_{max} values.

The present invention thus provides novel viscous alkaline photographic processing liquids that can be utilized for activating or initiating development of exposed silver halide in the presence of silver halide developing agents. Such processing liquids, as described above, are useful in processes for forming diffusion transfer prints wherein images from light-sensitive photographic elements containing at least one silver halide emulsion layer are allowed to diffuse to superposed receiving sheets for such images, processing liquid being positioned between the light-sensitive elements and the receiving sheets. Photographic products comprised of the light-sensitive element and the receiving sheet with the subject alkaline processing liquid in at least one pressure rupturable container positioned therebetween are useful photographic products that have particular utility for in-camera processing as described above.

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 utilizing in said alkaline liquid as a thickening agent hydroxyethyl cellulose having a viscosity of more than about 10,000 cps. in 2% solution in water at 25° C.

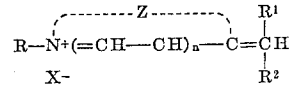
2. The process as described in claim 1 wherein the alkaline liquid contains an onium compound diffusible in the alkaline liquid.

3. The process as described in claim 1 wherein the alkaline liquid contains a silver halide solvent.

4. The process as described in claim 1 wherein the photographic element contains a substantially colorless and water-insoluble hydroquinone that is diffusible in the presence of the alkaline liquid.

5. 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 utilizing in said alkaline liquid as a thickening agent hydroxyethyl cellulose having a viscosity of more than about 10,000 cps. in 2% solution in water at 25° C.

6. 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 aqueous 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 utilizing in said alkaline liquid as a thickening agent hydroxyethyl cellulose having a viscosity of more than about 10,000 cps. in 2% solution in water at 25° C., and a heterocyclic quaternary ammonium compound capable of forming a diffusible methylene base in said alkaline liquid and having the formula



wherein:

a. n is an integer of 0 to 1,
b. Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus,
c. X is an anion,
d. R is selected from the group consisting of an alkyl radical, an aryl radical and an aralkyl radical, and
e. R^1 and R^2 are each selected from the group consisting of a hydrogen atom and a lower alkyl radical.

7. In the processing of an exposed photographic element comprising a support, superposed red, green and blue light-sensitive gelatino-silver halide emulsion layers, and a dye developer which is both a silver halide developing agent and a dye in a sublayer contiguous to each of the respective gelatino-silver halide emulsion layers, said processing being effected by treating said photographic element with a viscous aqueous alkaline liquid, developing latent images in the regions of exposure of the gelatino-silver halide emulsions and thereby immobilizing the dye developers in said regions of exposure, remaining dye developers in undeveloped regions corresponding to a positive image diffusing imagewise to the surface of said photographic element, and transferring the resulting diffused positive image in register to a dye developer receiving sheet superposed on said photographic element, the improvement which comprises using as a thickening agent for said alkaline liquid about 2% to 5% by weight based on the weight of the alkaline liquid of hydroxyethyl cellulose having a viscosity of more than about 10,000 cps. to 25,000 cps. in 2% solution in water at 25° C.

8. In the processing of an exposed photographic element comprising a support, superposed red, green and blue light-sensitive gelatino-silver bromoiodide emulsion layers, and a dye developer which is both a silver halide developing agent and a dye in a sublayer contiguous to each of the respective silver bromoiodide emulsion layers, said processing being effected by treating said photographic element with an aqueous alkaline liquid having a viscosity of at least about 5,000 cps. to 200,000 cps. at 25° C. and containing at least .01 N hydroxyl ion, developing latent images in the regions of exposure of the gelatino-silver bromoiodide emulsions and thereby immobilizing the dye developers in said regions of exposure, remaining dye developers in undeveloped regions corresponding to a positive image diffusing imagewise to the surface of said photographic element, and transferring the resulting diffused positive image in register to a dye developer receiving sheet superposed on said photographic element, the improvement which comprises using as a thickening agent for said alkaline liquid about 2% to 5% by weight based on the weight of the alkaline liquid of hydroxyethyl cellulose having a viscosity of more than about 10,000 cps. to 25,000 cps. in 2% solution in water at 25° C.

9. The process as described in claim 8 wherein the aqueous alkaline liquid contains an onium salt selected from the group consisting of 1-phenethyl-2-picolinium bromide and 1-benzyl-2-picolinium bromide, and the photographic element contains a hydroquinone selected from the group consisting of 4'-methylphenyl hydroquinone, 4'-chlorophenyl hydroquinone, phenyl hydroquinone, phenoxy hydroquinone and 2,5-dioctyl hydroquinone.

10. A viscous alkaline photographic processing liquid suitable for activating development of exposed silver halide in the presence of a silver halide developing agent, the improvement which comprises utilizing as a thickening agent for said processing liquid hydroxyethyl cellulose having a viscosity of more than about 10,000 cps. in 2% solution in water at 25° C.

11. An aqueous alkaline photographic processing liquid having a viscosity of at least about 5,000 cps. to 200,000 cps. at 25° C. and containing at least .01 N hydroxyl ion suitable for activating development of exposed silver halide in the presence of a silver halide developing agent, the improvement which comprises using as a thickening agent for said processing liquid about 2% to 5% by weight based on the weight of the alkaline liquid of hydroxyethyl cellulose having a viscosity of more than about 10,000 cps. to 25,000 cps. in 2% solution in water at 25° C.

12. An aqueous alkaline photographic processing liquid as described in claim 11 containing a heterocyclic quaternary ammonium compound diffusible in the processing liquid.

13. An aqueous alkaline photographic processing liquid as described in claim 11 containing a silver halide antifoggant.

14. A photographic product capable of forming diffusion transfer prints comprising a light-sensitive photographic element containing at least one silver halide emulsion layer, a receiving sheet for receiving images from said light-sensitive element superposed on said light-sensitive element, and an alkaline processing liquid in a pressure rupturable container positioned between said light-sensitive photographic element and said receiving sheet, the improvement which comprises utilizing in said alkaline processing liquid as a thickening agent hydroxyethyl cellulose having a viscosity of more than about 10,000 cps. in 2% solution in water at 25° C.

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