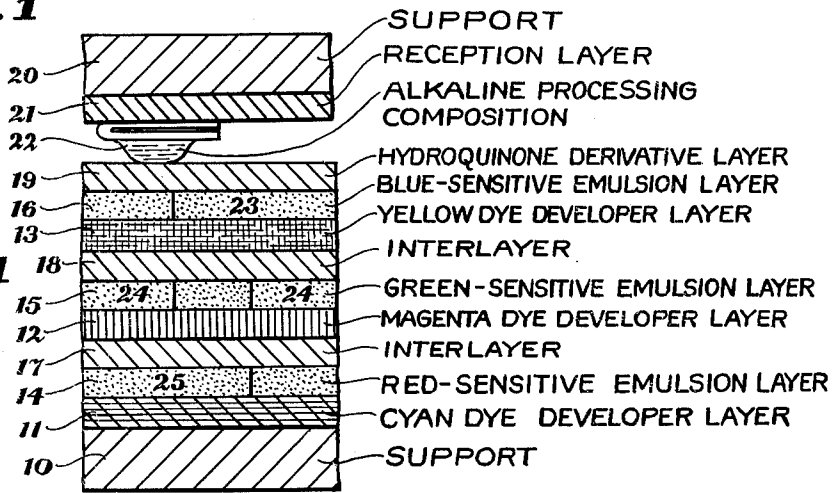


Oct. 19, 1965

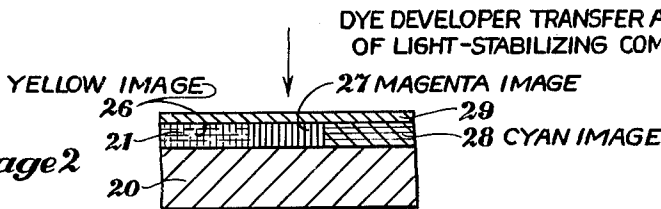
W. M. SALMINEN
PHOTOGRAPHIC MULTICOLOR DIFFUSION TRANSFER
PROCESS USING DYE DEVELOPERS
Filed March 27, 1961

3,212,893

Fig. 1



Stage 1



Stage 2

Fig. 2

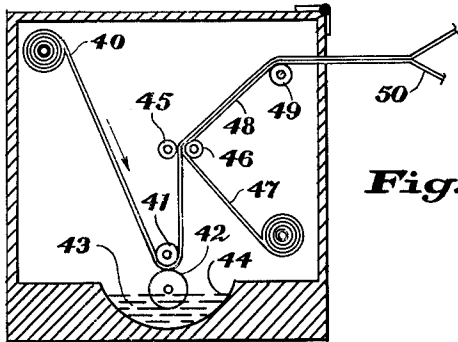
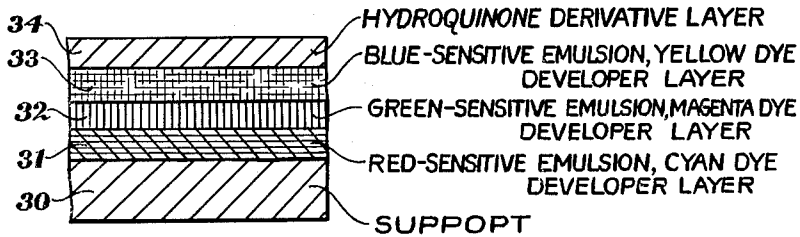


Fig. 3

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3,212,893

PHOTOGRAPHIC MULTICOLOR DIFFUSION TRANSFER PROCESS USING DYE DEVELOPERS

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Filed Mar. 27, 1961, Ser. No. 98,620

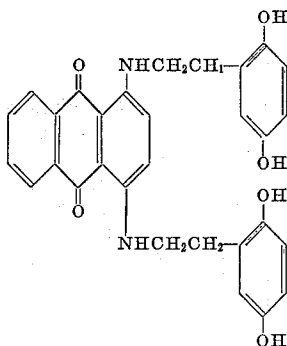
7 Claims. (Cl. 96—55)

This invention relates to the art of photography and more particularly to a multicolor diffusion transfer process in photography and materials adapted to use in the process.

A diffusion transfer color process has been described in a number of patents, including British Patent 804,971 published November 26, 1958, wherein photographic elements containing silver halide emulsion layers and layers containing diffusible dye developers (dyes having a silver halide developing function) are exposed to record the latent image in the silver halide and then treated with an alkaline processing composition which permeates the emulsion layers and layers containing the dye developers which then develop the latent images to silver images. At the same time oxidation products of the dye developers are formed in situ with the silver images and which are relatively non-diffusing in the colloid vehicle of the layers. The non-diffusing character of the oxidized dye developers is apparently due at least in part to a decrease in solubility in the alkaline processing liquid, and may also be due to a hardening effect of the oxidized developer upon the colloid vehicles of the layers which retards the diffusion of the oxidized dye developers. The residual unoxidized dye developers remaining in the layers in image-wise distribution are transferred by diffusion to a superposed reception element substantially to the exclusion of the silver image and oxidized dye developer to provide a positive dye image.

When an element containing differentially sensitized silver halide emulsion layers is used and subtractively colored dye developers are present in or contiguous to the respective emulsion layers, upon treatment with the processing liquid the dye developers are oxidized and rendered non-diffusing in the developed regions of the layers and the residual dye developer images in the positive regions are transferred by diffusion and in register to the reception element to provide a multicolor reproduction.

When the process is carried out with the typical cyan dye developers such as 1,4-bis[β-(2,5-dihydroxyphenyl)ethylamino]-anthraquinone.



this dye developer diffuses unchanged from the undeveloped areas of the sensitive element to the reception layer to provide the cyan dye image of a subtractive color sys-

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tem. The dye possesses light absorption properties such that it is well adapted to use with other dye developers providing the yellow and magenta color components of the color system. However, as in the case of the other dyes, this dye developer as well as other cyan, magenta and yellow dye developers mentioned below, is adversely affected by exposure to light, such as daylight, rich in ultraviolet radiations which either fade the dye developer or changes its color depending upon the particular dye developer. Naturally, the result is that the color prints are thrown out of color proportion to the length of time the prints are exposed to the source of ultraviolet radiations.

I have discovered that if the colored images composed of dye developers are treated with a mixture of polyvinyl alcohol and one or more of the following substances a very substantial improvement in light stability of the dye developer images synergistic in character is obtained, i.e. a mixture of either (1) polyvinyl alcohol with a monosaccharide or a disaccharide, (2) polyvinyl alcohol with a water soluble polymeric condensation product of dicyandiamide and formaldehyde or (3) polyvinyl alcohol with 3,3,5,5-tetrahydroxymethyltetrahydro-pyran-4-ol. Moreover, I have discovered that the stabilizing activity of these mixtures (1), (2) and (3) above is not confined to colored images composed of dye developers inasmuch as the conventional dye images obtained in color development by reaction of primary aromatic amino silver halide developing agents with phenolic couplers, 1-naphtholic couplers, 5-pyrazolone couplers and open-chain reactive methylene couplers containing the $-\text{CO}-\text{CH}_2-\text{CO}-$ group, are likewise rendered more stable to light. Similar results can be expected when other dye images are treated with the polyvinyl alcohol compositions (1), (2) and (3), such as dye images obtained in the well known silver dye bleach process wherein the dye images result from bleaching of azo and other dyes in regions of a developed silver image.

No substantial improvement in stability of the colored images is obtained if the dyes are transferred to a receiving layer containing a mixture of polyvinyl alcohol and one of the substances mentioned. It appears necessary to apply the mixtures containing polyvinyl alcohol to the surface of the dye print.

The light stabilizing effect obtained with polyvinyl alcohol in combination with the mentioned substances is a synergistic effect because none of the substance is nearly as effective as a stabilizer alone as it is in combination with polyvinyl alcohol. The cause of the stabilizing effect is not known. While these compounds, including polyvinyl alcohol, are characterized by containing methylol groups, similar compounds such as hexahydroxy cyclohexane also containing methylol groups are not nearly as effective in combination with polyvinyl alcohol.

Representative disaccharides are e.g. sucrose, lactose and maltose.

The monosaccharides include e.g. the hexoses and pentoses e.g. dextrose, sorbose, mannose, levulose (also called fructose), sorbitol, mannitol, arabinose, ribose, stereoisomers thereof, and oxidation products such as glucuronic acid.

The dicyandiamide-formaldehyde condensate may be prepared by well-known methods involving acid or alkaline condensation of dicyandiamide with formaldehyde until a water-soluble polymeric condensate is obtained.

The polyvinyl alcohol used (designated as PVA herein) is not especially critical and well-known types, e.g. polyvinyl alcohols obtained by acid or alkaline de-esterification of polyvinyl esters of varying viscosities can be used. Minor amounts of other polymeric units such as vinyl acetate or vinyl acetate units be present in the polyvinyl alcohol molecule but ordinarily substantially fully hydro-

lyzed polyvinyl esters are preferred. Commercially available polyvinyl alcohols can be used such as those sold under the tradename Elvanol, by the E. I. du Pont de Nemours and Co., Inc., e.g. Elvanol 71-30, a medium viscosity polyvinyl alcohol (99-100% hydrolyzed polyvinyl ester). Elvanol 52-22 (87-89% hydrolyzed) is not as useful in the invention presumably because of the relatively high residual polyvinyl ester content. Higher viscosity polyvinyl alcohols, e.g. Elvanol 72-60 (99-100% hydrolyzed) is useful but less preferred because 5% solutions are too viscous to use and lower concentrations, e.g. 2% do not deposit as much polymer on the print surface as is desired. Similarly, the low viscosity polyvinyl alcohols are useful but require use of rather high concentrations to obtain the best results. Suitable polyvinyl alcohols are readily prepared by acid or alkaline hydrolysis of medium viscosity polyvinyl esters, e.g. by alcoholysis of polyvinyl acetate using alcoholic alkali as is well known in the art.

One object of my invention is to provide the methods and materials for use in the preparing and stabilizing of dye images, particularly dye images composed of the dye developers. In the following description typical sensitive elements will be provided as well as processing solutions and processing variations which yield the most useful dye images, and reception elements adapted to receive the dye images transferred thereto by diffusion. Camera and processing equipment particularly adapted to providing the dye developer images will also be described.

In a typical process (shown in FIG. 1 of the drawings) for producing the dye developer images, and stabilizing the images, a sensitive element comprising a plurality of silver halide emulsion layers differentially light-sensitive (sensitive to different regions of the spectrum), having contiguous dyes developers which may be subtractively colored with respect to the sensitivity of the corresponding emulsion layer, and preferably contiguous hydroquinone derivatives, is exposed to a colored subject and processed by wetting with an alkaline processing solution such as one containing hydroxyethyl cellulose as a thickening agent, in contact with the reception layer and preferably with onium compounds, especially a quaternary ammonium salt, to develop the exposed silver halide in the emulsion layers and thereby render the dye developers non-diffusing in the regions of development, allowing the dye developers in the undeveloped regions to transfer imagewise by diffusion and in register to the reception layer to yield a multicolor dye developer image thereon, and stabilizing the image with the mentioned compositions.

In the accompanying drawings are shown in greatly enlarged cross-sectional view the appearance of representative elements employed in the mentioned typical process of the invention.

In FIG. 1 of the drawings the process is shown in flow-sheet form according to which in stage 1 the sensitive element comprises a support 10, layers 11, 12 and 13 containing subtractively colored alkali-soluble cyan, magenta and yellow dye developers, the light sensitive halide emulsion layers 14, 15 and 16 sensitive to red, green and blue light respectively, the interlayers 17 and 18 separating the green-sensitive emulsion and its contiguous subtractively colored magenta dye developer layer from the other layers and the overcoating layer 19 containing one of the hydroquinone compounds mentioned below. The reception element containing support 20 and reception layer 21 (which may contain the onium salt) is positioned so as to receive dye images transferring by diffusion from the sensitive element, with a rupturable container of alkaline processing solution 22 therebetween. Upon rupture of the container 22 as by means of passing the assembly between rollers in a camera so as to distribute the contents uniformly across a predetermined area of the sensitive element, the solution penetrates layer 19 dissolving the water-insoluble alkali-soluble and diffusible

hydroquinone derivative and transporting it to the underlying layers where the latent images in the silver halide of areas 23, 24 and 25 are developed to silver and the dye developers in the areas contiguous to areas 23, 24 and 25 each become immobilized and rendered non-diffusing. The unreacted dye developers of layers 11, 12 and 13 diffuse imagewise in register to the reception layer 21 and form the dye images thereof. Thereafter, a thin stratum 29 of the polyvinyl alcohol-containing light-stabilizing composition is applied to layer 21 to stabilize the dye developer images against the effects of light. The method of preparation of the described sensitive element and its use in the processes of the invention is described herein-after.

In FIG. 2 of the drawings is shown an element in which the dye developers are incorporated into the differentially sensitized emulsion layers 31, 32 and 33, and the hydroquinone derivative is present in the layer 34 outermost from the support. This element may likewise be used to provide the dye developer images to be stabilized in the manner of the invention.

In FIG. 3 of the drawings is shown in schematic form, a light-impervious enclosure useful for processing an exposed roll of film containing silver halide emulsions and dye developers so as to wet the film with alkaline activator solution and bring it into contact with a mordanted reception sheet for transfer of several multicolor dye developer images to the sheet. The resulting dye images can be stabilized in succession immediately after their diffusion to the receiving surface, or at a later time, e.g. by application of the stabilizing composition with the enclosure or after passage of the images out of the enclosure, as is desired.

In the mentioned process using the dye developers it has been discovered that partly due to the inefficiency of the dye developers as silver halide developing agents, the lack of discrimination of the dye developers for the silver halide they should develop, and other factors, when sensitive elements containing a plurality of differently sensitized silver halide emulsion layers and contiguous dye developers for subtractive color reproduction are used in the process the development products of one emulsion tend to effect the development of the other emulsions, the diffusion of a dye developer from a lower layer can be affected, i.e. be hindered, by a dye developer or other substance in an upper layer, the exhaustion of the processing solution by an outer layer may affect development of a lower layer and one layer may not develop to the extent of another layer, and particularly one dye developer may not be immobilized sufficiently to prevent it from transferring and causing color contamination of a dye image of another color. Also, a given dye developer may develop some grains of silver halide in the wrong emulsion layer with the result that an insufficient amount of that dye developer is available for transfer and the corresponding colors are unsaturated thus a magenta dye developer may develop some grains of red sensitive silver halide and become immobilized thus decreasing the magenta available to produce red colors which then appear unsaturated.

It has been mentioned that the onium compounds and certain hydroquinone derivatives are preferably used in formation of the dye developer images. These materials are employed to alleviate the mentioned disadvantageous characteristics of the process such as color contamination. It is believed that the onium compounds interact with the dye developers to form salts thereof and that the improvements in reduced "color contamination," "color drop off" and minimum density obtained by their use are at least due in part to the effect of such salt formation on the solubility and diffusibility of the dye developers. There is evidence that the onium compounds actually temporarily delay the migration of the dye developers so that the initial diffusion rates of the dye developers are

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reduced, yet more of the dye developers transfers from less exposed areas to increase the density. The beneficial effects of the hydroquinone derivatives include a decrease in "color contamination" of the dye developer prints which is apparently due to their effecting a more complete and uniform immobilization of the dye developers in the regions of development.

"Color contamination" usually appears in the prints as a degradation of one or more colors by one or more other colors and may be due to the failure of one or more dye developers to be immobilized sufficiently to prevent them from transferring from regions where they should have been immobilized. "Drop-off" appears as a degradation in color quality of the prints apparently caused by one dye developer developing silver halide grains in the wrong emulsion layer, e.g. the magenta dye developer developing some red sensitive silver halide grains with the result that more magenta dye developer is immobilized than should be and the red colors are deficient in magenta and are thus less saturated.

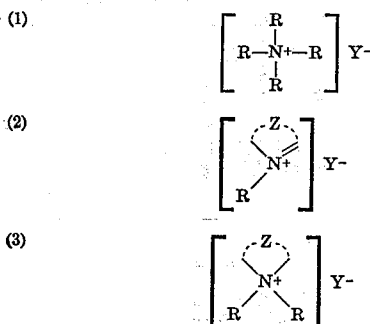
Onium compounds have been used in the photographic art for quite some time. For example, U.S. Patent No. 2,648,604 discloses the use of non-surface-active quaternary ammonium compounds as development accelerators and U.S. Patents Nos. 2,271,623, 2,271,622 and 2,275,727 disclose the use of quaternary ammonium, quaternary phosphonium and tertiary sulfonium compounds as sensitizers for silver halide emulsions. Notwithstanding the fact that such onium compounds have been previously used as sensitizers and as development accelerators, the mentioned results obtained by using onium compounds in conjunction with the dye developers in the diffusion-transfer processes of this invention are worthy of note. In the processes disclosed in the above-mentioned U.S. patents, there is an increase in silver density in the negative due to the use of the onium compounds; however, the increase in density in such processes takes place in the exposed areas of the negative and is attributable to the above-mentioned ability of the onium compounds to sensitize an emulsion or to accelerate development. In the present processes, when an increase in density is obtained it takes place in the positive image and is primarily the result of increased transfer of the dye developer from unexposed areas of the negative. The fact that the onium compounds would coact with dye developers to increase the transfer of such dye developers from unexposed areas of the negative in no way was expected from the prior use made of such compounds as sensitizers or development accelerators.

The fact that the onium compounds would also act, especially in the presence of the hydroquinone derivatives, to inhibit transfer of the oxidized dye developers from the exposed areas and thus improve the highlights, was similarly unexpected. This improvement in highlights is believed to be due to the ability of the onium compounds to control, especially in the exposed areas, the diffusibility of such dye developers.

Especially useful results have been obtained through the use of quaternary ammonium compounds. As is known, quaternary ammonium compounds are organic compounds containing a pentavalent nitrogen atom. Generally, they can be considered as derivatives of ammonium compounds wherein the four valences usually occupied by the hydrogen atoms are occupied by organic radicals. Generally, the organic radicals are joined directly to the pentavalent nitrogen through a single or double carbon-to-nitrogen bond. The term quaternary ammonium, as used herein, is intended to cover compounds wherein the pentavalent nitrogen is one of the nuclear atoms in a heterocyclic ring as well as those wherein each of the four vacancies is attached to separate organic radicals, e.g., tetraalkyl quaternary ammonium compounds. As illustrations of quaternary ammonium

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compounds, mention may be made of those represented by the following formulae:



wherein each R is an organic radical, Y is an anion, e.g., hydroxy, bromide, chloride, toluene sulfonate, etc., and Z represents the atoms necessary to complete a heterocyclic ring. As examples of compounds within Formulae 1, 2 and 3, mention may be made of tetraethylammonium bromide, N-ethylpyridinium bromide, N,N-diethylpiperidinium bromide, ethylene-bis-pyridinium bromide, 1-ethylpyridinium bromide, 1-phenethyl-3-picolinium bromide, tetraalkylammonium salts, cetyltrimethylammonium bromide, polyalkylene oxide bis-quaternary ammonium salts such as polyethylene oxide bis-pyridinium perchlorate, the heterocyclic quaternary ammonium salts mentioned which form the methylene bases including 3-methyl-2-ethylisoquinolinium 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 and the pyridinium salts below.

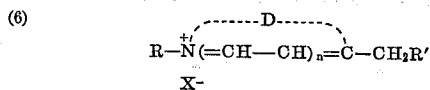
The tertiary sulfonium and quaternary phosphonium compounds may be represented by the formulae:



wherein each R is an organic radical, e.g., alkyl, aralkyl, aryl, etc. groups, and X is an anion, e.g., hydroxy, bromide, chloride, toluene sulfonate, etc. As examples of tertiary sulfonium and quaternary phosphonium compounds, mention may be made of lauryldimethylsulfonium p-toluene-sulfonate, nonyl-dimethyl sulfonium p-toluene sulfonate and octyldimethylsulfonium p-toluene sulfonate, butyldimethylsulfonium bromide, triethylsulfonium bromide, tetraethylphosphonium bromide, dimethylsulfonium p-toluene sulfonate dodecyldimethylsulfonium p-toluene sulfonate, decyldimethylsulfonium p-toluene sulfonate and ethylene-bis-oxyethyltriethylphosphonium bromide.

The onium compounds may be used as the hydroxide or as the salt. When the onium compounds are used as the salt, the anion may be a derivative of any acid. However, it should be noted that when the anion is iodide, such iodide may have deleterious effects on the emulsion and suitable precautions should be taken. Especially good results were obtained when the onium compounds were employed as the bromide.

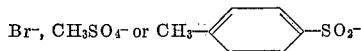
The particularly efficacious heterocyclic quaternary ammonium compounds which form the methylene bases diffusible in alkaline solution have the general formula



wherein D represents the non-metallic atoms necessary to complete the heterocyclic nucleus of the quaternary ammonium compound containing 1 or more of the reactive methyl groups $-CH_2R'$ in one or more of the nuclear positions, the other nuclear positions being substituted or

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not, such as quaternary salts of the pyridine, quinoline, benzoquinoline, benzoxazole, benzoselenazole, thiazole, benzothiazole, naphthothiazole, benzimidazole, isoquinoline series, etc., n is 0 or 1, R is an alkyl group, an aryl or aralkyl group of the benzene series, or substituted alkyl, aryl or aralkyl groups of the benzene series, the alkyl chains preferably being lower alkyl of from 1 to 4 carbon atoms, R' is a hydrogen atom or one of the groups represented by R, and X represents OH⁻ or an acid anion such as



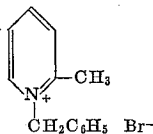
One or more of these quaternary ammonium compounds can be used alone or in combination with the onium compounds having the Formulae 1, 2, 3, 4 and 5 above, and are advantageously employed in either the processing solution, the reception element, or both, and less desirably in the light-sensitive element per se, to improve the print quality by a mechanism not fully understood. When the hydroquinone derivatives are also present a co-action with the quaternary compound takes place such that a greatly improved effect is obtained distinguishable from the effect of either the hydroquinone derivative or the quaternary compound. The dye prints obtained exhibit appreciably less color contamination and improved color saturation, density and contrast.

The onium compounds can be used in varying amounts depending upon the particular compound. When used in the alkaline processing solution, useful results can be obtained with from about 0.2 to 15% of onium compound. In some cases about 0.2 to 3% is best. Similarly, the amount used in the sensitive element and receiving sheet will vary with the onium compound selected.

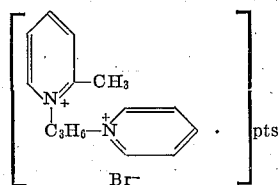
The quaternary ammonium compounds comprising a preferred embodiment of the invention are pyridinium salts which form the diffusible methylene bases and which have the above Formula 6, the pyridinium nucleus being substituted with from 1 to 3 active methyl groups —CH₂R' present in at least one of the 2, 4 or 6 positions, e.g. a lower alkyl group such as methyl, ethyl, propyl or substituted lower alkyl groups such as hydroxyalkyl, e.g. hydroxyethyl, which alkyl groups act as methylene base precursors. Positions 3 and 5 may or may not be substituted with e.g. halogen, lower alkyl and haloalkyl groups such as chlorine, methyl, ethyl, propyl or chloroethyl groups.

Typical salts having the above Formula 6 are as follows:

1-benzyl-2-picolinium bromide

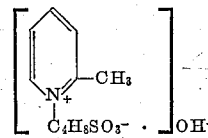


- 1-(3-bromopropyl)-2-picolinium-p-toluenesulfonate
- 1-phenethyl-2-picolinium bromide
- 1-γ-phenylpropyl-2-picolinium bromide
- 2,4-dimethyl-1-phenethylpyridinium bromide
- 2,6-dimethyl-1-phenethylpyridinium bromide
- 5-ethyl-2-methyl-1-phenethylpyridinium bromide
- 2-ethyl-1-phenethylpyridinium bromide
- 1-[3-(N-pyridinium bromide)propyl]-2-picolinium-p-toluene sulfonate

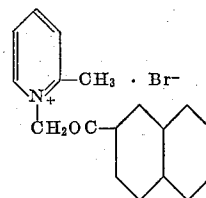


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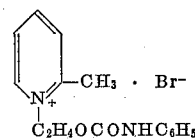
Anhydro-1-(4-sulfobutyl)-2-picolinium hydroxide



α-picoline-β-naphthoilmethylbromide



1-β-phenylcarbamoyloxyethyl-2-picolinium bromide



- 1-methyl-2-picolinium pts
- 1-phenethyl-2,4,6-trimethylpyridinium bromide
- 1-phenethyl-4-n-propylpyridinium bromide
- 4-γ-hydroxypropyl-1-phenethylpyridinium bromide and
- 1-n-heptyl-2-picolinium bromide

A number of pyridinium salts having the above general formula do not form methylene bases sufficiently diffusible in alkaline solution to be of practical use in the process e.g.

- 1-n-decyl-2-picolinium bromide
- 1,2-dibenzyl pyridinium bromide
- 6-amino-1-phenethyl-2-picolinium bromide
- 2-amino-1-phenethyl-4-picolinium bromide
- 2-benzyl-1-phenethyl pyridinium bromide
- 4-benzyl-1-phenethyl pyridinium bromide

The following which do not form methylene bases in alkali solutions are also less useful.

- 45 1-phenethyl pyridinium bromide
- 1-ethyl pyridinium bromide
- 1-phenethyl-3-picolinium bromide
- 1-n-nonylpyridinium pts

The hydroquinones which have the requisite properties are substantially colorless, substantially water-insoluble, and soluble and diffusible in alkaline solution through organic colloid layers such as gelatin and are exemplified by the following

- 55 Phenylhydroquinone
- 2'-hydroxyphenylhydroquinone
- Phenoxyhydroquinone
- 4'-methylphenylhydroquinone
- 1,4-dihydroxynaphthalene
- 60 2-(4-aminophenethyl)-5-bromohydroquinone
- 2-(4-aminophenethyl)-5-methylhydroquinone
- 4'-aminophenethylhydroquinone
- 2,5-dimethoxyhydroquinone
- 2,5-dibutoxyhydroquinone
- 65 m-Xylohydroquinone
- Bromohydroquinone
- 3,6-dichlorohydroquinone
- 2-dimethylaminomethyltoluhydroquinone
- 2-cyclohexylhydroquinone
- 70 Sec. butylhydroquinone
- 2,5-dichlorohydroquinone
- 2,5-diisopropylhydroquinone
- 2,5-diiodohydroquinone
- 3-chlorotoluhydroquinone
- 75 Tetrachlorohydroquinone

2,5-diphenylhydroquinone
2,5-diresorcylohydroquinone
2,5-dioctylhydroquinone
Dodecylhydroquinone

The useful hydroquinone derivatives are particularly distinguished from the dye developers containing hydroquinonyl moieties mentioned hereinafter, in being substantially colorless and therefore do not impart any color to the print.

The processes of the invention are thus carried out with the silver halide emulsions and dye developers preferably in contiguity with both the quaternary ammonium salts and the hydroquinone derivatives. That is, the quaternary salt may be present in either or both the alkaline processing fluid, the reception sheet, less desirably in the sensitive element, and the hydroquinone derivative in any of the layers of sensitive element such as an overcoating layer, emulsion layer, dye developer layer, an interlayer, or in the reception sheet. Thus, the reception sheet or reception layer may be composed of a mordant for the dye developers such as mentioned below, e.g., poly-4-vinylpyridine and in addition may contain at least one of the hydroquinone derivatives above. Similarly, the reception layer or sheet may contain the combination of a mordant for the dye developers, at least one of the hydroquinone derivatives and at least one of the onium compounds mentioned, particularly the heterocyclic quaternary ammonium compounds forming the methylene bases. For some purposes the hydroquinone derivatives may be present in the processing fluid containing the hydroxyethyl cellulose; however, in the present invention use in the fluid is much less desirable since the hydroquinone derivatives are unstable in such solutions and readily undergo oxidation accompanied by discoloration of the prints, unless prepared and stored in absence of air or other precautions are taken to prevent oxidation.

The hydroquinone derivatives used as described, are preferably incorporated into emulsion layers, overcoating, interlayers or other layers, as dispersions in the hydrophilic organic colloid vehicle of the layer. The hydroquinone derivatives may be dissolved in alkaline solution and precipitated into aqueous gelatin solutions by raising the acidity of the solution. However, this is a less desirable procedure because of the instability of the compounds in alkaline solution. The hydroquinone derivatives may be dissolved in a solvent, such as a lower alcohol, and precipitated into aqueous gelatin solutions for coating on the sensitive element. They may be added to gelatin solutions which are ball-milled to reduce the crystal size. However, the hydroquinones are preferably dissolved in a low molecular weight water-insoluble organic crystalloidal solvent permeable to the alkaline processing solutions and having a boiling point above about 175° C. such as dibutyl phthalate and added to an aqueous gelatin solution which is passed through a colloid mill until the desired degree of subdivision has been attained. An auxiliary organic solvent can also be used such as one having a solubility in water greater than that of the crystalloidal solvent, of the order of at least about 2 parts per 100 parts of water. Thus the auxiliary organic solvent can be washed from a chilled gelatin dispersion in the presence of the other solvent. The auxiliary solvent may be one having a boiling point at least about 25° C. lower than the crystalloidal solvent in order that it can be removed by volatilization during the drying of a coating to leave the hydroquinone derivative dispersed in only the crystalloidal solvent. As a result, the hydroquinone derivatives are quickly and uniformly dissolved by the alkaline processing composition and transported throughout the sensitive element to produce more uniform development than when the hydroquinone derivatives are incorporated into the element by other means.

The hydroquinone derivatives may be used in one or more layers of the sensitive element in quantities of the order of from about 10 to 100 mgs. or more per square

foot. However, the quantity used depends in part upon the amount of silver halide, the layer in which it is contained, the amount of dye developer and the amount of pyridinium salt in the sensitive element or processing solution of reception element. In some instances it may be desirable to form a complex of the hydroquinone derivatives by reaction with sulfur dioxide in a well-known manner and to incorporate the complex in the overcoating layer, outer emulsion or other layer of the sensitive element. These hydroquinone-sulfur dioxide complexes tend to be more stable than the hydroquinone derivatives themselves.

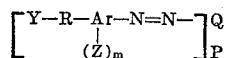
The dye developers which are used in the emulsion layers or in layers adjacent to the emulsion layers are compounds which are both a silver halide developing agent and a dye. They are characterized by being relatively non-diffusible in the colloid layers at a neutral pH but diffusible in the layers in the presence of the alkaline processing solutions. For the most part the dye developers are insoluble in water per se, which property usually necessitates the use of organic solvents to incorporate the dye developers into the organic colloid layers of the sensitive elements. Otherwise, the solubility of the dye developers is not particularly important and so long as the dye developers are capable of being immobilized in the layers in the presence of the alkaline processing solution and they are transferrable to the reception element, they are useful in the process of the invention. The dye developers are particularly characterized by containing both a chromophore moiety and at least one moiety such as a hydroquinonyl radical having a silver halide developing agent function and which radical imparts silver halide development activity to the dye developer molecule as a whole with the result that during development of a silver halide image, the dye developers are oxidized to less diffusible compounds in the region of exposure and development and the residual dye developers in the undeveloped regions are transported imagewise to mordanted reception layers to provide a dye image thereon. The dye developers of course should not have a desensitizing action toward silver halide emulsions.

Representative dye developers of use in the sensitive elements of the invention have the general formula

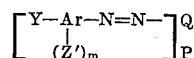


in which M is an aromatic or heterocyclic ring or ring system such as a benzene, naphthalene, tetralin, anthracene, anthraquinone, pyrazole, quinoline, etc., ring and may also be substituted, as by hydroxyl amino, keto, nitro, alkoxy, aryloxy, acyl, alkylamido, arylamido, alkyl, aryl, carboxamido, sulfonamido, 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 may be substituted with amino, alkylamino, alkyl, hydroxyl, alkoxy or halogen groups.

A very useful type of dye developers disclosed in Australian Patent 220,279 accepted December 17, 1958, and German Patent 1,036,640, August 14, 1958 have the general formula



and



wherein P=1 or 2; R=an alkylene group of from 1 to 5 carbon atoms; Ar=an aryl group of the benzene or naphthalene series; each Z=a lower alkyl group such as methyl or ethyl, or halogen e.g. chlorine; Z'=a lower alkoxy group such as methoxy or ethoxy, halogen or lower alkyl group; m=0, 1 or 2; Y=a 2,5- or 2,3- or 3,4-dihydroxyphenyl group which may be substituted by alkyl or halogen groups; Q=the residue of a coupling component such

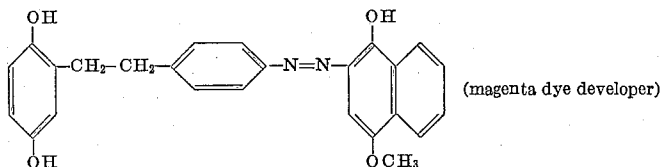
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as a phenol, naphthol, 5-pyrazolone or open chain reaction methylene coupler containing the group



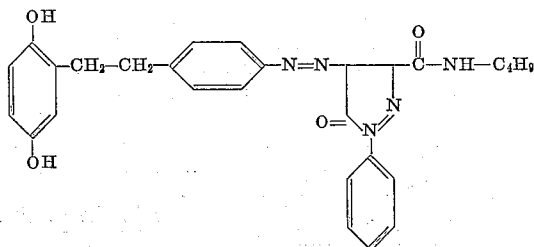
for example:

- 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

(Compound II)

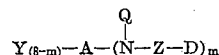


- 1-phenyl-3 - N-n-butyl-carboxamido - 4 - [p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone.
 1-phenyl-3-N-n-hexylcarboxamido-4 - [p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone (Compound III).
 1-phenyl-3-carbomethoxy-4-[p-(2',5' - dihydroxyphenethyl)-phenylazo]-5-pyrazolone.
 2-[p-(2',5' - 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 '-

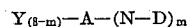
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hydroquinonylethyl)-phenylazo] - 5 - hydroxypyrazole lactone.

- Another class of dye developers disclosed by British Patent 804,971, November 26, 1958, and British Patent 804,973, November 26, 1958 have the general formula

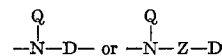


or



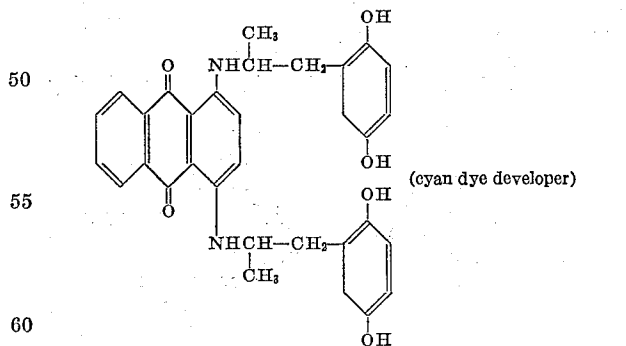
- wherein A represents an anthraquinone nucleus, D represents an organic radical having a developing function and containing an aryl nucleus such as benzene or naphthalene nuclei, substituted by at least two substituents selected from hydroxyl, amino and substituted amino groups so

that the resulting compound is capable of developing exposed silver halide, Q represents a hydrogen atom or an alkyl group or, when the substituents on the aryl nucleus of D are hydroxyl groups, Q may also be an acyl group, which may be aliphatic, e.g., acetyl or aromatic, e.g. benzoyl, Z is a bivalent organic radical containing at least one methylene ($-\text{CH}_2-$) group, m is a positive integer less than 5 and each Y may be a hydrogen or halogen atom or an amino, alkyl, aryl, nitro, alkylamino, arylamino, aryloxy, alkoxy, hydroxyl, sulphonamido, carboxamido, carboxy, sulpho,



group.

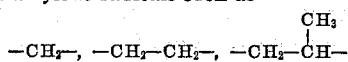
Examples of these dye developers are 1,4-bis(2',5'-dihydroxyanilino)-anthraquinone, 1,5-bis-(2',5'-dihydroxyanilino) - 4,8 - dihydroxy-anthraquinone, 1,4-bis[β -(3',4' - dihydroxyphenyl) - ethylamino]-anthraquinone,



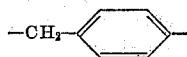
- 1,4-bis[β -(2',5' - dihydroxyphenyl) - isopropylamino]-anthraquinone,
 1,4-bis[β -(2',5' - dihydroxyphenyl) - ethylamino]-anthraquinone,
 1-chloro-4-[β -(2',5' - dihydroxyphenyl) - ethylamino]-anthraquinone,
 N-monobenzoyl-1,4-bis[β -(3',4'-dihydroxyphenyl) - ethylamino]-anthraquinone,
 N-monobenzoyl-1,4-bis[β -(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)-ethyl-amino]-anthraquinone;
 1-(β -hydroxy- α -ethyl-ethylamino) - 4 - β -hydroquinonyl- α -methylethylamino-anthraquinone and
 1-(butanol-2'-amino)-5,8-dihydroxy - 4 - hydroquinonyl-isopropylamino-anthraquinone.

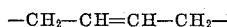
In the formulas above the expression bivalent organic radical Z refers to organic radicals having the two free valences attached to different atoms. As examples of such suitable bivalent organic radicals, mention may be made of alkylene radicals such as



as well as bivalent radicals such as



It is also intended that Z may be saturated, unsaturated, such as



or substituted, such as chloroalkylene or hydroxyalkylene. Where Z is an alkylene group, best results are obtained by the use of a lower alkylene group, e.g. an alkylene group, containing less than about six carbons, and preferably an ethylene ($-\text{CH}_2\text{CH}_2-$) group. Alkylene groups containing more carbon atoms may be used, however, providing that the resulting dye developer is capable of being dissolved in the liquid processing composition described herein, and its oxidation product rendered immobile in the developed emulsion layer.

Acylation of amino-nitrogen atoms which are part of the chromophoric system has the effect of shifting the visible absorption band of the compound toward higher frequencies (shorter wavelengths). Thus, acylating one amino-nitrogen of the cyan, 1,4-bis-[(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone changes its color to a magenta, and acylating both the amino-nitrogen atoms changes its color to an orange-yellow. Similarly the acylation of hydroxyl groups of the above types of dye developers can be expected to shift the color of the dye developers. Thus, the dye developers may undergo a change in structure and/or color during the development reaction, for example through hydrolysis, and the dye which is transferred may have a color different than that of the dye developer originally present in the sensitive element.

Additional dye developers are disclosed in Belgium Patent 554,935, British Patents 804,971, 804,973-5 and French Patent No. 1,168,292.

The following dye developers are also useful in the sensitive elements and processes of the invention:

Cyanurated dye developers such as 2-hydroquinone-amino-4-(p-phenylazo)anilino-6-hydroxy-4-triazine (Canadian Patent No. 579,038).

Anthraquinone dye developers such as 1,4-bis-(2',5'-dihydroxyanilino)-anthraquinone and 1,4 - diamino-N-(β -2',5'-dihydroxyphenyl- α -methyl - ethyl) - 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 -aminoethyl-amino)-anthraquinone with homogentisic acid lactone or acid chloride, or gentisic acid chloride e.g. 1-phenyl-3-(2',5'-dihydroxyphenylacetamido)-4-phenylazo - 5-pyrazolone (Blout et al. Canadian Patent 577,021 dated June 2, 1959).

Naphthamide dye developer such as 1-(2,5-dimethoxyphenylazo)-2-hydroxy - N - (2',5' - dihydroxyphenyl)-3-naphthamide (French Patent 1,168,292 dated August 25, 1958).

Disazo dye developers such as 2-[p-(1-hydroxy-3,6-di-

sulfo-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.

5 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.

10 Thiohydroquinoly dye developers, e.g. 1 - phenyl-3-methyl-4-[p-(2',5' - dihydroxyphenylthioethyl) - phenylazo]-5-pyrazoline (Belgium Patent 568,344).

Ortho coupled dye developers exhibiting limited sensitivity to changes of pH e.g. 2-(p-[2'',5''-dihydroxyphenoxyl]phenylazo)-4-methoxy-1-naphthol and 1-phenyl-3-methyl-4-[p-hydroquinolylsulfonyl] - phenylazo] - 5-pyrazolone.

15 Oxalyl ester dye developers, e.g. 1-phenyl-3-amino-4-[p-(2',5'-bis-ethoxalylloxyphenethyl) - phenylazo] - 5-pyrazolone.

20 Leuco compounds may 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.

The dye developers may be incorporated into the emulsion layers or into the layers thereunder by several methods. For example, the dye developers may be dissolved in organic solvents and precipitated into gelatin solution or the dye developers may be ball-milled in gelatin solutions to reduce their particle size. However, particularly favorable results are obtained when the hydroquinone derivatives of the invention are present in one or more of the layers of the sensitive element and the dye developers have been incorporated into the gelatin layers under the emulsion layers (as shown in FIG. 1) by dissolving the dye developers in high boiling solvents such as ditetrahydrofurfuryl adipate or 2-(2-butoxyethoxy)ethyl acetate and milling the mixture in gelatin solution in a colloid mill. When high boiling solvents having low solvent activity for the dye developers, such as dibutyl phthalate, are used it is desirable to dissolve the dye developer in a mixture of the high boiling solvent and a low boiling solvent such as cyclohexanone, methanol, etc., which evaporates readily from the coatings during the subsequent drying operation. Many of the dye developers can be used with the high boiling solvents (in absence of low boiling solvents) such as the following:

- Ditetrahydrofurfuryl phthalate
- β -Methoxyethyl phthalate
- Ethyl N,N-di-n-butylcarbamate
- 55 Guaiacol acetate (o-methoxyphenyl acetate)
- Tetrahydrofurfuryl propionate
- Triethyl citrate
- Acetyl triethyl citrate
- Tricresyl phosphate
- 60 Tri-p-tert.butylphenyl phosphate
- Triethylphosphate
- Tri-n-butylphosphate
- Triphenylphosphate
- Isoamyl acetate
- 65 Ditetrahydrofurfuryl succinate
- Methyl acetate
- Ditetrahydrofurfuryl adipate
- Tetrahydrofurfuryl benzoate
- N-n-amyolphthalimide
- 70 Ethyl N,N-di-n-butylcarbamate
- Diethyl lauramide
- Dibutyl lauramide
- Lauroyl piperidine
- 75 N-n-butyl acetanilide

Tetraethyl phthalamide
 N-n-amyI succinimide
 4-methyl-2-pentanol
 2,4-di-n-amyIphenol
 Ethylene glycol monobenzyl ether
 Methyl isobutyl carbinol
 Furfuryl alcohol
 Cyclohexanone
 2-(2-butoxyethoxy)ethyl acetate

The isomeric 2-, 3- and 4-methylcyclohexanones are particularly useful lower-boiling solvents for use with the above high-boiling solvents for dispersion of dye developers such as the cyan dye developers, 1,4-bis-(2,5-dihydroxyphenylisopropylamino)anthraquinone, 5,8-bis-[(β -hydroquinoyl- α -methyl)ethylamino]quinizarin and 1,4-bis(2,5-dihydroxyphenylisopropylamino) - 5-hydroxyanthraquinone, and the magenta dye developer 4-methoxy-2-[p-(β -hydroquinoyl)ethyl]-phenylazo]-1-naphthol. As a result the gelatin solutions containing dispersions of dye developers produce stable dried coatings in which the dye developers do not tend to crystallize out.

The dye developers are employed in the sensitive elements contiguous to the silver halide of the emulsion layers, that is, they may be present in one or more of the emulsion layers or preferably in a hydrophilic organic colloid layer immediately next to and particularly under the silver halide emulsion layer. Especially good results are obtained when the dye developers are positioned so as to be present in the layer immediately under the emulsion layer, the sensitivity of which is complementary to the color of the dye developer as shown in FIG. 1 of the drawings. It appears less desirable to locate the dye developer in a layer positioned above the corresponding layer of silver halide emulsion. 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 may be present in a matrix surrounding a particle or globule containing silver halide grains.

In multilayer sensitive elements of the type shown in FIG. 1 the order of arrangement of the differentially sensitized silver halide emulsion layers on the support can be different, e.g. reversed so as to have the blue-sensitive emulsion layer on the support and the red sensitive emulsion layer outermost. In such arrangements of layers the sensitivities of the silver halide emulsions should be adjusted so as to prevent recording unwanted blue light images in the emulsions primarily sensitive to the red and green regions of the spectrum, e.g. a silver bromide emulsion can be used for the blue sensitive emulsion and silver chloride emulsions for the other layers. In instances of this type it may be desirable to utilize the leuco compounds mentioned above in place of one or more of the dye-developers which, since they may have some blue absorption, might tend to exert an undue filtering action on the blue sensitive bottom emulsion layer.

The hydrophilic organic colloid vehicle of the emulsion layers, overcoating layers, of the dye developer layers and of interlayers can be varied somewhat, for example, gelatin, gelatin derivatives such as dibasic acid esters of gelatin, polyvinyl alcohol and cellulose acetate hydrogen phthalate, or mixtures of the hydrophilic organic colloid vehicles, may be used. However, the best and most consistent results, and consequently prints of the highest quality, are obtained when gelatin is used as a colloid vehicle throughout all layers of the sensitive element. In fact, when gelatin interlayers are used as shown in FIG. 1 of the drawings, they should be at least about 75% of the measured thickness of the yellow dye developer layer and contain at least about two times the amount of gelatin present in that layer in order to prevent undue wandering of the dye developer and development products from layer to layer. Other hydrophilic organic colloids yield less desirable results when used in the layers. For example, when some of the layers contain gelatin vehicle and interlayers of polyvinyl alcohol or cellulose

acetate hydrogen phthalate are used, the layers tend to strip apart particularly when dry. Also, when gelatin is used through more uniform transfer of the alkaline processing solution and hydroquinone derivative through the layers is obtained and the dye developers comprising the final print transfer more readily to the reception layer.

The processing solution used to initiate development of the exposed sensitive elements containing the dye developers and hydroquinone derivatives, and which may contain the quaternary ammonium salt, should be strongly alkaline to accelerate the development activity of the dye developer as much as possible. Alkali metal hydroxides such as sodium hydroxide or alkaline salts such as sodium carbonate are advantageously used in the activator composition for this purpose. However, quaternary ammonium hydroxides or volatile amines such as diethyl amine, which have the advantage of being volatilized from the prints and therefore leave no residue of alkali thereon which might tend to decompose the dye images, may also be used. As mentioned previously, since the hydroquinone derivatives may tend to be unstable in the strongly alkaline activator, they are preferably not incorporated in the processing solution although when the pyridinium salts are present, results are obtained which are satisfactory in other respects. The results most desired are obtained when the hydroquinone derivative is present in the layers of the sensitive elements. Therefore, no silver halide developing agent need be present in the processing solution. The alkaline processing solution may be replaced with water or a water solution of pH 7.5 or less if the contiguous receiving sheet contains an alkali or an alkali releasing material. If the water or water solution is integumented and incorporated in the light sensitive element or in the mordanted receiving sheet it may be released by suitable means such as by pressure or by heat.

The sensitive elements of the invention are, of course, adapted to use in a camera or taking pictures in the usual manner. Moreover, the development of the sensitive elements, i.e. the treatment with an alkaline activator solution to initiate development, can also be carried out in the camera by use of rupturable containers of processing solution used as illustrated in FIG. 1 of the drawings or other means may be used to spread the processing solution uniformly across the picture area of one or more consecutively exposed images and in contact with the reception layer. For this purpose, it may be desirable to use a processing solution containing in addition to strong alkali a thickening agent such as carboxymethyl cellulose or high-viscosity hydroxyethyl cellulose in suitable quantity to obtain the desired viscosity. Other means can be used such as spraying, dipping, roller coating, etc. to apply the processing solution to the exposed element and to initiate its development.

Thus, several consecutive exposures on a strip of the sensitive element can all be wetted with the alkaline processing solution and the dye developer images transferred to a single strip of reception material to provide several color prints in a single transfer operation.

One method for obtaining the color prints from a strip of the sensitive element containing a series of, for example, three or four consecutive exposures, is to apply the viscous processing solution from a releasably confining or rupturable container in a compartment such as a magazine, integral with a camera in the manner described below, to cause each of the exposed areas to be wetted with the processing composition at approximately the same time in contact with a strip of reception material and the corresponding multicolor images to transfer thereto provide a series of color images on a single strip of the reception material.

A different means for providing prints from the sensitive element containing a series of image exposures such as three or four consecutive exposures, is to expose the element to several subjects in a conventional camera not

necessarily adapted to use of rupturable containers of the processing composition, and withdrawing the exposed element from the camera in a convenient manner so as to prevent fogging of the emulsions. Thus, the element can be exposed and wound upon itself on a spool in an ordinary roll-film type of camera so as to exclude light, by use of a light-impervious covering such as black paper, a cassette or a magazine. The element can then be withdrawn from the camera and placed in a convenient portable light-impervious enclosure of small dimension such as shown in FIG. 3, for application of the viscous processing fluid to the element from, for example, a single rupturable container or several rupturable containers corresponding to the number of exposures recorded on the strip of sensitive element or by application of the fluid to the element by means of a wick, roller or similar applicator, so that each of the exposed areas is wetted. As a result the element comprising several image exposures on a single strip of differentially light-sensitive emulsion layers and subtractively colored dye developers contiguous to the silver halide of each emulsion layer, is wetted with the alkaline fluid in the presence of the onium salts, and preferably in the presence of the hydroquinone derivatives, and brought into contact with the reception layer for a time sufficient for adequate development of each image, to cause the silver halide in the several exposed areas of each emulsion layer to develop and thereby render the corresponding dye developers immobile and the dye developers in the unexposed portions of each of the several exposed areas to transfer to the reception layer and provide a series of prints thereon composed of the dye developers. In FIG. 3 is shown a schematic representation of an apparatus useful for this purpose and the process for making the series of prints from a sensitive element containing a series of exposures. The film 40 wound emulsion side inwards, having the structure shown in FIG. 1, Stage 1 and comprising a support having superposed thereon differentially sensitized emulsions and contiguous dye developers, which has been exposed so as to record a series of multicolor subjects, is quickly passed between rollers 41 and 42 so as to pick up the alkaline activator solution 43, such as Activator II, contained in pan 44, which is supplied by roller 42 dipping into the solution. Thence the film continues between rollers 45 and 46 where it is brought into contact with the mordanted receiving sheet 47, such as Receiving Sheet A, to form the sandwich 48. The exposed silver halide in each emulsion layer then develops, corresponding dye developers become immobilized and the unreacted dye developers then transfer to sheet 47, after which the sandwich passes out of the enclosure and is stripped apart to provide a series of positive dye developer images on sheet 47 at 50.

Camera apparatus of the type useful for exposing and processing the sensitive elements of the invention have been described, for example, in U.S. Patent 2,435,717. Such cameras permit successive exposure of individual frames of the photosensitive element from the emulsion side as well as processing of an exposed frame by bringing the exposed portion of the photosensitive element in superposed relation with a portion of the print receiving element while drawing these portions of the film assembly between a pair of pressure rollers which rupture the container associated therewith and spread the processing liquid 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 liquid 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 receiv-

ing element of the dye forming the final color image.

The reception layers to which the dye developers are transferred imagewise to obtain the multicolor images may be composed of various materials such as linear polyamides, proteins such as gelatin, polyvinyl pyrrolidone, poly-4-vinyl pyridine, polyvinyl alcohol, polyvinyl salicylal and methyl cellulose. These reception layers are coated on a suitable support such as a paper support, a polyethylene coated paper support, a transparent film or a white pigmented cellulose ester support to obtain a print or transparency as the case may be.

In the process of the invention it may be desirable to employ an antifoggant in the sensitive element, in the alkaline processing solution or the reception element or in each, and a development arresting compound in the reception element. When development arresting compounds are present in the reception element rather than in the sensitive element or solution they do not become effective until dissolved by the processing solution and have migrated to the sensitive element under development. As a result, the latent image is allowed to develop very rapidly and the development arresting effect is delayed until the development of the exposed areas has essentially reached completion before development is appreciably arrested. This results in the prevention of development in the unexposed areas and increases the amount of dye developer transferring. Additional improvement is obtained when the development arrestor is present in the reception layer and the mentioned quaternary salts are present in either the processing solution or the reception layer, or both. Suitable development arrestors are heterocyclic mercaptans such as mercaptotetrazoles and mercaptobenzothiazoles, e.g. 1-phenyl-5-mercaptotetrazole, 2-mercaptobenzothiazole, etc. Many compounds usually considered to be anti-foggants for silver halide do not arrest development as desired.

In a further variation of the invention a small amount of a silver halide solvent such as alkali metal or ammonium thiosulfate or thiocyanate may be incorporated into the alkaline processing composition or the receiving layer, or both, with the result that the effective photographic speed of the process is increased. However, the effect of the silver halide solvent becomes most apparent when either or both the mentioned hydroquinones and quaternary salts are present. Ordinarily the amount of silver halide solvent used is not sufficient to cause any appreciable amount of silver halide to be dissolved from the unexposed and undeveloped areas of the sensitive element and to be transferred to the reception layer.

The invention contemplates sensitive elements wherein the emulsion layers, contiguous hydroquinone derivatives and dye developer layers are integral with the support, e.g. coated on a support capable of receiving the dye developer images, the support being of a nature such that it can be stripped away from the sensitive layers or a stripping layer may be provided between the reception layer and the other layers to facilitate the stripping operation. The viscous alkaline fluid can thus be supplied as described above or in case the alkali is contained in one of the layers the fluid may merely be an aqueous solution supplied to release the alkali.

The silver halide emulsions of the sensitive elements of the invention include well-known silver halides and mixtures thereof, for example, silver bromide, silver bromoiodide or silver chlorobromide emulsions.

The dye developer images which are obtained by transfer to absorbent receiving surfaces from the sensitive elements in the manner described above, are treated with the polyvinyl alcohol-containing stabilizing compositions as described, and with the results shown in the following representative examples.

EXAMPLE 1

A sensitive element having the structure shown in

Stage 1 of FIG. 1 was prepared by coating a subbed film support 10 with suitably hardened gelatin layers as follows:

Layer 11.—An aqueous gelatin solution containing the cyan dye developer (Compound I above) dissolved in a mixture of N-n-butylacetanilide, 4-methyl cyclohexanone and dispersing agent Alkanol B, and the mixture passed through a colloid mill several times, coated and dried so as to volatilize the 4-methyl cyclohexanone.

Layers 14, 15 and 16.—Gelatin silver bromoiodide emulsion layers sensitized, respectively, to the red, green and blue regions of the spectrum.

Layers 17 and 18.—Gelatin interlayers.

Layer 12.—An aqueous gelatin solution containing the magenta dye developer (Compound II above) dissolved in a mixture of cyclohexanone, N-n-butylacetanilide and Alkanol B, and the mixture passed through a colloid mill several times, coated and dried to volatilize the cyclohexanone.

Layer 13.—An aqueous gelatin solution containing the yellow dye developer (Compound III above) dissolved in a mixture of ditetrahydrofurfuryl adipate, ethylene glycol monobenzyl ether, and Alkanol B, and the mixture passed through a colloid mill several times, the resulting dispersion chilled to set it, washed to remove ethylene glycol monobenzyl ether followed by coating upon Layer 18 and drying.

Layer 19.—Hydroquinone derivative dispersion D-1

Part A

4'-methylphenylhydroquinone	136 g.	Heat at 70° C. to dissolve then cool to 40° C.
Methyl alcohol	136 ml.	
Di-n-butyl phthalate	272 ml.	

Part B

10% gelatin solution	1360 g.	Heat to 40° C.
Water	1360 ml.	
Alkanol B (5% aqueous solution)	136 ml.	

Part A was slowly added to Part B with the aid of mechanical agitation. The solution obtained was then passed through a Manton-Gaulin laboratory 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 Layer 19 was prepared as follows:

Part I

Dispersion D-1	3775 g.	Heat to 40° C.
Water	2225 ml.	

Part II

10% galatin solution	3180 g.	Heat to 40° C., adjust pH to 5.5
Water	12,000 ml.	
Mucochloric acid (2.7% aqueous solution)	515 ml.	

Parts I and II were then combined and diluted with water to 22,700 ml. This solution was coated as Layer 19 of FIG. 1 to yield a coverage of approximately 120 mg. of gelatin per sq. ft. and 40 mg. per sq. ft. of 4'-methylphenylhydroquinone identified hereinafter as "MPHQ."

Samples of the resultant film were exposed under a step tablet through red, green and blue filters, and each wetted with the following activator in contact with the Receiving Sheet below with the result that the cyan, magenta and yellow dye developer images transferred from the undeveloped regions to the receiving sheets.

After about two minutes the receiving sheets containing the dye developer images (indicated as "Example 1 Control" sheet in the table below) were removed and the D max. values of various steps of the neutral scale of the dye images were recorded using red, green and blue filters in the usual manner.

Activator.—3.5% HEC (Hercules type 250, high vis-

cosity); 4.5% NaOH; 2.0% benzotriazole, 2.0% 1-phenethyl-2-picolinium bromide.

Receiving sheet.—A white pigmented cellulose ester support carrying a gelatin layer containing a mixture of poly-4-vinyl pyridine mordant and 1-phenyl-5-mercapto tetrazole.

Samples of the Example 1 Control image-bearing sheet were then tested with the various solutions given below in Examples 2-8 and the resultant samples exposed in fading tests for varying periods of times under a Xenon arc rich in ultraviolet radiations.

EXAMPLE 2

A 5% aqueous solution of a medium viscosity polyvinyl alcohol (Elvanol 71-30) was coated upon a sample of the Example 1 Control sheet the excess solution drained off, followed by drying the coating before subjecting it to the fading tests. (The technique used for applying the solution conveniently approximates that which the average person would be expected to use in stabilizing individual prints by hand coating rather than machine coating methods.) Known machine coating methods, where applicable, can be expected to give more uniform coatings of the compositions and, of course, more uniform stabilization of the images.

EXAMPLE 3

A 5% aqueous solution of 3,3,5-tetrahydroxymethyl-tetrahydro-pyran-4-ol (designated as "AEH") was coated upon the Example 1 Control sheet, the excess solution drained off, followed by drying.

EXAMPLE 4

An aqueous solution containing 5% PVA (Elvanol 71-30) and 5% of the compound AEH of Example 3 was applied to a sample of the Example 1 Control sheet in the manner of Example 2, followed by drying. The resulting print provided with the stabilizing mixture of PVA and AEH appears somewhat as shown in FIG. 1, Stage 2 of the drawings, a sufficient amount of stabilizing composition having been applied to the dye developer images to provide a thin stratum 29 over the layer 21 containing the cyan, magenta and yellow dye developer.

In this, and the following examples the ratio of polyvinyl alcohol (PVA) to the other component of the stabilizing composition can be varied appreciably within a range of about 1 to 0.5 to 1 to 2 and still obtain useful results. For example, from about 1 part of PVA per 0.5 part of fructose to 1 part of PVA per 2 parts of fructose can be used.

EXAMPLE 5

Five cc. of an aqueous 40% solution of a condensation polymer of formaldehyde and dicyanodiamide sold under the tradename "Perma Fix 45" by the Refined Products Co. of Lyndhurst, New Jersey was diluted with 100 cc. of water and the resultant solution applied to the Control sheet as in Example 2 followed by drying.

EXAMPLE 6

To 100 cc. of a 5% aqueous PVA (Elvanol 71-30) solution were added 5 cc. of Perma Fix 45 of Example 5, and the resulting solution applied to the Control sheet as in Example 2 followed by drying.

EXAMPLE 7

A 5% aqueous solution of fructose was applied to the Control sheet as in Example 2, followed by drying.

EXAMPLE 8

An aqueous solution containing 5% fructose and 5% PVA was applied to the Control sheet as in Example 2, followed by drying.

Samples of Example 1-8 coatings were then subjected to 50 and 100 hours fading tests under the Xenon arc and the cyan, magenta and yellow dye densities then recorded

at the first, fifth, tenth, fifteenth and twentieth steps of their images. The resulting densities are given in the following table.

the sheet radiated 40 hours as in Example 9 with the result that the sucrose-PVA treatment was found to prevent loss of the dye density to a great extent.

NEUTRAL SCALE DENSITIES (RED, GREEN, AND BLUE FILTERS)

Example	Number and feature	Color transfer print step No.	Cyan density			Magenta density			Yellow density		
			Original	Xenon after 50 hrs.	Xenon after 100 hrs.	Original	Xenon after 50 hrs.	Xenon after 100 hrs.	Original	Xenon after 50 hrs.	Xenon after 100 hrs.
1	101-2, control, no stabilization.	1	0.15	0.12	0.14	0.18	0.12	0.14	0.24	0.15	0.15
		5	0.17	0.14	0.14	0.22	0.14	0.14	0.28	0.16	0.15
		10	0.58	0.46	0.38	0.80	0.34	0.30	0.98	0.42	0.30
		15	1.96	1.62	1.30	2.11	1.18	0.87	2.32	1.50	1.00
		20	2.08	1.72	1.40	2.28	1.24	0.92	2.46	1.64	1.10
2	101-3, PVA	1	0.16	0.10	0.10	0.20	0.12	0.10	0.24	0.15	0.14
		5	0.20	0.12	0.10	0.22	0.14	0.10	0.27	0.16	0.14
		10	0.60	0.46	0.38	0.82	0.34	0.29	0.90	0.47	0.32
		15	1.94	1.62	1.30	2.16	1.42	1.04	2.30	1.90	1.30
		20	2.04	1.72	1.42	2.32	1.56	1.16	2.44	2.04	1.48
3	101-4, AEH	1	0.16	0.14	0.11	0.18	0.15	0.14	0.22	0.17	0.15
		5	0.20	0.15	0.12	0.23	0.16	0.14	0.26	0.19	0.16
		10	0.68	0.58	0.44	0.74	0.50	0.35	0.88	0.60	0.44
		15	1.96	1.58	1.30	2.26	1.32	0.96	2.35	1.70	1.18
		20	2.06	1.66	1.34	2.42	1.34	1.00	2.50	1.82	1.24
4	101-5, PVA and AEH	1	0.14	0.12	0.12	0.19	0.15	0.14	0.23	0.20	0.20
		5	0.16	0.14	0.13	0.20	0.16	0.14	0.24	0.21	0.19
		10	0.61	0.68	0.61	0.80	0.80	0.78	0.84	0.84	0.80
		15	1.96	2.04	2.00	2.18	2.22	2.18	2.30	2.26	2.15
		20	2.12	2.18	2.14	2.36	2.32	2.22	2.45	2.36	2.27
5	101-6, condensation polymer	1	0.15	0.13	0.12	0.18	0.13	0.14	0.20	0.16	0.15
		5	0.16	0.14	0.13	0.20	0.14	0.14	0.24	0.18	0.16
		10	0.66	0.46	0.40	0.80	0.48	0.30	0.87	0.58	0.36
		15	2.00	1.57	1.28	2.13	1.15	0.88	2.23	1.60	1.09
		20	2.11	1.69	1.39	2.28	1.24	0.94	2.38	1.76	1.20
6	101-7, PVA and condensation polymer	1	0.15	0.13	0.10	0.18	0.13	0.10	0.23	0.16	0.14
		5	0.18	0.13	0.11	0.20	0.14	0.11	0.24	0.16	0.14
		10	0.62	0.56	0.45	0.82	0.56	0.37	0.84	0.68	0.48
		15	2.00	1.81	1.54	2.18	1.74	1.30	2.33	2.22	1.82
		20	2.10	1.94	1.68	2.32	1.92	1.44	2.42	2.38	2.02
7	101-8, fructose	1	0.20	0.14	0.12	0.22	0.14	0.12	0.25	0.17	0.14
		5	0.22	0.15	0.12	0.25	0.15	0.12	0.27	0.19	0.16
		10	0.64	0.51	0.40	0.78	0.48	0.35	0.88	0.58	0.40
		15	1.97	1.57	1.30	2.18	1.27	0.94	2.31	1.67	1.34
		20	2.13	1.75	1.42	2.32	1.30	1.01	2.44	1.76	1.20
8	101-9, PVA and fructose	1	0.18	0.15	0.13	0.19	0.16	0.14	0.26	0.22	0.21
		5	0.18	0.15	0.14	0.22	0.17	0.17	0.28	0.23	0.22
		10	0.68	0.68	0.59	0.82	0.73	0.50	0.94	0.80	0.60
		15	1.98	2.06	1.96	2.17	1.90	1.55	2.30	2.15	1.90
		20	2.14	2.16	2.13	2.38	2.10	1.69	2.45	2.26	2.07

From the table it can be readily seen that each of the dyes of the Example 1 Control sample, having had no stabilization treatment, undergo serious loss of dye density after 50 and 100 hours of exposure to the Xenon arc lamp. Even the PVA (polyvinyl alcohol) treatment per se of Example 2 does not substantially improve the resistance to light fading. Similarly, the coatings of Examples 3, 5 and 7 which contained, respectively, "AEH", "Permaflox-45" or fructose but which do not contain polyvinyl alcohol, do not adequately stabilize dye images. However, the coatings of Examples 4, 6 and 8 which were similar, respectively, to the coatings of Examples 3, 5 and 7 except that they contained, in addition, polyvinyl alcohol, were found to impart substantial protection to all dye developer images and thereby reveal the mentioned synergistic effect. For example, the data of the table for Example 4, shows that the cyan density of 2.12 at the 20th step was substantially unchanged (2.14) after 100 hours radiation, the magenta density also changed only from 2.36 to 2.22 and the yellow density decreased only from 2.45 to 2.27 under the same conditions. Yet, neither the Example 3 sample containing no PVA nor the Example 1 and 2 samples containing no "AEH" withstood the fading effects of the ultraviolet radiations of the Xenon arc.

EXAMPLE 9

A 5% aqueous sucrose solution was applied to the Control Sheet as in Example 2 and when subjected to radiation under the Xenon arc for 40 hours sustained substantial loss in dye density particularly of the yellow and magenta dye developers.

EXAMPLE 10

An aqueous solution containing 5% sucrose and 5% PVA was applied to a Control Sheet as in Example 2 and

EXAMPLE 11

An aqueous solution of 5% levulose and 5% PVA was applied to a Control Sheet as in Example 2. It was found that radiation under the Xenon arc had little or no effect upon the dye developer images.

EXAMPLE 12

The following saccharides were used with PVA as in Example 10:

Dextrose	β -Lactose
Arabinose	Mannose
Sorbose	Maltose
Ribose	Glucuronic acid
Sorbitol	Mannitol

each of the saccharides was found to be effective (only in combination with polyvinyl alcohol) in preventing loss of dye developer density under the Xenon arc.

EXAMPLE 13

To 100 cc. of 5% aqueous PVA solution was added 5 cc. of AEH (Example 3) and 5 cc. of Permaflox 45 (Example 5) and the mixture applied to a Control Sheet as in Example 2 with the result that the Xenon arc did not materially fade the sheet upon exposure for about 50 hours.

EXAMPLE 14.—LIGHT-STABILIZATION OF DYE IMAGES OBTAINED BY COLOR DEVELOPMENT

A color product of a well known type containing conventional couplers producing dye images with p-phenylenediamine developing agents was prepared, having a paper support, a blue sensitive silver halide emulsion containing a yellow dye forming coupler such as disclosed in Weissberger U.S. Patent 2,298,443 and McCrosen et al. U.S. Patent 2,875,057, e.g. N-(p-benzoyl-acetamino-

benzenesulphonyl)-N-iso-amylaniline, N-(p-benzoyl-acetaminobenzenesulphonyl) - N - (γ - phenylpropyl) - (o) -, (m) -, or (p) -toluidine, N-(p-anisoylacetaminobenzenesulphonyl)-N-(m-methylbenzyl)aniline, α -benzoyl-5-[α -(2,4 - di - tert.amylphenoxy)butyramino] - 2 - methoxyacetanilide, α -{4-[α -(2,4 - di - tert - amylphenoxy)acetamido] - benzoyl} - 2 - methoxyacetanilide, over that layer a green sensitive emulsion containing a magenta dye forming coupler such as disclosed in Loria et al. U.S. Patent 2,600,788, e.g. 1-(2',4'-dichlorophenyl)-3-[3''-(2''',4''') - di - tert.amylphenoxyacetamino) - benzamido]-5 - pyrazolone, 1 - (2',4',6' - trichlorophenyl) - 3 - [3'' - (2''',4''') - di - tert. amylphenoxy-acetamido]benzamido] - 5 - pyrazolone, 1 - (2',4',6' - trichlorophenyl) - 3 - [β -2''',4''') - di - tert.amylphenoxy] - propionamide] - 5 - pyrazolone, and thereover a red sensitive emulsion containing a cyan dye forming coupler such as disclosed by Weissberger et al. U.S. Patent 2,474,293, Salminen et al. U.S. Patent 2,423,730, e.g. 2-[α -(4'-tert.amylphenoxy)-n-butyrylamino]-5-methyl-1-phenol, 1-hydroxy-2-[β -(2'-4' - di - tert.amylphenoxy) - ethyl] - 4 - chloronaphthamide, 1 - hydroxy 2 - [δ - 2',4' - tert.amylphenoxy)-propyl] - naphthamide, 2 - (2,4-diamylphenoxy) - acetamino - 4,6 - dichloro - 5 - methylphenol. The element was exposed to a multicolor negative subject composed of color developed negative dye images, and developed with an alkaline solution containing a p-phenylenediamine color developing agent such as disclosed by Weissberger U.S. Patent 2,193,015, e.g. N-ethyl- β -methane-sulfonamidoethyl-3-methyl-4-aminoaniline, followed by bleaching and fixing to remove the residual silver halide and silver images. Samples of the resulting color positive now containing cyan, magenta and yellow dye images of the well known azomethine and indophenol types of dyes were then coated with 5% aqueous PVA solution, 5% levulose solution and an aqueous solution of 5% PVA + 5% levulose. Only the sample coated with the latter solution imparted light-stability to the dye images when exposed for 100 hours under the Xenon arc, the effect being most pronounced on the yellow dye image.

Other images obtained by the diffusion transfer process of Example 1 and containing other dye developers mentioned above, may be stabilized to light in the manner of the examples by use of the compositions containing a mixture of polyvinyl alcohol and the mono- and disaccharides, "AEH" or a dicyandiamide-formaldehyde condensation polymer.

What I claim is:

1. A method for light-stabilizing photographic images composed of dye developers, said dye developer being a compound which is both a dye and a silver halide developing agent, which comprises applying over the surface of said images an aqueous solution of a mixture of polyvinyl alcohol and at least one member of the class consisting of a monosaccharide, a disaccharide, a water-soluble, polymeric dicyandiamide-formaldehyde condensation product, and 3,3,5,5-tetrahydroxymethyltetrahydro-pyran-4-ol.

2. A method for light -stabilizing photographic images composed of dye developers, said dye developer being a

compound which is both a dye and a silver halide developing agent, which comprises applying over the surface of said image an aqueous solution of a mixture of polyvinyl alcohol and a monosaccharide.

3. A method for light-stabilizing photographic images composed of dye developers, said dye developer being a compound which is both a dye and a silver halide developing agent, which comprises applying over the surface of said image an aqueous solution of a mixture of polyvinyl alcohol and a disaccharide.

4. A method for light-stabilizing photographic images composed of dye developers, said dye developer being a compound which is both a dye and a silver halide developing agent, which comprises applying over the surface of said image an aqueous solution of a mixture of polyvinyl alcohol and levulose.

5. A method for light-stabilizing photographic images composed of dye developers, said dye developer being a compound which is both a dye and a silver halide developing agent, which comprises applying over the surface of said image an aqueous solution of a mixture of polyvinyl alcohol and sucrose.

6. A method for light-stabilizing photographic images composed of dye developers, said dye developer being a compound which is both a dye and a silver halide developing agent, which comprises applying over the surface of said image an aqueous solution of a mixture of polyvinyl alcohol and a water-soluble polymeric condensate of formaldehyde and dicyandiamide.

7. A method for light-stabilizing photographic images composed of dye developers, said dye developer being a compound which is both a dye and a silver halide developing agent, which comprises applying over the surface of said image an aqueous solution of a mixture of polyvinyl alcohol and 3,3,5,5-tetrahydroxymethyltetrahydro-pyran-4-ol.

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