May 18, 1971 R. F. W. CIECIUCH ET AL 3,579,334

DYE DEVELOPERS WHICH ARE NON-REVERSIBLY SPECTRALLY SHIFTED BY ALKALINE HYDROLYSIS IN COLOR DIFFUSION TRANSFER PROCESSES AND ELEMENTS

Filed Aug. 30, 1968

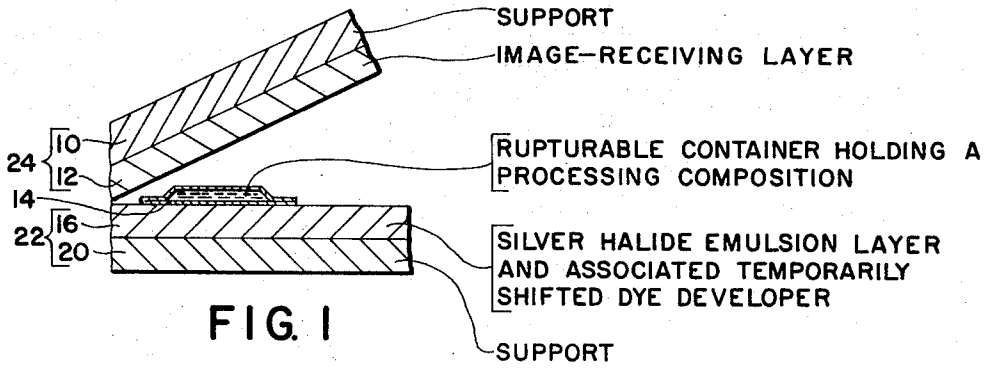


FIG. 1

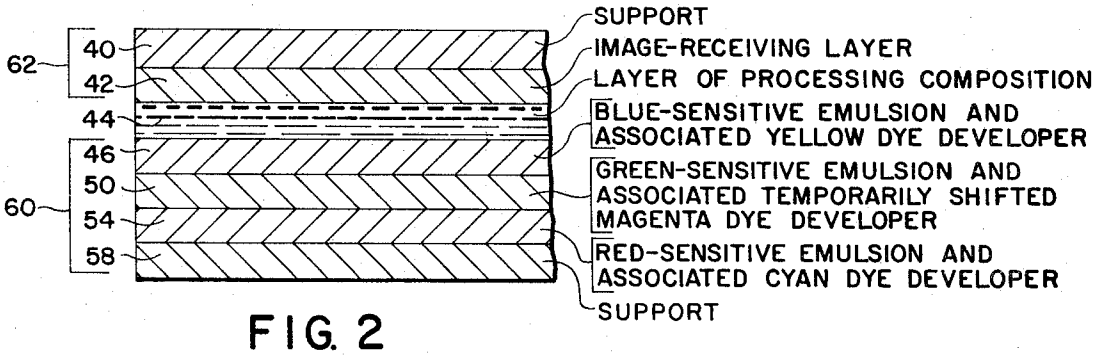


FIG. 2

INVENTORS
Ronald F. W. Cieciuch
and
Myron S. Simon
BY Brown and Mikulka
and
Robert M. Ford
ATTORNEYS

United States Patent Office

3,579,334

Patented May 18, 1971

3,579,334

DYE DEVELOPERS WHICH ARE NON-REVERSIBLY SPECTRALLY SHIFTED BY ALKALINE HYDROLYSIS IN COLOR DIFFUSION TRANSFER PROCESSES AND ELEMENTS

Ronald F. W. Cieciuch, Boston, and Myron S. Simon, Newton Center, Mass., assignors to Polaroid Corporation, Cambridge, Mass.

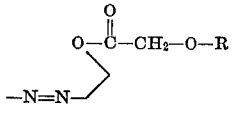
Filed Aug. 30, 1968, Ser. No. 756,481

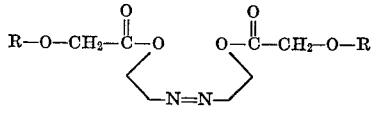
Int. Cl. G03c 5/54, 7/00

U.S. Cl. 96—29 13 Claims

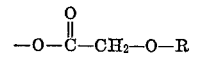
ABSTRACT OF THE DISCLOSURE

Transfer images in color are formed by exposing a photosensitive element containing a silver halide emulsion and a mono or disazo dye which contains not less than one or more than two groups selected from the group represented by the formulae.





wherein R is a lower alkyl group, said dyes also containing not less than one nor more than two dihydroxyphenyl silver halide developing radicals; permeating the photosensitive element with an aqueous alkaline processing composition, and deacylation of the



groups by hydrolysis to provide hydroxyl groups, thereby providing a non-reversible bathochromic shift of the spectral absorption characteristics of dye; immobilizing the dye as a result of the development of the exposed areas of the emulsion; and transferring, by diffusion, at least a portion of the imagewise distribution of dyes to a superposed image receiving layer to provide a positive dye image therein.

This invention relates to photography and, more particularly, to an improvement in photographic diffusion-transfer reversal processes for obtaining color images.

It has been proposed, in U.S. Pat No. 2,983,606, issued May 9, 1961, to form color images by diffusion-transfer reversal processes utilizing dye developers. In a process of this type, a photosensitive element containing a dye developer and a silver halide emulsion is exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing

composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation and especially as regards its solubility in alkaline solution. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. Under certain conditions, the layer of liquid processing composition may be utilized as the image-receiving layer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the transferred dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

The dye developers, as noted above, are compounds which contain, in the same molecule, both the chromophoric system of a dye and also a silver halide developing function. By "a silver halide developing function" is meant a grouping adapted to develop exposed silver halide. A preferred silver halide development function is a hydroquinonyl group. Other suitable developing functions include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the development function includes a benzenoid developing function, that is, an aromatic developing group which forms quinonoid or quinone substances when oxidized.

The preferred dye developers possess the characteristics of relatively high absorption of actinic radiation over a desired segment of the spectral range as well as substantially no absorption over the remaining portion of the spectrum. For example, in a diffusion-transfer reversal process for three-color substractive photography, the preferred dye developers utilized should comprise, respectively, a yellow, a magenta, and a cyan dye developer, each of said dye developers, having a high transmittance over approximately two-thirds of the visible spectrum, and a high absorption in the remaining one-third.

Where such dye developers are initially colored and

situated in an appropriately sensitized emulsion layer, that is, an emulsion layer sensitized to areas of the visible spectrum coinciding with the absorption maximum of the respective associated dye developers, it is obvious that the amount of actinic energy necessary to accomplish suitable excitation of the sensitized silver halide crystals contained within said emulsion is substantally increased.

The resultant effect of the dye developers absorption of a substantial proportion of the actinic energy available for silver halide crystal excitation is necessarily a substantial decrease in the relative speed of the associated photosensitive emulsion.

As previously stated, in multicolor photographic processes, the respective preferred dye developers should theoretically absorb actinic radiation over a selected portion of the spectral range equal to the color absorption desired and further should exert no influence on and/or absorption over the remaining portions of the spectrum. Thus, each dye developer associated emulsion layer unit, comprising a multilayer photosensitive element for use in obtaining multicolor images, should theoretically absorb spectral radiation of a predelineated area of the spectral range. Therefore, in an integral multilayer photosensitive element which comprises three appropriately sensitized silver halide emulsions having associated therewith, respectively, a yellow, a magenta and a cyan dye developer, the preferred yellow dye developer should be one with relatively high absorption in the blue area of the spectrum and thus would affect or control only the amount of blue light passing through said dye developer, but would have substantially little, if any, influence on the passage of red or green light. The magenta dye developer should be one with relatively high absorption in the green area of the spectrum and thus would affect and/or control only the amount of green light passing through said dye developer but would have substantially little, if any, influence on the passage of red or blue light. The cyan dye developer should be one with relatively high absorption in the red area of the spectrum and thus would affect or control only the amount of red light passing through said dye developer but would have substantially little, if any, influence on the passage of blue or green light.

Therefore, in an integral multilayer photosensitive element of the type previously described, upon exposure to actinic radiation comprising the visible spectrum, said radiation preferably traversing through a blue-sensitive emulsion perpendicular to the plane of said photosensitive element, the respective yellow dye developer or developers should theoretically absorb only the blue portion of the spectrum, thus allowing undiminished red and green wave lengths to contact a subsequent green-sensitive magenta dye developer containing silver halide emulsion. The magenta dye developer, in turn, should theoretically absorb only the blue portion of the spectrum, thus allowing undiminished red and green wavelengths to contact a subsequent green-sensitive magenta dye developer containing silver halide emulsion. The magenta dye developer, in turn, should theoretically absorb only the green wavelengths of the spectrum and thus allow the red wavelengths to contact, with undiminished energy, a subsequent red-sensitive cyan dye developer containing silver halide emulsion. Many yellow, magenta and cyan dye developers exhibit substantial spectral absorption in areas of the spectrum other than their preferred theoretical areas.

The unavailability of dye developers with desired absorption characteristics, that is, over one-third of the spectrum, and desired transmission characteristics, that is, over two-thirds of the spectrum, necessitates formulating a method of pre- and/or post-correcting of each emulsion layer to avoid the loss of a substantial amount of actinic energy upon exposure due to the undesirable absorption of the dye developer associated emulsion layers through which the actinic radiation must traverse in order to expose subsequent photosensitive emulsion layers.

As disclosed in U.S. Pats. Nos. 3,307,947 and 3,336,287, issued Mar. 7, 1967 and Aug. 15, 1967, it has been discovered that the necessity of correcting or compensating for the aforementioned undesirable absorption, that is, internal absorption within the respective emulsion layer decreasing the speed of said emulsion, as well as decreasing the actinic radiation transmitted through said emulsion, may be substantially obviated by effecting temporarily, that is, at least for the duration of exposure of a photosensitive element, a hypsochromic shift of the absorption characteristics of the respective dye developers such that the absorption of said dye developers is rendered negligible and transmission of the preferred spectral rays of light approximates the magnitude desired.

Dispersion of an associated dye developer in the photosensitive emulsion generally results in a substantial loss of the sensitivity of the emulsion due to the dye developer absorbing actinic energy in the corresponding region of maximum emulsion sensitivity. This is apparently due to the fact that photographic dye developers associated with a photosensitive silver halide emulsion generally possess a color, that is, a spectral absorption curve, which is substantially the same as that of the light, that is, the region of the spectrum, which the sensitized emulsion is intended to record. In such instances, the dye developer has its light absorption maximum, that is, $\lambda_{max.}$, at a wavelength within the maximum sensitivity of the photosensitive emulsion with which it is associated.

A hypsochromic shift of the light absorption spectrum of the respective dye developer is preferred since the absorption bands of the dye fall off more sharply on the long wavelength side of the $\lambda_{max.}$ A hypsochromic shift of the $\lambda_{max.}$ approximately 100 mμ susbtantially avoids absorption of spectral energy by the respective dye developer in the spectral region to which the associated emulsion is sensitized. However, it must be noted that a hypsochromic shift of the $\lambda_{max.}$ approximating 20 to 30 mμ may substantially obviate the filtering effect of the respective dye developer's absorption on photosensitive emulsions in a rearward position required by the conventional arrangement of integral multilayer photosensitive elements.

It has now been discovered that the aforementioned temporary shift of the dye developer's absorption characteristics may be attained by the utilization of mono- and disazo dye developers wherein the bathochromic effects of auxochromic hydroxy or amino substituted radicals substituted at specific positions in relation to the azo configuration, have been temporarily reduced by appropriately isolating said radicals from interaction with the azo chromophore.

From the standpoint of the color of dyes, an auxochrome is best defined as a substituent atom or group which increases the intensity (ϵ) of the absorption of light due to a chromophore. An auxochrome may also shift the main absorption band ($\lambda_{max.}$) to a longer wave length, just as a second chromophore conjugated with the first increases the ϵ in addition to shifting it to a longer $\lambda_{max.}$ It must be noted, however, that a given auxochrome may increase the ϵ only for certain chromophores, and only when it is situated in a suitable position with reference to said chromophore, to thus form an auxochromophoric system. In an auxochromophoric system, it is believed that the absorption of light results from the electronic interaction between auxochromes and chromophores by which the contribution of highly conjugated and polarized structures to the resonance of the dye molecule is increased.

Auxochromic hydroxyl and amino groups play a vital role in influencing the absorption characteristics of the azo dye developers of this invention by reason of electronic interaction between the azo chromophore and the respective hydroxyl or amino group. The position of the respective substituent in relation to the azo linkage largely determines the auxochromic effect, since resonance effects are inoperative in the meta position, auxochromic

substituents are mainly effective in the ortho and para positions with respect to the azo chromophore.

Diffusion-transfer reversal processes employing a photosensitive element, comprising not less than one silver halide emulsion having associated therewith not less than one image-forming component, should thus employ an image-forming component possessing a temporarily shifted light-absorption spectrum. The photosensitive element may be exposed to a predetermined actinic energy pattern and the resultant latent silver halide image or images formed thereby developed in said emulsion or emulsions to effect, as a result of development, immobilization of the respective associated image-forming components in the exposed areas of said photosensitive element which may be, at least in part, transferred by imbibition from the unexposed areas to a superposed image-receiving layer. A non-reversible restoration of at least a portion of the temporarily shifted image-forming components to their original spectral absorption characteristics is effected, at some stage subsequent to exposure, so as to impart to the image-receiving layer a reversed positive dye image of the latent image exhibiting the desired spectral absorption characteristics.

It is a primary object of the present invention to provide novel photographic diffusion transfer reversal processes and novel products for utilization therein.

Another object of the present invention is to provide novel photosensitive elements, comprising not less than one silver halide emulsion and not less than one dye developer, possessing increased emulsion speed and improved exposure control.

A further object of the present invention is to provide novel photographic compounds, processes and products for obtaining color images by diffusion-transfer reversal processes, wherein the light absorption characteristics of the dye developers utilized to provide said color images are temporarily shifted so that said dye developers absorb actinic energy at wave lengths substantially shorter during exposure than the wave lengths of the respective dye developers ultimately desired.

A still further object of the present invention is to provide novel photographic compounds, processes and products for obtaining color images by diffusion-transfer reversal processes, wherein the light absorption characteristics of the dye developers utilized to provide said color images are temporarily shifted so that said dye developers absorb actinic energy at wave lengths substantially shorter during exposure than the wave lengths to which the dye developer's associated silver halide emulsion is sensitized.

A still further object of the present invention is to provide novel photographic compounds, processes and products for obtaining multicolor transfer images, using integral multilayers photosensitive elements, whereby unwanted absorption, that is, absorption at the wave lengths of emulsion sensitization, is avoided.

A still further object of the present invention is to provide novel photographic processes whereby temporarily shifted dye developers, that is, dye developers the spectral absorption bands of which have been temporarily shifted to lower wave lengths prior to exposure of a photosensitive element containing said dye developers, may be restored to their original spectral absorption characteristics subsequent to exposure of said photosensitive element.

A still further object of the present invention is to provide dye developers, the spectral absorption characteristics of which are modified to effect a temporary hypsochromic shift in the wave lengths absorbed during exposure of an associated photosensitive emulsion and which, subsequent to said exposure, may be restored to their original absorption characteristics.

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

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

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

FIG. 1 is a diagrammatic cross-sectional view of one embodiment of a photographic product for use in obtaining monochromatic images in accordance with this invention and comprising a photosensitive element, an image-receiving element and a rupturable container holding a processing composition; and

FIG. 2 is a diagrammatic cross-sectional view of one embodiment of this invention, for use in obtaining multicolor images, during processing and comprising a multilayer photosensitive element, an image-receiving element and a processing composition.

The expression "temporarily shifted dye developer" as used herein is intended to signify a dye developer which has been modified chemically so that its spectral absorption bands have been relocated at substantially shorter wave lengths, that is, a hypsochromic shift of the absorption spectrum, for at least the time interval necessary to accomplish photo-exposure of a photosensitive silver halide emulsion associated therewith, and which dye developer is subject to restoration of the dye developer's original absorption characteristics upon simple chemical treatment such as, for example, hydrolysis, methanolysis, ammonolysis, etc.

It has been taught in the aforementioned U.S. Pat. No. 3,307,947 that the previously characterized advantages achieved by the utilization of temporarily shifted dye developers in photographic systems may be obtained by the employment of dye developers wherein specified auxochromic systems have undergone bathochromic shifts which result in a change in the electronic interaction between the respective auxochromes and chromophores. Alternation of the last-mentioned electronic interaction between auxochromic hydroxyl or amino groups substituted in ortho and/or para position with respect to a chromophoric azo linkage, may be affected by any suitable technique, but a most preferred means was disclosed to be temporary acylation of the respective auxochrome substituent or substituents. Restoration of the original auxochromophoric system may be then readily secured by hydrolysis of such acyl group by means of contact with an aqueous alkaline photographic processing composition.

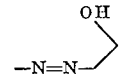
While the last-mentioned disclosed acylation of the selected auxochromic substituent does accomplish a hypsochromic shift in the spectral absorption characteristics of the selected auxochromophoric system, where the selected auxochromic substituent comprises an amino group substituted in ortho or para position with relation to a chromophoric azo linkage and/or a hydroxyl group substituted in para position to such an azo linkage, it has additionally been taught in the above patent that acylation of an auxochromic hydroxyl group substituted in ortho position with relation to a chromophoric azo linkage provides a hypsochromic shift of such extended magnitude as to be totally unexpected in view of, and unrelated in comparison with, the magnitude of hypsochromic shift provided the previously identified components.

As stated hereinbefore, a temporary hypsochromic shift of the dye developer's $\lambda_{max.}$, at least for the period during which exposure of a photographic film unit retaining same is accomplished, constituting a magnitude of 20 to 30 mμ, may be sufficient to substantially avoid a filtering effect, in the transmission of actinic energy to a rearwardly positioned photosensitive emulsion, in many desired instances. In certain instances, therefore, acylation of an auxochromic hydroxyl group substituted para to a chromophoric azo linkage may be sufficient to provide the desired radiation

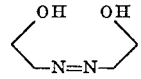
absorptive characteristics to a given photographic film unit. In many instances, however, the maximum magnitude of such shift is considerably less than that desired to provide the optimum radiation absorbing characteristics to the film unit. In such circumstances, it is preferred that acylation of an auxochromic hydroxyl group substituted in ortho position with respect to a chromophoric azo linkage, in accordance with the present disclosure, be employed to provide the desired photographic optical properties.

The preferred group of dye developers, the spectral absorption curve of which may be subjected to a temporary hypsochromic shift by isolation of an appropriate auxochromic substituent, comprises mono- and disazo dye developers characterized in that they contain an auxochromic hydroxyl group substituted on an aryl nucleus in ortho or ortho'ortho positions to one or both azo linkages, that is, mono- and disazo dye developers characterized in that said dye developers contain not less than one and not more than two groups selected from the groups represented by the formulae:

(1)



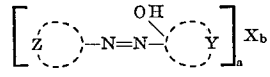
(2)



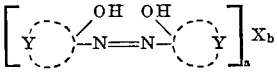
and said dye developers being further characterized in that they contain not less than one and preferably not more than two groups selected from the group consisting of p-dihydroxyphenyl and o-dihydroxyphenyl groups and halogen and alkyl substituted derivatives thereof.

It will be apparent that preferred members of the aforementioned mono- and disazo dye developers may also be represented by the formulae:

(3)



(4)



(5)



wherein *a* is one or two; *b* is one or two; X is a p-dihydroxyphenyl or an o-dihydroxyphenyl group and the halogen and alkyl substituted derivatives thereof; each Y represents the non-metallic atoms necessary to complete an aryl nucleus, preferably a benzene or naphthalene nucleus, which aryl nuclei may be the same or different; and Z represents the residue of an azo coupler.

As examples of ortho-hydroxy and/or ortho, ortho'-dihydroxy substituted mono- and disazo dye developers preferred for use in the practice of the present invention, mention may be made of the following:

2-(4'-[4''-(2''',5'''-dihydroxyphenethyl)-phenylazo]-naphthalene azo)-4-methoxy-1-naphthol

p-(1-hydroxy-4-methoxy-2-naphthalene azo)-phenethyl catechol

2-(p-[B-(hydroquinonyl)-ethyl]-phenylazo)-4-methoxy-1-naphthol

2-(p-[B-(hydroquinonyl)-ethyl]-phenylazo)-4-n-propoxy-1-naphthol

the preparations of which are disclosed in the copending U.S. application of Elkan R. Blout, Milton Green, and Howard G. Rogers, Ser. No. 612,045, filed Sept. 25, 1956, abandoned and replaced by Ser. No. 144,816, filed Oct. 18, 1961 (now U.S. Pat. No. 3,134,672, issued May 26, 1964);

2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-4-methoxy-1-naphthol

the preparation of which is disclosed in the copending U.S. application of Helen P. Husek and Myron S. Simon, Ser. No. 612,054, filed Sept. 25, 1956, now abandoned and replaced by Ser. No. 197,283, filed May 24, 1962 (now U.S. Pat. No. 3,236,645, issued Feb. 22, 1966) and Ser. No. 197,259, filed May 24, 1962 (now U.S. Pat. No. 3,134,763, issued May 26, 1954);

2-(2',5'-dimethoxy-4'-[p-2'',5''-dihydroxy phenethyl)-phenylazo]-phenylazo)-4-methoxy-1-naphthol

the preparation of which is disclosed in the copending U.S. application of Helen P. Husek, Ser. No. 612,055, filed Sept. 25, 1956, now abandoned and replaced by Ser. No. 192,355, filed May 4, 1962 (now U.S. Pat. No. 3,236,643, issued Feb. 22, 1966) and Ser. No. 192,354, filed May 4, 1962 (now U.S. Pat. No. 3,134,762, issued May 26, 1954);

2-p-[4'-methyl-2',5'-dihydroxyphenylthioethyl]-phenylazo)-4-methoxy-naphthol

the preparation of which is disclosed in the copending U.S. application of Milton Green and Howard G. Rogers, Ser. No. 633,905, filed June 6, 1957, now abandoned and replaced by Ser. No. 193,326, filed May 8, 1962 (now U.S. Pat. No. 3,222,169, issued Dec. 7, 1965);

2-(p-[2',5'-dihydroxyphenoxy]-phenylazo)-4-methoxy-1-naphthol

the preparation of which is disclosed in the copending U.S. application of Milton Green, Ser. No. 680,403, filed Aug. 26, 1957, now abandoned;

2-(p-[hydroquinonylsulfonyl)-phenylazo]-4-methoxy-1-naphthol

the preparation of which is disclosed in the copending U.S. application of Milton Green, Ser. No. 680,434, filed Aug. 26, 1957, now abandoned and replaced by Ser. No. 230,287, filed Oct. 12, 1962 (now U.S. Pat. No. 3,230,086, issued Jan. 18, 1966);

2-(2',5'-dimethoxy-3'-[2'',-(2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-4-methoxy-1-naphthol

the preparation of which is disclosed in the copending U.S. application of Elkan R. Blout, Milton Green, Howard G. Rogers, and Myron S. Simon, Ser. No. 685,081, filed Sept. 20, 1957, now abandoned and replaced by Ser. No. 222,702, filed Sept. 10, 1962 (now U.S. Pat. No. 3,208,991, issued Sept. 28, 1965) and Ser. No. 222,656, filed Sept. 10, 1962 (now U.S. Pat. No. 3,142,565, issued July 28, 1964);

2-(4'-[p-(hydroquinonyl)-phenylcarboxamido)-phenylazo]-4-methoxy-1-naphthol

the preparation of which is disclosed in the copending U.S. application of Milton Green, Ser. No. 703,515, filed Dec. 18, 1957, now abandoned;

4,4'-bis-(4''-[2''',5'''-dihydroxyphenethyl]-phenylsulfamyl)-1-hydroxy-1,2'-azonaphthalene

4-(4'-[2'',5''-dihydroxyphenethyl]-N-methyl-phenylsulfamyl)-2-(2',5'-dimethoxyphenylazo)-1-naphthol

the preparations of which are disclosed in the copending U.S. application of Elkan R. Blout, Milton Green, Howard G. Rogers, and Robert B. Woodward, Ser. No. 707,109, filed Jan. 6, 1958, now abandoned;

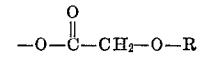
2-(4'-[4''-(2''',5'''-dihydroxyphenethyl)-phenylcarbamyl]-phenylazo)-4-methoxy-1-naphthol

the preparation of which is disclosed in the copending U.S. application of Milton Green and Howard G. Rogers, Ser. No. 748,145, filed July 14, 1958, now abandoned and replaced by Ser. No. 190,804, filed Apr. 27, 1962 (now U.S. Pat. No. 3,186,982, issued June 1, 1965); and

1-(4'-[2'',5''-dihydroxyphenethyl]-2'-hydroxyphenylazo)-2-naphthol

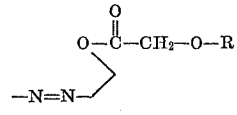
the preparation of which is disclosed in the copending U.S. application of Milton Green and Myron S. Simon, Ser. No. 788,893, filed Apr. 15, 1964, now abandoned and replaced by Ser. No. 359,998, filed Apr. 15, 1964 (now U.S. Pat. No. 3,299,041, issued Jan. 17, 1967).

In compounds comprising the last-mentioned class of dye developers, the auxochromic hydroxyl group may be selectively isolated from interaction with the azo chromophore by acylation of said hydroxyl group according to the following procedure, in order to provide the preferred dye developers for use in the practice of the present invention. These dye developers comprise novel mono- and disazo dye developers characterized in that said dye developers contain not less than one and not more than two groups of the formula:

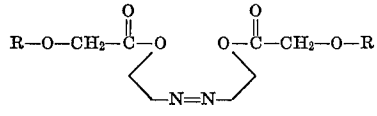


ortho to at least one azo group, and not more than one of said groups is ortho to the same nitrogen atom of said azo group; and which dyes may also be characterized in that they contain not less than one and not more than two groups represented by the formulae:

(6)

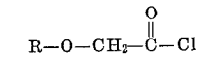


(7)



wherein each R is an alkyl group, preferably a lower alkyl of from one to ten carbon atoms, more preferably one to eight, such as methyl, ethyl, propyl, butyl, octyl, etc.; and said dye developers being further characterized in that they contain not less then one and preferably not more than two groups selected from the group consisting of a p-dihydroxyphenyl an o-dihydroxyphenyl group.

It has been discovered that the compounds within the aforementioned formulae may be prepared by oxidizing to the quinone, the p-dihydroxyphenyl or o-dihydroxyphenyl groups, or derivatives thereof of mono- or disazo dyes, said dyes characterized in that they contain not less then one and not more than two ortho-hydroxyazo and/or ortho, ortho'-dihydroxyazo configurations, and said dyes being further characterized in that they contain not less than one and not more than two groups selected from the group consisting of p-dihydroxyphenyl and o-dihydroxyphenol groups, including specifically the halogen and alkyl substituted derivatives thereof; said oxidation being accomplished, for example, with an oxidizing agent such as benzoquinone, chloranil, etc.; acylating the hydroxyl, groups substituted ortho and/or ortho' to one or more azo groups by reacting the oxidation product with an acylating agent of the formula:



said acylation being accomplished under anhydrous conditions.

Preferably, a solvent is employed, such as chloroform, carbon tetrachloride, methylene chloride, and the like. Optionally, potassium carbonate is employed to remove any hydrochloric acid that may be formed during the process. It is critical, however, that rigidly anhydrous conditions be maintained.

The p-dihydroxyphenyl group or o-dihydroxyphenyl group or derivatives thereof, are regenerated by, subsequent to acylation, reduction, said reduction being accomplished, for example, with a reducing agent such as xylohydroquinone or hydrogen in the presence of a suitable catalyst, such as a palladium/charcoal catalyst.

It is contemplated, within the scope of this invention that, where desirable, the dyes may contain one or more hydroxyl groups substituted thereon in addition to those previously mentioned. Under such conditions, the acylation action may be continued until substantially complete acylation is attained, that is, acylation of each free hydroxyl group of the respective dye molecules.

As illustrative examples of the preferred alkoxy acetyl chloride acylation agents within the scope of the present invention mention may be made of:

methoxy acetyl chloride
ethoxy acetyl chloride
propoxy acetyl chloride
butoxy acetyl chloride
octyloxy acetyl chloride
isopropoxy acetyl chloride
isobutoxy acetyl chloride

It will be recognized, from the preceding discussion that, within the scope of the invention claimed, the alkyl group represented by the term "R" is intended to encompass the equivalents thereof, and, accordingly may comprise a substituted alkyl or aliphatic group which may be saturated or unsaturated, in accordance with the specific acylating agent optionally chosen to conform to the desires of the operator.

The novel dye developers of the present invention provide advantages over prior art compositions. For example, more complete hydrolysis of the dye is achieved in the positive image thus insuring a truer color. In addition, a relatively short induction time is required and a greater dye transfer is exhibited as well as a more effective silver development. As will be seen in the following example, it is possible to use the dye developer of the present invention *in* the gelatin emulsion layer in addition to coating it *on* an emulsion layer. Prior to the present invention, dye developers have not been as suitable for use in the emulsion phase.

With specific regard to the p-dihydroxyphenyl and o-dihydroxyphenyl groups, or radicals, the remaining hydrogen atoms in the phenyl ring system may be suitably substituted by hydroxyl groups, amino groups, alkyl groups, or halogen atoms such as chloride and bromide atoms, and the like, which do not interfere with the photographic silver halide developing characteristics of the specified dihydroxyphenyl ring system.

In accordance with the present invention, it is contemplated to utilize a temporarily shifted dye developer and, specifically, a dye developer of the class detailed hereinbefore, in both monochromatic and multicolor diffusion-transfer reversal processes. It is contemplated to use at least one of the dye developers employed in multicolor diffusion-transfer reversal processes in the form of a temporarily shifted dye developer. Significant improvements may result from the use of even one temporarily shifted dye developer in a multicolor process. It is also contemplated to employ a plurality of temporarily shifted dye developers containing varying modifying groups to effect temporary shift of the respective dye developers' spectral characteristic.

The novel temporarily shifted dye developers of the present invention also find extensive application in sub-

tractive color correction processes, such as the integral masking procedures utilizing temporarily shifted dye developers.

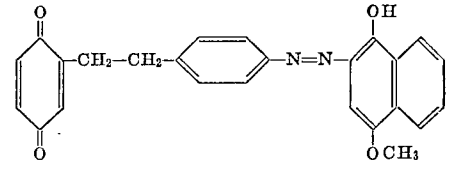
FIG. 1 of the accompanying drawing illustrates one method of processing a silver halide emulsion to obtain a monochromatic transfer image in accordance with this invention. A photosensitive element **22** comprises a support **20**, a layer **16** containing a temporarily shifted dye developer, and a silver halide emulsion. As shown in the particular embodiment depicted in FIG. 1, the photosensitive element **22** is shown in a spread-apart relationship (as, for example, during exposure) with an image-receiving element **24** having mounted thereon a rupturable container **14** holding a processing composition. The image-receiving element **24** comprises a support **10** and an image-receiving layer **12.** After exposure, the image-receiving element **24** is brought into superposed relationship with photosensitive element **22**, rupturable container **14** is ruptured by application of suitable pressure, for example, by advancing between a pair of rolls (now shown), and a layer of the liquid processing composition is spread between the superposed elements. The processing composition permeates the silver halide emulsion and develops a latent image contained therein. Subsequent to exposure, the temporarily shifted dye developer is restored to its original spectral absorption characteristics. In unexposed areas, the dye developer will transfer to the superposed image-receiving element **24**, to constitute thereon a positive dye image in terms of exposure, said image exhibiting the spectral absorption characteristics of the desired restored dye developer. The image-receiving element **24** is separated from its superposed relationship with the photosensitive element **22** after at least a portion of the dye developer has been transferred.

It should be noted that it is within the scope of the present invention to form images which comprise mixtures of temporarily shifted dye developers and non-shifted or restored dye developers. The restoration of the respective dye developer's original spectral absorption characteristics may be effected by reacting said dye developer with one or more processing compositions, subsequent to photoexposure, but prior to, concurrent with or subsequent to photographic processing. If desired, an image-receiving element containing a transferred dye developer may be contacted with said process-compositions subsequent to dissociation of said image-receiving element from its superposed relationship to the photosensitive element. For example, a temporarily shifted esterified dye developer retained in an image-receiving element, may be subjected to caustic hydrolysis by contact with a second processing composition prior to or subsequent to the aforementioned dissociation to provide an increased quantity of hydrolyzed dye developer therein.

In the following examples, all parts are given by weight except where otherwise noted and all operations involving light-sensitive materials are carried out in the absence of actinic radiation. These examples are intended to be illustrative only of the synthesis and employment of temporarily shifted dye developers wherein, subsequent to photoexposure, at least a portion of said temporarily shifted dye developer is restored to the desired subtractive color absorption spectrum to provide a reversed positive transfer image of the photographed subject and should not be considered as limiting the invention in any way.

EXAMPLE 1

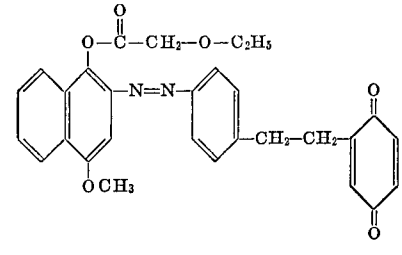
10 gm. of 2-(p-[B(hydroquinonyl)-ethyl]phenylazo]-4-methoxy-1-naphthol, the preparation of which is disclosed in the aforementioned copending U.S. application Ser. No. 612,045, abandoned and replaced by Ser. No. 144,816, filed Oct. 18, 1961 (now U.S. Pat. No. 3,134,672, issued May 26, 1964) and 10.5 gm. of benzoquinone are refluxed for 3.5 hours in 150 cc. of chloroform to provide 3 gm. of



4-methoxy - 2 - (p-[B(p'-quinonyl)-ethyl]-phenylazo)-1-naphthol.

EXAMPLE 2

8 gm. (.02 M) of dry 4-methoxy-2-(p-[B-(p'-quinonyl) ethyl]-phenylazo-1-naphthol are warmed under anhydrous conditions in 100 ml. of freshly purified chloroform. 8 g. (.058 M) of anhydrous potassium carbonate are added and the mixture brought to reflux, 3.6 ml. (.029 M) of ethoxy acetyl chloride are added and refluxing continued for 48 hours. Another 8 g. of potassium carbonate, and 3.6 ml. of ethoxy acetyl chloride are added, and refluxing continued for four days. The reaction is cooled and filtered under slightly reduced pressure, and then the solvent is removed under vacuum. The resulting hot orange-red oil is treated with 200 ml. of boiling hexane, and, from the quickly decanted solvent, the product is filtered off and washed with hexane to remove unreacted acid chloride. The product is dissolved in 100 ml. of dry benzene by boiling, 50 ml. of hot hexane is added and mixed quickly to precipitate the product as a red-brown oil. Precipitation is repeated twice to provide 4.3 g. of the product:



which melted at 132–133° F.

EXAMPLE 3

3.6 g. of the product of Example 2 was reduced at atmospheric pressure in 100 ml. of ethyl acetate using 10% palladium barium sulfate catalyst. At 27° F., the material took up the calculated volume of hydrogen in 12 minutes. The product, 4 - methoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-ethoxy acetate was recrystallized from boiling benzene in an 84% yield. The product melted at 123–125° F. and exhibits a spectral absorption curve which displays a $\lambda_{max.}$ at 397 mμ in methyl cellulose, ϵ=15,200.

EXAMPLE 4

310 gm. of dry 4-isopropoxy-2-[p-(B-quinonyl-ethyl)-phenylazo]-1-naphthol and 218 gm. of ethoxy acetyl chloride in 3 l. carbon tetrachloride were refluxed for 60 hours under anhydrous conditions. The product, 4-isopropoxy-2 - [p - (B-quinonylethyl) - phenylazo] - naphthalene-1-ethoxy acetate, is separated and purified by ethyl acetate-hexane crystallization, to yield 178 gm. of the product which melted at 119–120° F., and exhibited a spectral absorption curve which displays a $\lambda_{max.}$ at 341 mμ in acetone; ϵ=18,600.

EXAMPLE 5

Employing the procedure of Example 4, substituting octyloxy acetyl chloride for ethoxy acetyl chloride, 4-isopropoxy-2-[p-(B-quinonylethyl) - phenylazo] - naphthalene-1-octyloxy acetate was prepared having a melting point of 84–85° F. and exhibiting a spectral absorption curve which displays a $\lambda_{max.}$ at 341 mμ in methyl cellulose; ϵ=19,400.

EXAMPLE 6

Employing the procedure of Example 4, substituting propoxy acetyl chloride for ethoxy acetyl chloride, 4-isopropoxy - 2 - [p-(B-quinonylethyl)-phenylazo]-naphthalene-1-propoxy acetate was prepared.

EXAMPLE 7

Employing the procedure of Example 4, substituting butoxy acetyl chloride for ethoxy acetyl chloride, 4-isopropoxy - 2 - [p-(B-quinonylethyl)-phenylazo]-naphalene-1-butoxy acetate was prepared.

EXAMPLE 8

A photosensitive element was prepared as follows: 5.0 g. of 4-methoxy - 2 - [p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-ethoxy acetate was dissolved in 7.5 cc. of diethyl decanamide and 5.0 cc. of triethyl phosphite. This solution was emulsified by means of a high shear mechanical agitator, with an aqueous solution of 33.3 g. of 15% gelatin and a dispersing agent and then coated upon a subcoated film base with a green sensitive silver iodobromide emulsion and allowed to dry. This photosensitive element was exposed and processed by spreading, between the thus exposed photosensitive element and a superposed image-receiving element, an aqueous processing composition comprising:

Water—100 cc.
Potassium hydroxide—11.2 g.
Hydroxyethyl cellulose—3.8 g.
Benzotriazole—3.5 g.
N-benzyl-a-picolinium bromide—2.0 g.

The image-receiving element comprised baryta paper coated with a layer of a partial butyl ester of poly-(ethylene/maleic anhydride), followed by a layer of polyvinyl alcohol and a layer of 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinyl pyridine. Image-receiving elements of this type are disclosed and claimed in the copending aplication of Edwin H. Land, Ser. No. 234,864, filed Nov. 1, 1962 (now U.S. Pat. No. 3,362,819, issued Jan. 9, 1968).

After an imbibition period of aproximately one minute, the image-receiving element was separated and contained a magenta positive dye image having a $D_{max.}$ of 2.18 and a $\nu_{min.}$ of 0.2.

EXAMPLE 9

A photosensitive element was prepared by coating a gelatin subcoated film base with a solution comprising 0.3 g. of 4-methoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-ethoxy acetate which was dissolved in 7.5 cc. of 2% cellulose acetate hydrogen phthalate in acetone. After this coating dried, a green-sensitive silver iodobromide emulsion was coated thereupon and allowed to dry. This photosensitive element was exposed and processed as described in Example 8.

After an imbibition period of approximately one minute, the image-receiving element was separated and contained a magenta positive image having a $D_{max.}$ of 2.52 and a $D_{min.}$ of 0.4.

EXAMPLE 10

A photosensitive element was prepared as follows: 1.0 g. of 4-isopropoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-propoxy acetate was dissolved in 2 cc. of diethyl decanamide. This solution was emulsified by means of a high shear mechanical agitator, with an aqueous solution of 6.65 g. of 15% gelatin and then coated upon a subcoated film base, mixed with a green-sensitive silver iodobromide emulsion and allowed to dry. This photosensitive element was exposed and processed as described in Example 8.

After an imbibition period of approximately one minute, the image-receiving element was separated and contained a magenta positive image having a $D_{max.}$ of 1.56 and a $D_{min.}$ of 0.09.

EXAMPLE 11

A photosensitive element was prepared by coating a gelatin subcoated film base with a solution comprising 0.22 g. of 4-isopropoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-propoxy acetate which was dissolved in 5 cc. of 2% cellulose acetate hydrogen phthalate in acetone. After this coating dried, a green-sensitive silver iodobromide emulsion was coated thereupon and allowed to dry. This photosensitive element was exposed and processed as described in Example 8.

After an imbibition period of approximately one minute, the image-receiving element was separated and contained a magenta positive image having a $D_{max.}$ of 1.23 and a $D_{min.}$ of 0.21.

EXAMPLE 12

A photosensitive element was prepared by coating a gelatin subcoated film base with a solution comprising 0.22 g. of 4-isopropoxy-2-[p-(B-hydroxyquinonylethyl)-phenylazo]-naphthalene-1-butoxy acetate which was dissolved in 5 cc. of 2% cellulose acetate hydrogen phthalate in acetone. After this coating dried, a green-sensitive silver iodobromide emulsion was coated thereupon and allowed to dry. This photosensitive element was exposed and processed as described in Example 8.

After an imbibition period of approximately one minute, the image-receiving element was separated and contained a magenta positive image having a $D_{max.}$ of 0.94 and a $D_{min.}$ of 0.25.

EXAMPLE 13

A photosensitive element was prepared by coating a gelatin subcoated film base with a solution comprising 0.22 g. of 4-methoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-octyloxy acetate which was dissolved in 5 cc. of 2% cellulose acetate hydrogen phthalate in acetone. After this coating dried, a green-sensitive silver iodobromide emulsion was coated thereupon and allowed to dry. This photosensitive element was exposed and processed as described in Example 8.

After an imbibition period of approximately one minute, the image-receiving element was separated and contained a magenta positive image having a $D_{max.}$ of 0.66 and a $D_{min.}$ of 0.23.

As previously stated, the novel dye developers of the present invention unexpectedly provide advantageously shorter photoexposed silver halide development induction times than those capable of being achieved employing dye developers of the prior art. Thus increased dye transfer image definition control is provided by means of the present invention, which is especially preferred to provide the integrity of separate color image records which enhances the multicolor image acuity to be obtained from multicolor transfer processes.

Such decreased development induction periods are readily illustrated by reference to the following tabular compilation, which details, for comparative purposes, the induction periods obtained employing representative dye

developers of the present invention directly compared with representative dye developers of the prior art.

TABLE I

	Dye developer	Concentration of dye developer in grams	Example fabricated and processed in accordance with—	Induction of the development of photo-exposed silver halide in seconds
Control	4-methoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-acetate.	0.36	9	0.7
Test	4-methoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-ethoxy acetate.	0.297	9	0.4
Control	4-isopropoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-acetate.	0.38	9	1.9
Test	4-isopropoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-ethoxy acetate.	0.12	9	0.9
Test	do	5.0	8	0.6

In addition, more complete hydrolysis of the dye forming the transfer image, as compared with image dyes of the prior art, is advantageously provided employing the dye developers of the present invention as is readily illustrated by reference to the following tubular compilation, which denotes the ratio of transfer image optical densities at 560 and 434 mμ employing illustrative dyes of the present invention directly compared with illustrative dyes of the prior art.

TABLE II

	Dye developer	Ratio [1]
Control	4-isopropoxy-2-[p-(B-hydroquinonylethyl)-phentylazo]-naphthalene-1-acetate.	2.26
Test	4-isopropoxy-2-]p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-ethoxy acetate.	2.46
Control	4-isopropoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-undecoxy acetate.	1 10

[1] Equals $\frac{\text{O.D. at 560 m}\mu}{\text{O.D. at 434 m}\mu}$

The dye developers of the present invention also unexpectedly provide, compared with prior art compounds, increased dye transfer image maximum density, decreased dye transfer image minimum density, and more effective and efficient silver development, as directly illustrated in the following tabular compilation of experimental results.

TABLE III

	Dye developer	Concentration of dye developer	Example fabricated and processed in accordance with—	D_{max}	D_{min}	Silver image optical density of photosensitive element [1]	Fog silver optical density in photosensitive element [1]
Control	4-isopropoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-acetate.	0.38	9	0.75	0.54	0.89	0.61
Test	4-isopropoxy-2-[p-(B-hydroquinonylethyl)-phenylazo]-naphthalene-1-ethoxy acetate.	0.12	9	1.22	0.49	1.18	0.73

[1] 60 seconds development time.

It is also contemplated to utilize in the preparation of monochromatic images, a film structure wherein the photo-sensitive element is coated over the image-receiving layer and the processing composition must permeate through the emulsion before reaching the image-receiving layer. A structure of this type is described, for example, in U.S. Pat. No. 2,661,293, issued to Edwin H. Land on Dec. 1, 1953, and particularly with respect to FIG. 7 of said patent.

Multicolor images may be obtained using dye developers in diffusion-transfer reversal processes by several techniques. One such technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in the copending U.S. application of Howard G. Rogers, Ser. No. 748,421 (now U.S. Pat. No. 2,983,606, issued May 9, 1961), and also in the copending U.S. application of Edwin H. Land, Ser. No. 448,441, filed Aug. 9, 1956 (now U.S. Pat. No. 2,968,554, issued Jan. 17, 1961). In such an embodiment, each of the minute photosensitive elements has associated therewith an appropriate dye developer in or behind the silver halide emulsion portion. In general, a suitable photosensitive screen, prepared in accordance with the disclosures of the last-mentioned copending applications, comprises minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer.

Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multilayer photosensitive element such as is disclosed and claimed in the copending U.S. application of Edwin H. Land and Howard G. Rogers, Ser. No. 565,135 (now U.S. Pat. No. 3,345,163, issued Oct. 3, 1967) wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive halide emulsion stratum, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata may be separated from other sets by suitable interlayers, for example, by a layer of gelatin and/or polyvinyl alcohol.

A multilayer photosensitive element of this type just described is illustrated in FIG. 2 of the accompanying drawing and is depicted during processing. An exposed photosensitive element **60** comprises: a support **58**; a layer **54** containing a cyan dye developer and a red-sensitive silver halide emulsion; a layer **50** of a magenta dye developer exhibiting a temporarily shifted spectral absorption curve and a green-sensitive silver halide emulsion; a layer **46** containing a yellow dye developer and a blue-sensitive silver halide emulsion. As noted above, each set of silver halide emulsion and associated dye developer strata may be separated from other sets thereof by suitable interlayers (not shown), for example, by a layer of gelatin and/or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow

filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be employed. In such instances, a separate yellow filter may be omitted.

Referring again to FIG. 2, a multilayer photosensitive element 60 is shown in processing relationship with an image-receiving element 62 and a layer 44 of a processing composition. The image-receiving element 62 comprises a support 40 and an image-receiving layer 42. As noted in connection with FIG. 1, the liquid processing composition is effective to initiate development of the latent image in the respective exposed silver halide strata and also may effect restoration of the respective temporarily shifted magenta dye developer to its original absorption characteristics. After a suitable imbibition period, during which at least a portion of the dye developer associated with unexposed areas of each of said emulsions is transferred to the superposed image-receiving element 62, the latter element may be separated to reveal the positive multicolor image.

It should be noted that it is within the scope of this invention to utilize, in multicolor diffusion-transfer reversal processes, one or more of the requisite dye developers in the form of temporarily shifted dye developers. In certain instances, for example, it may be desirable to employ temporarily shifted dye developers in association with a red-sensitive and green-sensitive silver halide emulsion, together with a non-shifted dye developer associated with the blue-sensitive silver halide emulsion.

The dye developers utilized in the processes of this invention may be incorporated in the photosensitive elements, for example, in, on, or behind the respective silver halide emulsion. The dye developer may, for example, be in a coating or layer behind the silver halide emulsion and such a layer or dye developer may be applied by the use of a coating solution containing about 0.5 to 8%, by weight, of the respective dye developer. When the temporarily shifted dye developers, set forth in Examples 2 and 4, were placed in a dye carrier layer behind the green-sensitive emulsion in an integral multilayer photosensitive element of the type described in connection with FIG. 2, sensitivity of the rearwardly positioned red-sensitive emulsion was extended approximately 30mμ into the shorter wave lengths of the spectrum, that is, the sensitivity of the red-sensitive emulsion was extended from approximately 640mμ down to approximately 610mμ.

The liquid processing composition herein referred to comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate. If the liquid procesing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin uniform layer, it may also include a viscosity-increasing compound constituting a film-forming material of the type which, when said composition is spread and dried, forms a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric water-soluble ether which is inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time may also be used. The film-forming material is preferably contained in the processing composition in suitable quantities to impart to said composition a viscosity in excess of 1,000 centipoises at a temperature of approximately 24° C. and preferably of the order of 1,000 to 200,000 centipoises at said temperature. Illustrations of suitable liquid processing compositions may be found in the several patents and copending applications herein mentioned and also in examples herein given. Under certain circumstances, it may be desirable to apply a liquid processing composition to the photosensitive element prior to exposure, in accordance with the technique described in the copending U.S. application of Edwin H. Land Ser. No. 498,672, filed Apr. 1, 1955 (now U.S. Pat. No. 3,087,816, issued Apr. 30, 1963).

It will be noted that the liquid processing composition employed may contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4-diaminophenol, p-benzylaminophenol, hydroquinone, tolu-hydroquinone, phenylhydroquinone, 4'-methylphenylhydroquinone, etc. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed in U.S. Pat. No. 3,039,869, issued June 19, 1962. As examples of suitable combinations of auxiliary developing agents, mention may be made of 1-phenyl-3-pyrazolidone in combination with p-benzylaminophenol and 1-phenyl-3-pyrazolidone in combination with 2,5-bis-ethyleneimino-hydroquinone. Such auxiliary developing agents may be employed in the liquid processing composition or they may be initially incorporated, at least in part, in the silver halide emulsion strata or the strata containing the dye developers. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy-transfer reaction, with the oxidation product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposed silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed in the copending U.S. application of Milton Green and Howard G. Rogers, Ser. No. 50,851, filed Aug. 22, 1960 (now U.S. Pat. No. 3,173,786, issued Mar. 16, 1965).

The dye developers are preferably selected for their ability to provide colors that are useful in carrying out subsractive color photography, i.e., cyan, magenta and yellow. It should be noted that it is within the scope of this invention to use mixtures of dye developers to obtain a desired color, e.g., black. This it is to be understood that the expression "color" as used herein is intended to include the use of a plurality of colors to obtain black, as well as the use of a single black dye developer.

In all products employed in the practice of this invention, it is preferable to expose from the emulsion side. It is, therefore, desirable to hold the photosensitive element and the image-receiving element together at one end thereof by suitable fastening means in such manner that the photosensitive element and the image-receiving element may be spread apart from their superposed processing position during exposure. A camera apparatus suitable for processing film of the type just mentioned is provided by the Polaroid Land Camera, sold by Polaroid Corporation, Cambridge, Mass., or similar camera structure such, for example, as the roll film-type camera forming the subject matter of U.S. Pat. No. 2,435,717 or the film pack-type camera forming the subject matter of U.S. Pat. No. 2,991,702. Camera apparatus of this type permits successive exposure of individual frames of the photosensitive element from the emulsion side thereof as well as individual processing of an exposed frame by bringing said exposed frame into superposed relation with a predetermined portion of the image-receiving element while drawing these portions of the film assembly between a pair of pressure rollers which rupture a container associated therewith and effect the spreading of the processing liquid released by rupture of said container, between and in contact with the exposed photosensitive frame and the predetermined, registered area of the image-receiving element.

The nature and construction of rupturable containers such as that shown in FIG. 1 is well understood in the art; see, for example, U.S. Pat. No. 2,543,181, issued to Edwin H. Land on Feb. 27, 1951, and U.S. Pat. No. 2,634,886, issued to Edwin H. Land on Apr. 14, 1953.

The image-receiving element comprises an image-receiving layer of opaque or transparent material which is liquid permeable and dyeable from alkaline solutions and which has been illustrated for purposes of simplicity as comprising a single sheet of permeable material, for example, paper. This element, however, may comprise a support upon which at least one liquid-permeable and dyeable layer is mounted. The support layer may have a water-impermeable subcoat over which the stratum of permeable and dyeable material is applied. In certain instances, the dyeable layer may comprise a layer of liquid processing composition which is adapted to remain adhered to the support layer upon stripping.

As examples of useful image-receiving materials, mention may be made of nylon, e.g., N-methoxymethyl-polyhexamethylene adipamide, polyvinyl alcohol, and gelatin, particularly polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinyl pyridine, and other materials of a similar nature, as is well known in the art. The image-receiving element also may contain a development restrainer, e.g., 1-phenyl-5-mercaptotetrazole, as disclosed in the copending application of Howard G. Rogers and Harriet W. Lutes, Ser. No. 50,849, filed Aug. 22, 1960 now U.S. Pat. No. 3,265,498, issued Aug. 9, 1966.

While a rupturable container, such as container **14** in FIG. 1, provides a convenient means for spreading a liquid processing composition between layers of a film unit whereby to permit the processing to be carried out within a camera apparatus, the practices of this invention may be otherwise effected. For example, a photosensitive element, after exposure in suitable apparatus and while preventing further exposure thereafter to actinic light, may be removed from such apparatus and permeated with the liquid processing composition as by coating the composition on said photosensitive element or otherwise wetting said element with the composition following which the permeated, exposed photosensitive element, still without additional exposure to actinic light, is brought into contact with the image-receiving element for image formation in the manner heretofore described.

It is also to be understood that the invention may be successfully practiced without the use of a film-forming material in the liquid processing composition. As an illustration, a non-viscous liquid processing composition is particularly applicable with the processing technique last mentioned above and may be applied to the exposed photosensitive element by imbibition or coating practices and may be similarly applied to the image-receiving element before said elements are brought into superposed relation or contact for carrying out the transfer of non-immobilized color-providing substances.

It will be apparent that the relative proportions of the agents of the diffusion transfer processing composition may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of addition of preservatives, alkalis, silver halide solvents, etc., other than those specifically mentioned. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and, when desirable, adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photosensitive element and/or in the photosensitive emulsion.

In all examples of this specification, percentages of components are given by weight unless otherwise indicated.

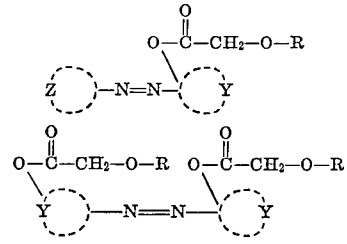
Throughout the specification the expression "positive image" has been used. This expression should not be interpreted in a restrictive sense since it is used primarily for purposes of illustration, in that it defines the image produced on the image-carrying layer as being reversed, in the positive-negative sense, with respect to the image in the photosensitive element. As an example of an alternative meaning for "positive image," assume that the photosensitive element is exposed to actinic light through a negative transparency. In this case, the latent image in the photosensitive element will be a positive and the image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

The dye developers of this invention may be used also in conventional photographic processes, such as tray or tank development of conventional photosensitive films, plates or papers to obtain black and white, monochromatic or toned prints or negatives. By way of examples, a developer composition suitable for such use may comprise an aqueous solution of approximately 1 to 2% of the dye developer, 1% sodium hydroxide, 2% sodium sulfite and 0.05% potassium bromide. After development is completed, any unreacted dye developer is washed out of the photosensitive element, preferably with an alkaline washing medium or other medium in which the unreacted dye developer is soluble. The expression "toned" is used to designate photographic images wherein the silver is retained with the precipitated dye, whereas "monochromatic" is intended to designate dye images free of silver.

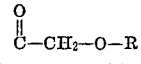
Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process of forming transfer images in color which comprises the steps of exposing a photosensitive element containing a silver halide emulsion and a dye selected from the group consisting of mono- and disazo dyes which contain not less than one and not more than two groups selected from the group represented by the formulae:



wherein each R represents a lower alkyl group and Y represents the atoms necessary to complete an aryl group and Z represents the residue of an azo dye coupler; said dyes further characterized in that they contain not less than one and not more than two dihydroxyphenyl silver halide developing radicals; permeating said photosensitive element with an aqueous alkaline processing composition, effecting thereby solubilization of said dye, and deacylation of said



groups, by hydrolysis, to provide hydroxyl groups and thereby a dye selected from the group consisting of ortho-dihydroxyazo, and ortho, ortho'-dihydroxyazo mono- and disazo dyes which contain not less than one and not more than two dihydroxyphenyl silver halide developing radicals, thereby providing a nonreversible bathochromic shift of the spectral absorption characteristics of said dye, and developement of said exposed silver halide emulsion; immobilizing said dye as a result of development of the exposed areas of said emulsion and thereby forming an

imagewise distribution of mobile dye, as a function of the point-to-point degree of exposure of said emulsion; and transferring, by imbibition, at least a portion of said imagewise distribution of dye to a superposed image-receiving layer to provide thereto a positive dye image.

2. A process of forming transfer images in color as defined in claim **1**, including the step of effecting said development in the presence of an additional, accelerating silver halide developing agent.

3. A process of forming transfer images in color as defined in claim **1** wherein said dye is 4-methoxy-2-[p-(β-hydroquinonyl ethyl) - phenylazo]-naphthalene-1-ethoxy acetate.

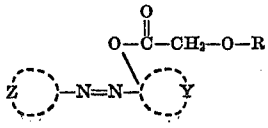
4. A process of forming transfer images in color as defined in claim **1** wherein said dye is 4-isopropoxy-2-[p - (β - hydroquinonyl ethyl)-phenylazo]-naphthalene-1-ethoxy acetate.

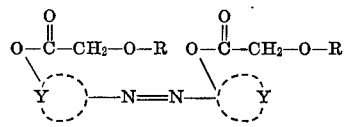
5. A process of forming transfer images in color as defined in claim **1** wherein said dye is 4-isopropoxy-2-[p-(β-hydroquinonyl ethyl)-phenylazo]-naphthalene - 1-octyloxy acetate.

6. A process of forming transfer images in color as defined in claim **1** wherein said dye is 4-isopropoxy-2-[p-(β-hydroquinonyl ethyl)-phenylazo]-naphthalene - 1-propoxy acetate.

7. A process of forming transfer images in color as defined in claim **1** wherein said dye is 4-isopropoxy-2-[p-(β-hydroquinonyl ethyl)-phenylazo]-naphthalene - 1-butoxy acetate.

8. A photographic product which comprises a plurality of layers, at least one of said layers comprising a silver halide emulsion, at least one of said layers containing dye selected from the group consisting of mono- and disazo dyes which contain not less than one and not more than two groups selected from the groups represented by the formulae:





wherein each R represents a lower alkyl group and Y represents the atoms necessary to complete an aryl group and Z represents the residue of anazo dye coupler; and said dyes further characterized in that they contain not less than one and not more than two dihydroxyphenyl silver halide developing radicals.

9. A product as defined in claim **8** wherein said dye is 4 - methoxy - 2-[p-(β-hydroquinonyl ethyl)-phenylazo]-naphthalene-1-ethoxy acetate.

10. A product as defined in claim **8** wherein said dye is 4-isopropoxy-2-[p-(β-hydroquinonyl ethyl)-phenylazo]-naphthalene-1-ethoxy acetate.

11. A product as defined in claim **8** wherein said dye is 4-isopropoxy-2-[p-(β-hydroquinonyl ethyl)-phenylazo]-naphthalene-1-octyloxy acetate.

12. A product as defined in claim **8** wherein said dye is 4-isopropoxy-2-[p-(β-hydroquinonyl ethyl)-phenylazo]-naphthalene-1-propoxy acetate.

13. A product as defined in claim **8** wherein said dye is 4-isopropoxy-2-[p-(β-hydroquinonyl ethyl)-phenylazo]-naphthalene-1-butoxy acetate.

References Cited

UNITED STATES PATENTS

2,860,974	11/1958	Williams	96—9
2,983,606	5/1961	Rogers	96—29
3,307,947	3/1967	Idelson et al.	
3,336,287	8/1967	Idelson et al.	

NORMAN G. TORCHIN, Primary Examiner

T. SURO PICO, Assistant Examiner

U.S. Cl. X.R.

96—3