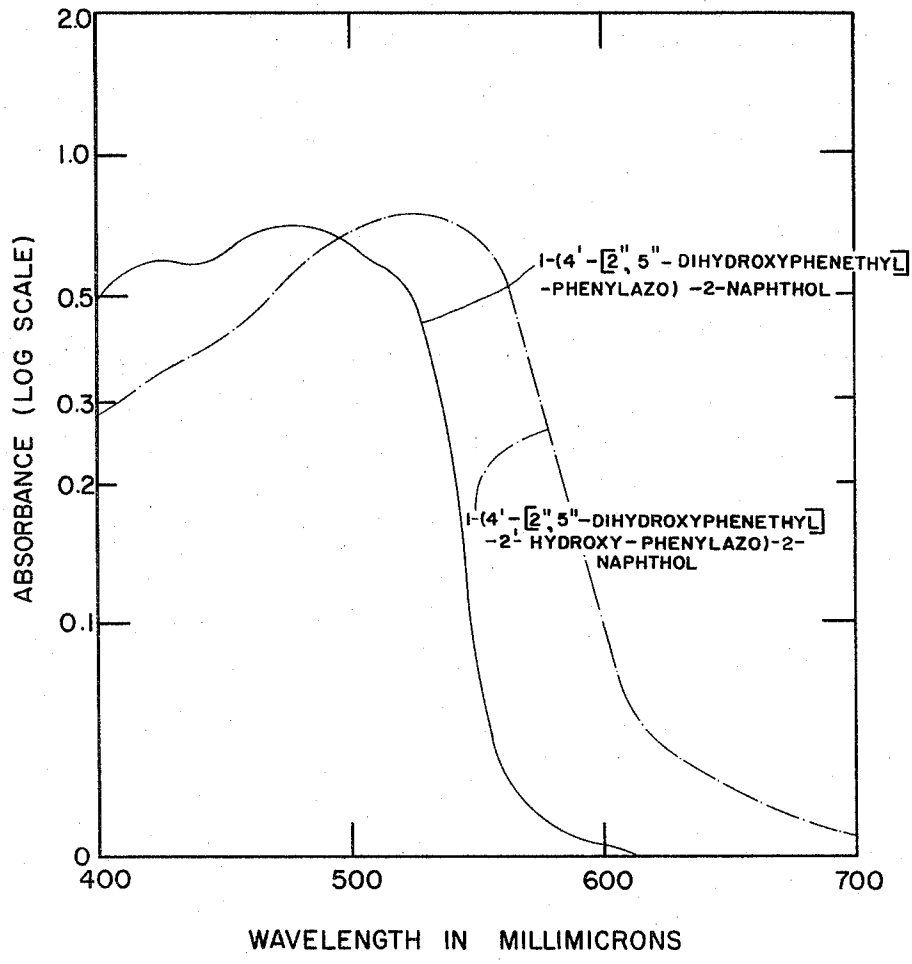
Jan. 17, 1967 M. GREEN ET AL 3,299,041

ORTHO- AND PARA-DIHYDROXYPHENYL SUBSTITUTED MONOAZO DYES

Filed April 15, 1964



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3,299,041

ORTHO- AND PARA-DIHYDROXYPHENYL SUBSTITUTED MONOAZO DYES

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4 Claims. (Cl. 260—197)

The present application is a continuation in part of our copending U.S. application Serial No. 788,893, filed January 26, 1959, and now abandoned.

This invention relates to photography and, more particularly, to compounds, products, compositions and processes for the development of photosensitive silver halide elements.

It is one object of the present invention to provide novel processes and compositions for the development of silver halide emulsions, in which colored developing agents are used to develop a latent image.

Another object is to provide novel processes and compositions for the development of silver halide emulsions, in which the novel developing agent is capable of developing a latent image and imparting a reversed or positive colored image of said latent image to a superposed image-receiving material.

A further object is to provide novel silver halide developing agents, and novel products, processes and compositions suitable for use in preparing monochromatic and multichromatic photographic images by employment of said novel silver halide developing agents.

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

The invention accordingly comprises the processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products and compositions 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: the solid line represents the spectral absorption curve of 1-(4′-[2″,5″-dihydroxyphenethyl]-phenylazo)-2-naphthol and the broken line represents the spectral absorption curve of 1-(4′-[2″,5″-dihydroxyphenethyl]-2′-hydroxy-phenylazo)-2-naphthol as measured over a predetermined portion of the spectrum.

The novel photographic developing agents employed in this invention possess the properties of both a dye and a photographic silver halide developing agent; thus they may be referred to as dye developers. The nature of these dye developers will be described hereinafter.

The photographic processes and compositions disclosed herein are particularly useful in the treatment of an exposed silver halide emulsion, whereby a positive dye image thereof may be imparted to another element, herein referred to as an image-carrying or image-receiving element.

U.S. Patent No. 2,983,606, issued May 9, 1961, discloses diffusion transfer reversal processes wherein a photographic negative material such as a photographic element comprising an exposed silver halide emulsion layer containing a latent image, is processed using a dye developer to impart to an image-receiving element a reversed or positive dye image of said latent image by permeating into said emulsion layer a suitable liquid processing composition and bringing said emulsion layer into superposed relationship with an appropriate image-receiving layer. It is an object of this invention to provide novel dye developers

particularly adapted for advantageous use in such processes.

In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on a sheetlike suport element, which may be utilized as an image-receiving element. In a preferred embodiment, the photosensitive element contains a layer of dye developer, and the liquid processing composition is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed position with an image-receiving element. The liquid processing composition permeates the emulsion to provide a solution of dye developer substantially uniformly distributed therein. As the exposed silver halide emulsion is developed, the oxidation product of the dye developer is immobilized or precipitated in exposed areas, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. 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 solutions. It may also be due, in part, to a tanning effect on the emulsion by the oxidized developing agent and, in part, to localized exhaustion of alkali due to development. 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 circumstances, the layer of the liquid processing composition may be utilized as the image-receiving layer. The latter element receives a depthwise diffusion, from the emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide a reversed or positive, colored image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. Imbibition periods of approximately one minute have been found to give good results, but this contact period may be adjusted where necessary to compensate for variations in temperature or other conditions. The desired positive image is revealed by stripping the image-receiving element from the photosensitive element at the end of the imbibition period.

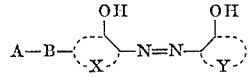
The dye developers of this invention may be utilized in the photosensitive element, for example in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer is placed behind the silver halide emulsion, i.e., on the side of the emulsion adapted to be located most distant from the photographed subject when the emulsion is exposed and preferably also adapted to be most distant from the image-receiving element when in superposed relationship therewith. Placing the dye developer behind the emulsion layer, as in the preferred embodiment, has the advantage of providing increased contrast in the positive image, and also minimizes any light-filtering action by the colored dye developer. In this preferred embodiment, the layer of dye developer may be applied by using a coating solution containing about 0.5 to 8%, by weight, of the dye developer. Similar concentrations may be used if the dye developer is utilized as a component of the liquid processing composition. In an especially useful mode of disposing the dye developers in a photosensitive element, the dye developer is dissolved in a water-immiscible solvent and then dispersed in a gelatin coating solution.

The liquid processing composition above referred to

comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate, and may contain the dye developer. In some instances, it may contain an additional silver halide developing agent. If the liquid processing 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 film-forming material of the type which, when spread over a water-absorbent base, will form 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 inert to an alkali solution, as, for example, hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time may also be used.

The novel compounds of the present invention may be represented by the formula:

(1)



wherein A is an ortho-dihydroxyphenyl or a para-dihydroxyphenyl group; B is a lower alkylene group containing from 1 to 5 carbon atoms, inclusive, such as methylene, ethylene, propylene, isopropylene, butylene, isobutylene, etc., group; X represents the atoms necessary to complete an arylene group selected from the group consisting of a phenylene and a naphthalene group; and Y represents the atoms necessary to complete an aryl group selected from the group consisting of a phenyl and a naphthyl group.

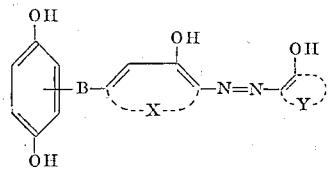
The novel dyes of the present invention may also be characterized by the formula:

(2) A—B—C—N=N—D

wherein A and B have the same significance as previously set forth; C is a phenylene or a naphthalene group; D is a phenyl or a naphthyl group; and each of said C and said D has a hydroxyl group substituted at a nuclear carbon atom in ortho position to the nuclear carbon atom substituted by a nitrogen atom of said —N=N— group.

One preferred group of the compounds of the present invention may be represented by the formula:

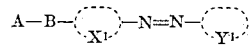
(3)



wherein B, X and Y have the same significance as previously set forth.

In general, the novel dyes of the present invention may be prepared by reacting a monoazo dye of the formula:

(4)



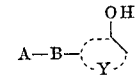
wherein A and B have the same significance as previously noted; X^1 represents the atoms necessary to complete a phenylene or a naphthalene group; Y^1 represents the atoms necessary to complete a phenyl or naphthyl group; and one of X^1 and Y^1 possesses a hydroxyl group substituted in ortho position to the azo group; and wherein A is preferably in the form of a protected derivative of a dihydroxyphenyl group, for example, an ester thereof; in the presence of copper, as, for example, an ionizable copper salt such as cupric sulfate, cupric chloride, or cupric acetate, with an oxygenating agent such as hydrogen peroxide, alkali peroxides, perborates, percarbonates, organic peracids, acyl peroxides, or chromic acid.

The resultant copper complexed dye may be demetallized, as, for example, by hydrolysis in the presence of

acid, for example, a mineral acid such as hydrochloric acid, to yield the dyes of Formula 1.

The novel dyes of the present invention also may be prepared by diazotizing an ortho-aminophenol or naphthol and coupling the diazotization product thereof into a coupling component of the formula:

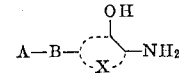
(5)



wherein A, B and Y have the same significance as previously noted, wherein A is preferably in the form of the protected derivative thereof and the para position of group Y, with respect to the hydroxyl group, is preferably effectively blocked from entering the coupling reaction, said coupling being effected in ortho position to the designated hydroxyl group on said coupling component.

Still another preparation of the novel dyes of the present invention comprises diazotizing an ortho-aminophenol or naphthol of the formula:

(6)



wherein A, B and X have the same significance as previously stated and wherein A is preferably in the form of a protected derivative thereof; and coupling the diazotization product thereof into a phenol or naphthol coupling component in ortho position to a hydroxyl group.

A second diazotization and coupling reaction may be employed, where desired, to provide disazo dyes.

As illustrations of suitable coupling components or couplers, mention may be made of couplers such as phenols and naphthols having a free position ortho to the hydroxyl group, including the substituted derivatives thereof, and particularly those couplers having a blocked para position.

Accordingly, in the preceding formulae, one of X and Y represents the atoms necessary to complete the radical of a diazotizable aromatic amine and the other of X and Y represents the atoms necessary to complete the radical of an aromatic azo dye coupler, where the aromatic nucleus of both X and Y comprises a benzene or naphthalene nucleus.

In order to provide the aforementioned esterified derivative of the designated dihydroxyphenyl group, represented by the term A in the pertinent formulae, the hydroxyl radicals may be acylated, with a conventional acylating agent, prior to reaction, thus insulating said radicals from the reaction. Subsequent to reaction and prior to use as a photographic dye developer, the protecting groups, for example, the acyl groups, may be removed by hydrolysis in the presence of alkali to yield the free hydroxyl radicals necessary for the development of a silver halide photographic latent image.

As examples of ortho-hydroxy substituted monoazo dyes for use in the preparation of the novel dye developers of the present invention, mention may be made of the following:

p-(1-hydroxy-4-methoxy-2-naphthaleneazo)-phenethylcatechol

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

2-[4′-(2″,5″-dihydroxyphenethyl)-phenylazo]-4-sulfo-1-naphthol

2-[2″,5″-dihydroxyphenethyl)-phenylazo]-4-acetamido-1-naphthol

2-[4′-(2″,5″-dihydroxyphenethyl)-phenylazo]-4-amino-1-naphthol

2-[4′-(2″,5″-dihydroxyphenethyl)-phenylazo]-4-methoxy-1-naphthol

2-[4′-(2″,5″-dihydroxyphenethyl)-phenylazo]-4-ethoxy-1-naphthol

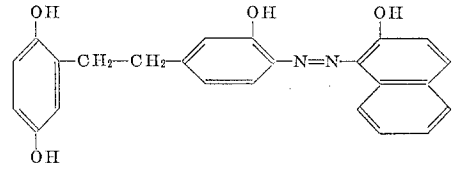
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-isopropoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-cyclohexoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-hexyloxy-1-naphthol
2-[4'-(3'',4''-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol
2-[4'-(2'',5''-dihydroxy-3''-methyl-phenethyl)-phenylazo]-4-n-propoxy-1-naphthol
2-[4'-(2'',5''-dihydroxy-3'',4'',6''-trimethyl-phenethyl)-phenylazo]-4-methoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-β-hydroxyethoxy-1-naphthol
2-[4'-(2'',5''-dihydroxy-4''-methyl-phenethyl)-phenylazo]-4-methoxy-1-naphthol
2-[4'-(2'',5''-dihydroxy-3'',4''-dimethyl-phenethyl)-phenylazo]-4-methoxy-1-naphthol
2-[4'-(2'',5''-dihydroxy-4''-methyl-phenethyl)-phenylazo]-4-N,N-diethyl-sulfonamido-1-naphthol
2-[4'-(2'',5''-dihydroxyphenylpropyl)-phenylazo]-4-n-propoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenylisobutyl)-phenylazo]-4-methoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-naphthylazo]-4-methoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-β-chloroethoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-ethoxyethoxyethoxy-1-naphthol
2-[3'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol
4-[4'1(2'',5''-dihydroxyphenethyl)-phenylazo]-5-hydroxyacenaphthene
2-[4'-(2'',5''1dihydroxyphenethyl)-phenylazo]-4-N-methyl-N1phenysulfonamido-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-3,6-bis-N,N-diethylsulfonamido-8-N-p-tolylsulfonamido-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-isobutoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-6'-methyl-phenylazo]-4-methoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenylpropyl)-phenylazo]-4-methoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-benzoyl-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-phenyl-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-chloro-1-phenol
1-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-6-methoxy-2-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-trifluoroethoxy-1-naphthol
1-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-5-methoxy-2-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-ethyl-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-methyl-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-sec.butoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-tert.butoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-butoxyethoxy-1-naphthol
2-[4'(2'',5''-dihydroxyphenethyl)-phenylazo]-4-methoxytriethoxy-1-naphthol
2-[4'-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-n-butoxy-1-naphthol
2-[p-(2',5'-dihydroxyphenethyl)-phenylazo-4-γ-phenylpropoxy-1-naphthol

2-[p-(2',5'-dihydroxyphenylpropyl)-phenylazo]-4-ethoxy-1-naphthol
4-acetyl-2-(4'-[2'',5''-dihydroxyphenethyl]-phenylazo)-1-naphthol
1-(4'-[2'',5''-dihydroxyphenethyl]-phenylazo)-3-(2',5'-dimethoxyphenylcarbamyl)-2-naphthol

the preparations of which are disclosed in the copending U.S. application of Elkan R. Blout, Milton Green and Howard G. Rogers, Serial No. 145,978, filed October 18, 1961, and now U.S. Patent No. 3,134,764.

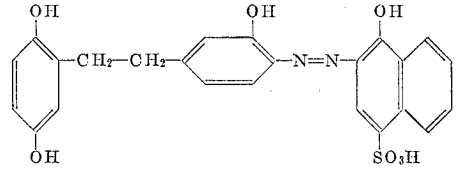
As examples of compounds contemplated within the scope of the present invention, mention may be made of the following:

(I)



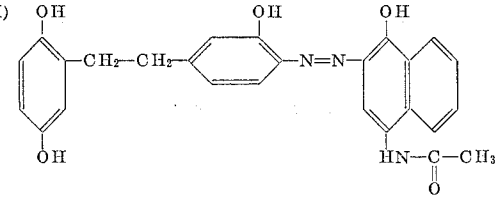
1-(4'-[2'',5''-dihydroxyphenethyl]-2'-hydroxy-phenylazo)-2-naphthol

(II)



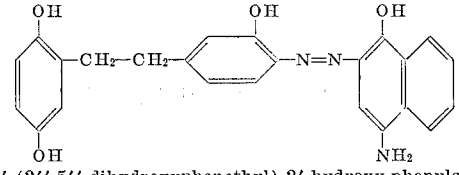
2-[4'-(2'',5''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-sulfo-1-naphthol

(III)



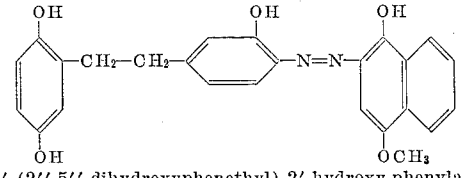
2-[4'-(2'',5''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-acetamido-1-naphthol

(IV)



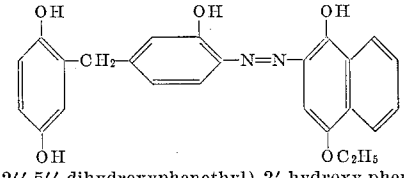
2-[4'-(2'',5''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-amino-1-naphthol

(V)



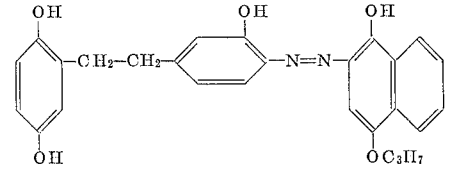
2-[4'-(2'',5''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-methoxy-1-naphthol

(VI)



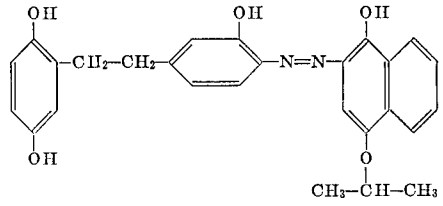
2-[4'-(2'',5''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-ethoxy-1-naphthol

(VII)



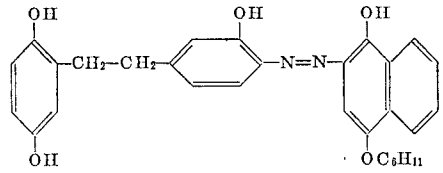
2-[4'-(2'',5''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-n-propoxy-1-naphthol

(VIII)



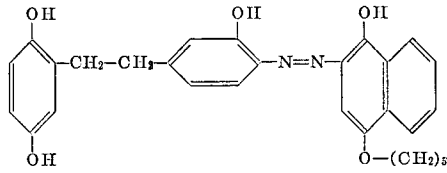
2-[4'-(2'',5''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-isopropoxy-1-naphthol

(IX)



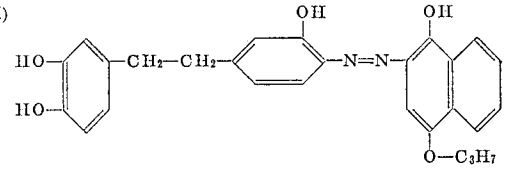
2-[4'-(2'',5''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-cyclohexyloxy-1-naphthol

(X)



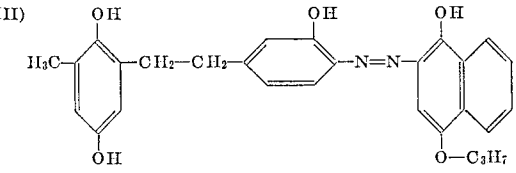
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(XI)



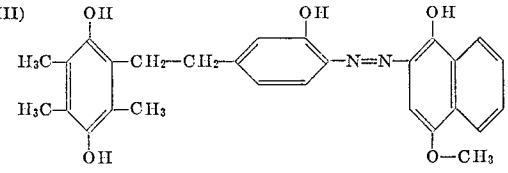
2-[4'(3'',4''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-n-propoxy-1-naphthol

(XII)



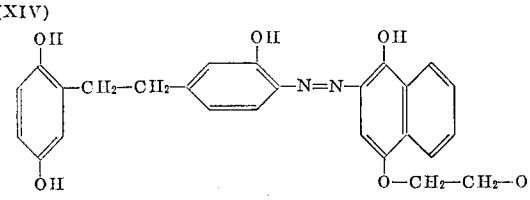
2-[4'-(2'',5''-dihydroxy-3''-methyl-phenethyl)-2'-hydroxy-phenylazo]-4-n-propoxy-1-naphthol

(XIII)



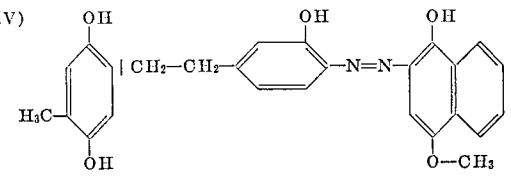
2-[4'-(2'',5''-dihydroxy-3'',4'',6''-trimethylphenethyl)-2'-hydroxy-phenylazo]-4-methoxy-1-naphthol

(XIV)



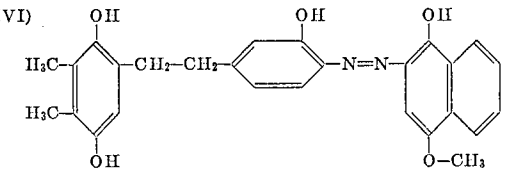
2-[4'-(2'',5''-dihydroxyphenethyl)-2'-hydroxy-phenylazo]-4-β-hydroxyethoxy-1-naphthol

(XV)



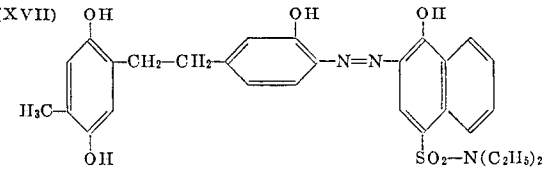
2-[4 (2'',5''-dihydroxy-4''-methyl-phenethyl)-2'-hydroxy-phenylazo]-4-methoxy-1-naphthol

(XVI)



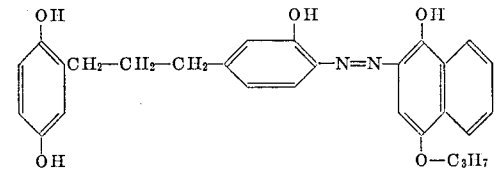
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(XVII)



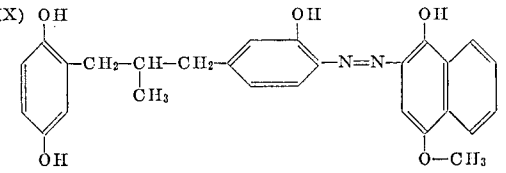
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(XVIII)



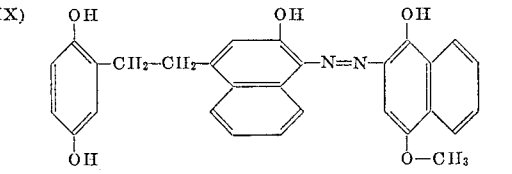
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(XIX)



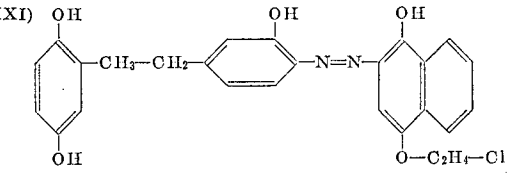
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(XX)



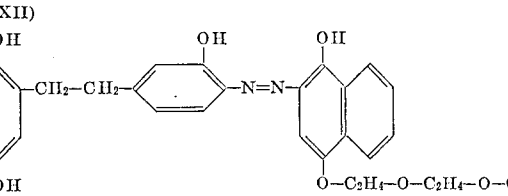
2-[4'(2'',5''-dihydroxyphenethyl)-2'-hydroxy-naphthyl-azo]-4-methoxy-1-naphthol

(XXI)



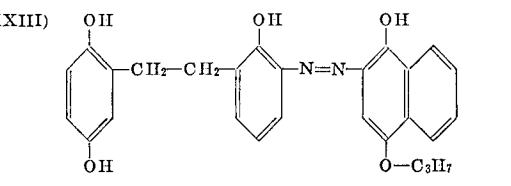
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(XXII)



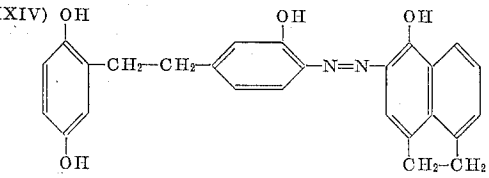
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(XXIII)



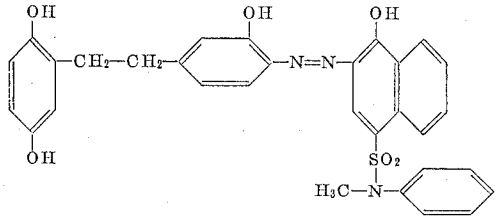
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(XXIV)



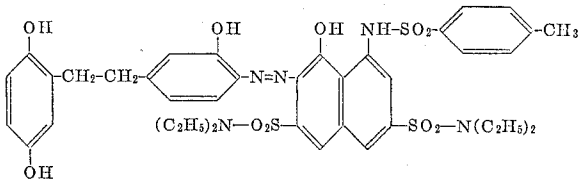
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(XXV)



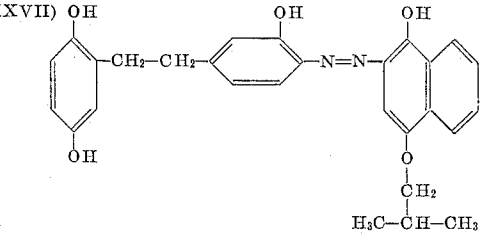
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(XXVI)



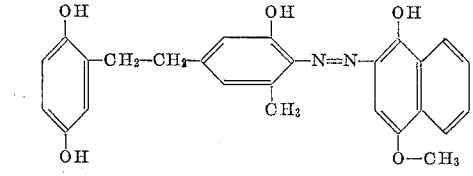
2-[4′-(2″,5″-dihydroxyphenethyl) - 2′ - hydroxy-phenylazo]-3,6 - bis - N,N-diethylsulfonamido-8-N-p-tolylsulfonamido-1-naphthol

(XXVII)



2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenylazo]-4-isobutoxy-1-naphthol

(XXVIII)



2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-6-methyl-phenylazo]-4-methoxy-1-naphthol

(XXIX)

2-[4′-(2″,5″-dihydroxyphenylpropyl)-2′-hydroxy-phenyl-azo]-4-methoxy-1-naphthol

(XXX)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-benzoyl-1-naphthol

(XXXI)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-phenyl-1-naphthol

(XXXII)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-chloro-1-phenol

(XXXIII)

1-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-6-methoxy-2-naphthol

(XXXIV)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-trifluoro-ethoxy-1-naphthol

(XXXV)

1-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-5-methoxy-2-naphthol

(XXXVI)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxyphenyl-azo]-4-ethyl-1-naphthol

(XXXVII)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-methyl-1-naphthol

(XXXVIII)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-sec. butoxy-1-naphthol

(XXXIX)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-tert. butoxy-1-naphthol

(XL)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-butoxy-ethoxy-1-naphthol

(XLI)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-methoxy-triethoxy-1-naphthol

(XLII)

2-[4′-(2″,5″-dihydroxyphenethyl)-2′-hydroxy-phenyl-azo]-4-n-butoxy-1-naphthol

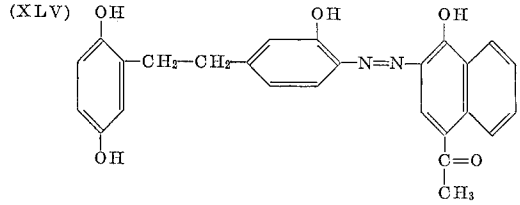
(XLIII)

2-[p-(2′,5′-dihydroxyphenethyl)-2′-hydroxy-phenylazo]-4-γ-phenylpropoxy-1-naphthol

(XLIV)

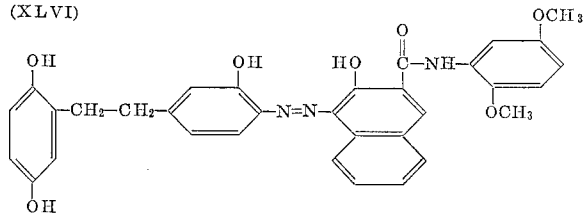
2-[p-(2′,5′-dihydroxyphenylpropyl)-2′-hydroxy-phenyl-azo]-4-ethoxy-1-naphthol

(XLV)



4-acetyl-2-(4′-[2″,5″-dihydroxyphenethyl]-2′-hydroxy-phenylazo)-1-naphthol

(XLVI)



1-(4′-[2″,5″-dihydroxyphenethyl]-2′-hydroxy-phenylazo)-3-(2′,5′-dimethoxyphenylcarbamyl)-2-naphthol

As will be recognized from examination of the preceding illustrative compounds, the respective aromatic groups may be substituted by those substituents or radicals customary in the art, for example, alkyl, sulfo, alkoxy, aryl, aryloxy, amino, keto, alkylamino, arylamino, hydroxyl, alkylamido, arylamido, halo, carboalkoxy, carboxamido, sulfonamido, etc.

The invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative preparations and photographic utilization of the novel compounds of this invention, which,

however, are not limited to the details therein set forth and are intended to be illustrative only.

Example 1

A solution of 1.38 g. of cupric sulfate pentahydrate, 1.5 cc. of 20% acetic acid, and 1.08 g. of anhydrous sodium acetate in 10 cc. of water, is added at 80° C. to a solution of 0.005 mole of 1-(4'-[2'',5''-bis-acetoxyphenethyl]-phenylazo)-2-naphthol in 150 cc. of diethylene glycol. A solution of 4 cc. of 30% hydrogen peroxide in 10 cc. of water is added at 80° C. to the resultant mixture dropwise over a period of 2 hours. The resultant solution is stirred overnight, poured into water and the precipitate formed filtered off. The precipitate is then dissolved in a dimethyl formamide solution containing 0.025 mole of cupric acetate monohydrate. Water is added to the solution until precipitation is complete.

The product, copper complexed 1-(4'-[2'',5''-bis-acetoxyphenethyl]-2'-hydroxy-phenylazo)-2-naphthol monohydrate, is a magenta dye the spectral absorption curve of which exhibits a $\lambda_{max.}$ at 546 mμ in pyridine; ϵ=19,000.

Analysis of the product.—Calculated as $C_{28}H_{24}O_7N_2Cu$: C, 59.6%; H, 4.3%; N. 5.0%; Cu, 11.3%. Found: C, 59.7%; H, 4.0%; N, 4.7%; Cu, 11.3%.

The product is dissolved in a methyl Cellosolve solution containing 10% concentrated hydrochloric acid. Water is added to the solution until a precipitate is formed. The resultant precipitate, 1-(4'-[2'',5''-bis-acetoxyphenethyl]-2'-hydroxy - phenylazo) - 2 - naphthol, is filtered off.

The precipitate is dissolved in methanol and hydrolyzed with an aqueous solution of sodium hydroxide. Precipitation with hydrochloric acid gives the desired dye developer, 1 - (4' - [2'',5''-dihydroxyphenethyl]-2'-hydroxyphenylazo)-2-naphthol [Formula I], a magenta dye the spectral absorption curve of which exhibits a $\lambda_{max.}$ at 525 mμ in pyridine; ϵ=14,400.

Example 2

A solution of 21 g. of 2,5-bis-acetoxyphenethyl aniline hydrochloride and 4.8 g. of sodium nitrite is diazotized. The product thereof is coupled into 11.2 g. of 4-acetyl-α-naphthol in a 1:3 mixture of acetone and water containing 5 cc. of pyridine and 17 g. of sodium bicarbonate. The solid product, 4-acetyl-2-(4'-[2'',5''-bis-acetoxyphenethyl]-phenylazo)-1-naphthol, $\lambda_{max.}$ 504 mμ in methyl Cellosolve, is filtered off, dissolved in methyl Cellosolve and precipitated with a saline solution containing 1% hydrochloric acid. The precipitate is filtered off, redissolved in methyl Cellosolve and reprecipitated with a saline-sodium acetate solution. The precipitate is filtered off, dissolved in a minimum amount of acetone. This solution is poured in a thin stream into 1000 cc. of diethylene glycol maintained at 80 to 90° C. with constant stirring. The resultant solution and a solution comprising 0.9 cc. of acetic acid and 3.1 g. of sodium acetate in 30 cc. of water are added simultaneously to a solution of 5.5 g. of cupric sulfate pentahydrate in 20 cc. of water. A solution of 16 cc. of 30% hydrogen peroxide in 40 cc. of water is added dropwise over a period of 2 to 3 hours at 80 to 90° C. with constant stirring. The resultant solution is stirred for 12 hours and a product precipitated with saline solution. The precipitate is twice dissolved in methyl Cellosolve containing 5% hydrochloric acid and reprecipitated with saline solution. The resultant precipitate, 4 - acetyl - 2 - (4'-[2'',5''-diacetoxyphenethyl]-2'-hydroxy-phenylazo-1-naphthol, is twice redissolved in methyl Cellosolve and reprecipitated with a saline-sodium acetate solution.

The product is suspended in methanol and treated with 10 cc. of a 10% sodium hydroxide solution/g. of product under nitrogen. The solution is warmed on a steam bath under nitrogen and neutralized with acetic acid. The desired dye developer, 4-acetyl-2-(4'-[2'',5''-dihydroxyphenethyl]-2'-hydroxy-phenylazo)-1-naphthol, [Formula XLV], a magenta dye the spectral absorption curve of which exhibits a $\lambda_{max.}$ at 520 mμ in methyl Cellosolve; 527 mμ in pyridine, is filtered off, dissolved in methyl Cellosolve, precipitated with a saline-sodium acetate solution, washed with water, and dried.

Example 3

A solution of 21 g. of 2,5-bis-acetoxyphenethyl aniline hydrochloride and 4.8 g. of sodium nitrite is diazotized. The product thereof is coupled into 19.4 g. of 3-(2',5'-dimethoxyphenylcarbamyl)-β-naphthol in a 1:3 mixture of acetone and water containing 5 cc. of pyridine and 17 g. of sodium bicarbonate. The solid product, 1-(4'-[2'',5''-bis - acetoxyphenethyl] - phenylazo)-3-(2',5'-dimethoxyphenylcarbamyl)-2-naphthol, melting point 125.5 to 126° C., $\lambda_{max.}$ 510 and 534 mμ in methyl Cellosolve; ϵ=29,000 and 28,000, is filtered off, dissolved in methyl Cellosolve and precipitated with a saline solution containing 1% hydrochloric acid. The precipitate is filtered of, redissolved in methyl Cellosolve and reprecipitated with a saline-sodium acetate solution. The precipitate is filtered off, dissolved in a minimum amount of acetone. This solution is poured in a thin stream into 1000 cc. of diethylene glycol maintained at 80 to 90° C. with constant stirring. The resultant solution and a solution comprising 0.9 cc. of acetic acid and 31 g. of sodium acetate in 30 cc. of water are added simultaneously to a solution of 5.5 g. of cupric sulfate pentahydrate in 20 cc. of water. A solution of 16 cc. of 30% hydrogen peroxide in 40 cc. of water is added dropwise over a period of 2 to 3 hours at 80 to 90° C. with constant stirring. The resultant solution is stirred for 12 hours and a product precipitated with saline solution. The precipitate is twice dissolved in methyl Cellosolve containing 5% hydrochloric acid and reprecipitated with saline solution. The precipitate, 1 - (4' - [2'',5''-bis-acetoxyphenethyl]-2'-hydroxy - phenylazo)-3-(2',5'-dimethoxyphenylcarbamyl)-2-naphthol, melting point 162 to 165° C., $\lambda_{max.}$ at 527 and 554 mμ in methyl Cellosolve, is twice redissolved in methyl Cellosolve and reprecipitated with a saline-sodium acetate solution.

The product is suspended in methanol and treated with 10 cc. of a 10% sodium hydroxide solution/g. of product under nitrogen. The solution is warmed on a steam bath under nitrogen and neutralized with acetic acid. The desired dye developer, 1-(4'-[2'',5''-dihydroxyphenethyl]-2' - hydroxy-phenylazo) - 3 - (2',5' - dimethoxyphenylcarbamyl)-2-naphthol [Formula XLVI], a magneta dye, is filtered off, dissolved in methyl Cellosolve, precipitated with a saline-sodium acetate solution, washed with water and dried.

Substitution of a second hydroxyl group ortho to an azo linkage in the respective dye molecule provides a pronounced bathochromic shift in the spectral absorption characteristics of the resulting compound. For example, 1-(4'-[2'',5''-dihydroxyphenethyl]-phenylazo) - 2 - naphthol, an ortho-hydroxyazo magenta dye developer, exhibits a spectral absorption which discloses a $\lambda_{max.}$ at 480 mμ, ϵ=14,000, in methyl Cellosolve, in contradistinction to the spectral absorption curve of the corresponding ortho,ortho'-dihydroxyazo dye developer disclosed in Example 2. The magnitude of the aforementioned bathochromic shift and characteristics of the resultant spectral curve are illustrated in the drawing wherein a portion of the spectral curve of the ortho-ortho'-dihydroxyazo product of Example 2 (broken line) is superposed on the spectral curve of the last-mentioned corresponding ortho-hydroxyazo dye developer (solid line).

In photographic subtractive color processes, and particularly photographic multicolor processes, image dyes are desired which possess the characteristics of relatively high absorption of actinic radiation over a specific segment of the spectral range, which segment preferably is complementary to the sensitivity spectrum of its specifically associated photosensitive emulsion, as well as possessing

substantially no absorption over the remaining areas of the visible spectrum, for purposes of accurate color rendition.

Specifically, in an integral multilayer photosensitive element which comprises three appropirately sensitized silver halide emulsions having associated therewith, respectively, a yellow, a magenta, and a cyan dye, the preferred yellow dye would be one with a relatively high absorption in the blue area of the spectrum and thus would affect and/or control only the amount of blue light passing through the image dye-containing layer but would have substantially little, if any, influence on the passage of red and green light. The magenta dye should preferably be one with a 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 the layer containing the image dye but would have substantially little, if any, influence on the passage of red or blue light. The cyan image dye should then be one with a relatively high absorption in the red area of the spectrum and thus would affect and/or control only the amount of red light passing through the image dye-containing layer but would have substantially little influence on the passage of blue or green light.

Therefore, in an integral multilayer photosensitive element of the type described, which preferably comprises, in order, from the exposure surface, a blue-sensitive silver halide emulsion, an associated yellow image dye, a green-sensitive silver halide emulsion, an associated magentia image dye, a red-sensitive silver halide emulsion, and an associated cyan image dye, upon exposure to actinic radiation comprising the visible spectrum, the respective yellow image dye would preferably absorb only the blue portion of the spectrum, said dye's absorption spectrum being substantially complementary to the sensitivity spectrum of its associated emulsion, thus allowing undiminished red and green wave lengths to contact with the subsequent green-sensitive silver halide emulsion stratum. The magenta image dye, in turn, would preferably absorb only the green wave lengths of the spectrum, complementary to the sensitivity spectrum of its associated emulsion, and thus allow red wave lengths to contact, with undiminished energy, the subsequent red-sensitive silver halide emulsion stratum. It will be recognized, however, that the specific deposition and order of the respective selectively sensitized emulsion strata and their associated image dyes may be chosen in accordance with the varied relationships disclosed in the art.

By reason of the present invention, a class of dyes having desired spectral absorption characteristics may be synthesized for utilization in photographic color processes. Specifically, various desired image dyes of the type set forth in the aforementioned copending U.S. application Serial No. 145,978 which have extremely desirable characteristics with regard to chemical and light stability, photographic kinetics, and/or economical methods of production, but which possess an absorption spectrum at wave lengths less than that optimum for employment in photographic color processes, may be treated in accordance with the present invention to provide a bathochromic spectral absorption shift sufficient to make the employment of such dyes photographically feasible and desirable, as illustrated in the drawing.

The novel dyes of this invention are to be additionally distinguished from the compounds disclosed in the prior art by the presence of the alkylene group B in combination with the state o,o'-dihydroxyazo configuration. The presence of this alkylene group B insulates the dihydroxyphenyl group A from conjugation with the chromophoric system of the rest of the molecule, and effectively avoids pH color sensitivity resulting from such conjugation. In addition, the presence of the alkylene group B helps to avoid color changes in the transfer dye image should the transferred dye developer subsequently be oxidized. The dye developers of this invention are additionally superior to dye developers such as orthohydroxyphenylazohydroquinone in that the resulting dye transfer images are more stable, particularly as to heat and humidity, and also to color changes from changes in pH.

As previously mentioned, the novel compounds of this invention are useful dye developers. In the following example, 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. This example is intended to be illustrated only of the photographic use of the dye developers and should not be construed as limiting the invention in any way.

Example 5

A photosensitive element is prepared by coating a gelatin-coated film base with a solution containing 4% of 1-(4'-[2'',5''-dihydroxyphenethyl] - 2' - hydroxy - phenylazo)-2-naphthol [Formula I as prepared in Example 1], in a 4% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran. After this coating has dried, a silver iodobromide emulsion is applied. This photosensitive element is exposed and processed by spreading an aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.75
1-phenyl-3-pyrazolidone	0.2
Sodium hydroxide	2.5
Potassium bromide	0.2

between said photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element comprises a cellulose acetate-coated baryta paper which has been coated with a solution comprising 4% N-methoxymethyl polyhexamethylene adipamide in 80% aqueous ethanol. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a magenta positive dye image of the photographed subject.

Example 6

A photosensitive element is prepared by coating a gelatin-coated film base with a solution containing 3% of 4-acetyl - 2 - (4' - [β - (hydroquinonyl) - ethyl]-2'-hydroxyphenylazo)-1-naphthol [Formula XLV as prepared in Example 2], in a 2% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran. After this coating has dried, a silver iodobromide emulsion is applied. This photosensitive emulsion is exposed and processed according to the procedure of Example 5 with an aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
1-phenyl-3-pyrazolidone	0.6
Sodium hydroxide	2.0
2,5-bis-ethyleneiminohydroquinone	0.4
6-nitrobenzimidazole	0.12

After an imbibition period of approximately one minute, the image-receiving element is separated and contains an orange-red dye image of the photographed subject.

The novel ortho,ortho'-dihydroxyazo dye developers of the present invention comprise an especially desirable class of compounds which find extensive application in the photographic diffusion-transfer processes, employing dye developers containing chelatable configurations, disclosed and claimed in the copending U.S. application of Howard G. Rogers, Serial No. 788,742, filed January 26, 1959 and now U.S. Patent No. 3,196,014, and U.S. Patent No. 3,081,167, issued March 12, 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'-methylphenylhy-

droquinone, etc. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as a 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed in U.S. Patent 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 quarternary ammonium compound, in accordance with the processes disclosed in the copending U.S. application of Milton Green and Howard G. Rogers, Serial No. 50,851, filed August 22, 1960, and now U.S. Patent No. 3,173,768.

In products employed in the diffusion transfer processes 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, or similar camera structure such, for example, as the roll film-type camera forming the subject matter of U.S. Patent No. 2,435,717 or the film pack-type camera forming the subject matter of U.S. Patent 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 require 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 is well understood in the art; see, for example, U.S. Patent No. 2,543,181, issued February 27, 1951, and U.S. Patent No. 2,634,886, issued April 14, 1953.

While a rupturable container 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 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 or addition of preservatives, alkalies, 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 are particularly useful in integral multilayer photosensitive elements for use in multicolor diffusion transfer processes for the reasons previously enumerated. As an example of such photosensitive elements, mention may be made of the photosensitive elements disclosed in the aforementioned U.S. Patent No. 2,983,606, and particularly with reference to FIG. 9 of the patent's drawings, 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 element. 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 silver halide emulsion stratum, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. In one of the preferred embodiments of photosensitive elements of this type, the dye developers are disposed in separate alkali-permeable layers behind the photosensitive silver halide emulsion stratum with which they are associated.

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 example, 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.

It should be noted that the dye developers of this invention are self-sufficient to provide the desired color image and do not depend upon coupling reactions to produce the desired color. They thus provide a complete departure from conventional photographic color processes in which the color is produced by a coupling reaction involving the oxidized developing agent.

The dye developers of this invention are preferably selected with a view to their usefulness in color photography and, in particular, their ability to provide the desired subtractive colors, i.e., magenta, yellow or cyan.

It will be apparent that, by appropriate selection of the image-receiving element from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency. Likewise, the inventive concepts herein set forth are adaptable for multicolor work by the use of special photographic materials, for example, film materials of the type containing two or more photosensitized elements associated with an appropriate number of image-receiving elements and adapted to be treated with one or more liquid processing compositions, appropriate dye developers suitable to impart the desired subtractive colors being incorporated in the photosensitized elements or in the liquid processing compositions. Examples of such photographic materials are disclosed in U.S. Patent No. 2,647,049 to Edwin H. Land.

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-vinylpyridine. 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, Serial No. 50,849, filed August 22, 1960.

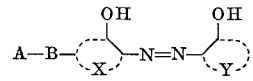
The inventive concepts herein set forth are also adaptable for the formation of colored images in accordance with the photographic products and processes described in U.S. Patent No. 2,968,554, issued January 17, 1961 to Edwin H. Land.

In the preceding portions of the specification the expression "color" has been frequently used. This expression 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.

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

What is claimed is:

1. An azo dye developer of the formula:



wherein A is selected from the group consisting of an ortho-dihydroxyphenyl group and a para-dihydroxyphenyl group; B is a lower alkylene group containing from 1 to 5 carbon atoms, inclusive; and one of X and Y represents the atoms necessary to complete a radical of a diazotizable aromatic amine and the other of said X and Y represents the atoms necessary to complete an aromatic azo dye coupler, wherein the aromatic nucleus of both of said X and Y is selected from the group consisting of benzene and naphthalene nuclei.

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

3. 4 - acetyl - 2 - (4' - [2'',5'' - dihydroxyphenylethyl] - 2' - hydroxy - phenylazo) - 1 - naphthol.

4. 1 - (4' - [2'',5'' - dihydroxyphenethyl] - 2' - hydroxyphenylazo) - 3 - (2',5' - dimethoxyphenylcarbamyl) - 2 - naphthol.

References Cited by the Examiner

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2,709,697	5/1955	Seruto	260—163

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