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3,236,643

PHOTOGRAPHIC PROCESSES, COMPOSITIONS AND PRODUCTS

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No Drawing. Filed May 4, 1962, Ser. No. 192,355
28 Claims. (Cl. 96—29)

This application is in part a continuation of my co-pending application, Serial No. 612,055, filed September 25, 1956 (now abandoned).

This invention relates to photography and more particularly to 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 novel colored silver halide developing agents are used.

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

Further objects are to provide said novel silver halide developing agents, and novel products, processes and compositions suitable for use in preparing monochromatic and multichromatic photographic images by the 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.

The objects of this invention may be accomplished by the use of certain novel dyes which have the ability to develop an exposed silver halide emulsion; thus these dyes may be referred to as dye developers. These novel dyes or dye developers will be further described hereinafter.

The dye developers and the photographic processes and compositions disclosed herein are particularly useful in the treatment of an exposed silver halide emulsion, whereby a positive dye image 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, to Howard G. Rogers, discloses diffusion transfer processes wherein a photographic negative material, such as a photographic element comprising an exposed silver halide emulsion, is developed in the presence of a dye developer to impart to an image-receiving layer a reversed or positive dye image of the developed image by permeating into said emulsion a suitable liquid processing composition and bringing said emulsion into superposed relationship with an appropriate image-receiving layer. The inventive concepts herein set forth provide novel dye de-

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velopers which may be advantageously used 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 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 situ with the developed silver, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. This immobilization is apparently due, at least in part, to 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. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer. The image-receiving layer 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 or negative 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 separating the image-receiving layer from the silver halide emulsion at the end of the imbibition period.

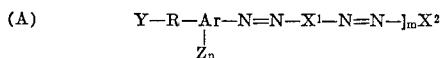
The dye developers of this invention may be utilized in the photosensitive element, for example, in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer 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 layer 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, e.g., 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 the photosensitive elements, the dye

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developer is dissolved in a water-immiscible solvent and then dispersed in a gelatin coating solution.

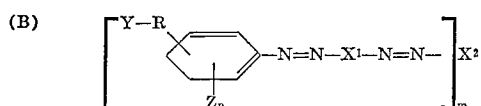
The liquid processing composition which is used in the processes herein disclosed comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate, and may contain the dye developer. In some instances, it may contain an additional silver 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, a 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 azo dye developers of this invention may be represented by the formula:



wherein R is an alkylene group, preferably a lower alkylene group containing no more than five carbons and more preferably an ethylene ($-\text{CH}_2\text{CH}_2-$) or trimethylene ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) group; Ar is an aryl nucleus, such as benzene or naphthalene nucleus; each Z is an alkyl group, preferably a lower alkyl group such as methyl or ethyl, an alkoxy group, preferably a lower alkoxy group such as methoxy, or a halogen, such as chlorine; n is 0, 1 or 2; Y is a para-dihydroxyphenyl or an ortho-dihydroxyphenyl group which also may be nuclear substituted by alkyl or halogen groups; m is 1 or 2; and X^1 and X^2 are each the radical of an azo coupling component, which coupling component or coupler may be the same or different, i.e., similar or dissimilar.

In a preferred embodiment, the aryl nucleus Ar is a benzene nucleus, and such dye developers may be represented by the formula:



wherein Y, R, Z, n , X^1 , X^2 and m have the same meaning as above.

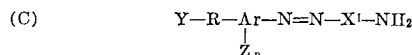
As illustrations of suitable coupling components or couplers from which X^1 and X^2 may be derived, mention may be made of phenols and aromatic amines having a free position ortho or para to the hydroxyl or amino group, e.g., phenol, anilines, naphthols, anthrols, naphthylamines, etc.; heterocyclic aromatic compounds containing hydroxyl or amino groups, such as pyrazolones or pyrroles; aliphatic or alicyclic activated methylene couplers, i.e., compounds having an aliphatic or alicyclic methylene group activated by two adjacent keto, aldehyde, ester or nitrile groups, which may be the same or different, or a keto, aldehyde, ester or nitrile group in combination with an amide group, e.g., 1,3-diketones or β -ketonic acid arylamides; etc., and substituted derivatives thereof. Examples of groups which may be present in such substituted derivatives include alkyl, sulfo, alkoxy, aryl, aryloxy, amino, keto, alkylamino, arylamino, hydroxyl, cyano, alkylamido, arylamido, carbalkoxy, carbamido, sulfonamido, etc.

As used herein with reference to X^1 and X^2 , the expression "radical of a phenolic coupler" is intended to refer to hydroxyphenyl, hydroxynaphthyl, hydroxyan-

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thryl, etc. radicals, and substituted derivatives thereof; the expression "radical of an aromatic amino coupler" is intended to refer to aminophenyl, aminonaphthyl, etc. radicals, and substituted derivatives thereof; and the expressions "radical of a heterocyclic aromatic coupler," "radical of an aliphatic activated methylene coupler" and "radical of an alicyclic activated methylene coupler" are to be similarly construed.

The novel dye developers of this invention may be prepared by diazotizing a compound of the formula:



wherein Ar, R, Z, X^1 , n and Y have the same meaning as above, and particularly a derivative wherein the hydroxyl groups of Y are protected, e.g., an O-acylated derivative, and coupling the diazotized compound into the desired coupling component providing X. Preferably Ar is a benzene nucleus. The preparation of amino compounds within the Formula C, and the protected derivatives thereof, are disclosed and claimed in the co-pending applications of Elkan R. Blout, Milton Green and Howard G. Rogers, Serial No. 612,045, filed September 25, 1956 (now abandoned), and in Serial Nos. 144,816 and 145,978, both filed October 18, 1961, as continuations-in-part of said Serial No. 612,045, now U.S. Patents Nos. 3,134,672 and 3,134,764, both issued May 26, 1964.

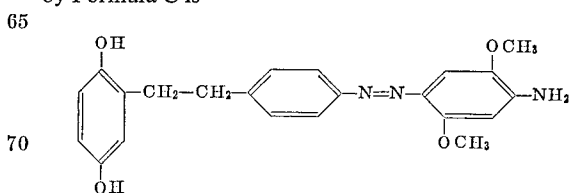
As examples of compounds which may be employed in the preparation of compounds within Formula C, e.g., by diazotizing the corresponding O,O-diacetate and coupling into the desired azo coupler providing the radical X^1 , mention may be made of:

- 35 p-Aminophenethyl-hydroquinone
- 2-(4'-aminonaphthylethyl)-hydroquinone
- 2-(p-aminophenethyl)-5-methyl-hydroquinone
- 2-(p-aminophenethyl)-5-chloro-hydroquinone
- 2-(3'-methyl-4'-aminophenethyl)-hydroquinone
- 40 2-(p-aminophenethyl)-5,6-dimethyl-hydroquinone
- 2-(p-aminophenethyl)-3,5,6-trimethyl-hydroquinone
- 2-m-aminophenethyl-hydroquinone
- p-Aminophenylmethyl-hydroquinone
- 2-(m-aminophenethyl)-5-methyl-hydroquinone
- 45 1,2-dihydroxy-4-(p-aminophenethyl)-benzene
- 2-[γ -(4-aminophenyl)- β -methyl-propyl]-hydroquinone
- 2-[γ -(4-aminophenyl)-propyl]-hydroquinone
- 2-(4'-amino-3'-methoxy-phenethyl)-hydroquinone
- 2-[γ -(3'-amino-4'-methylphenyl)-propyl]-hydroquinone
- 50 2-(p-aminophenethyl)-6-methyl-hydroquinone
- 2-(p-aminophenethyl)-5-bromo-hydroquinone
- 2-(5'-aminonaphthylethyl)-hydroquinone

These compounds are disclosed and claimed in the co-pending application of Elkan R. Blout, Milton Green, Howard G. Rogers, Myron S. Simon and Robert B. Woodward, Serial No. 98,287, filed March 27, 1961, as a continuation-in-part of Serial No. 612,051, filed September 25, 1961, now U.S. Patent No. 3,019,107, issued January 30, 1962.

The monoazo intermediates conveniently are employed without removal of the protective, e.g., acetoxy, groups.

The preferred compound within the group represented by Formula C is



2,5 - dimethoxy-4-[p-(2',5'-dihydroxyphenethyl)-phenyl-azo]-aniline.

As noted above, R preferably is a lower alkylene group. It will be understood that the selection of particular alkylene, alkyl and alkoxy groups in the compounds of Formula C may be varied as desired, so long as the resulting dye developer is capable of being dissolved in the alkaline photographic processing solution and of transferring by diffusion within a reasonable imbibition time. The selection of solubilizing groups as substituents of the azo coupler radical, including their exclusion or inclusion, provides a useful means of modifying the solubility and diffusion properties of the resulting dye developer to meet the requirement of any particular application.

The azo coupling is generally performed at a pH which is preferably not greater than about 9. The hydroxy groups of Y are protected during diazotization and coupling, as by the formation of a bis-acetoxy derivative; such bis-acetoxy derivatives are described in the aforementioned application of Milton Green and Helen P. Husek.

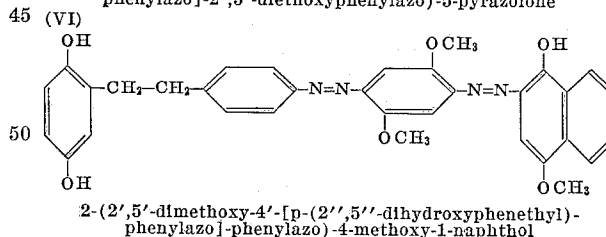
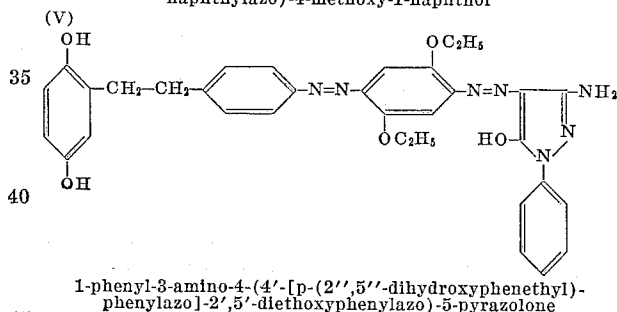
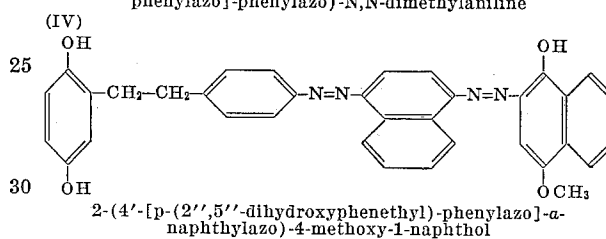
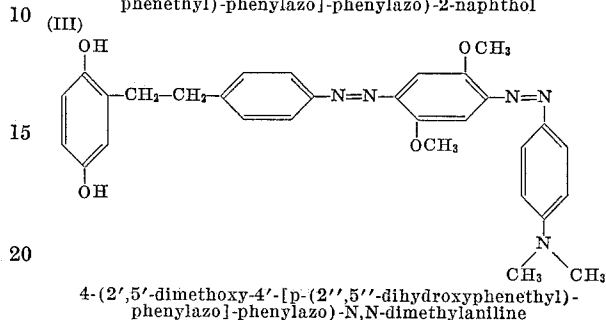
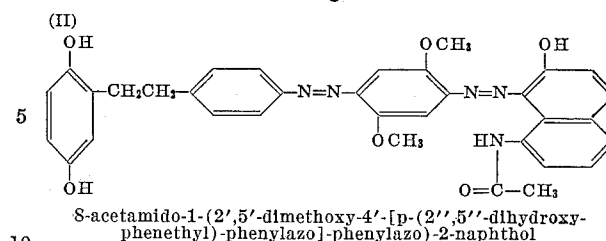
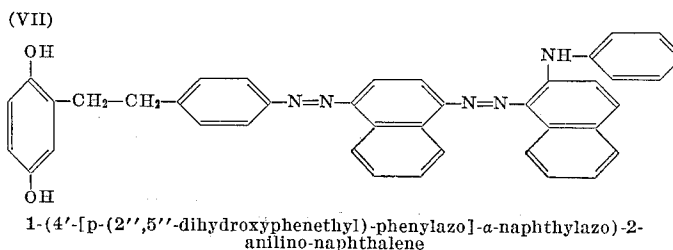
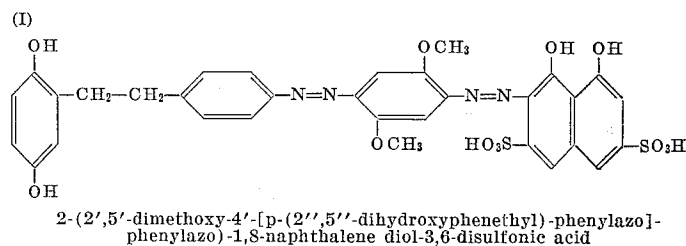
By the use of two moles of the diazonium salt to each mole of the coupling component, one may couple twice into certain of the azo coupling components which provide the azo coupling radical X², and which have two available coupling positions, as, for example, phenols and aromatic amines such as 1,6-dihydroxy naphthalene and 1,5-diaminonaphthalene.

Where the azo coupling component is a phenolic coupler, and particularly an α -naphthol, it has been found that coupling ortho to the hydroxyl group gives a dye developer of superior color properties. It has also been found that such ortho-coupled dye developers exhibit essentially no pH sensitivity over a fairly wide range on either side of neutral.

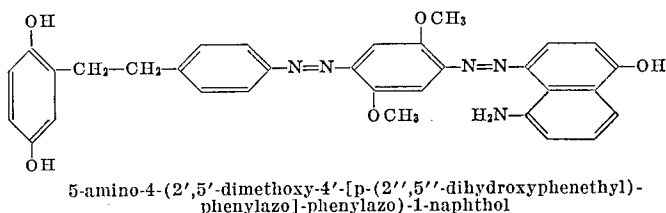
The coupling component employed to provide the residue X¹ is preferably a coupler containing a diazotizable amino group. It is to be understood, however, that one may employ a coupler having a group convertible to a diazotizable amino group, e.g., a nitro group. The diazotizable amino group may be on a ring or nucleus other than the one substituted by the azo grouping.

It will be noted that, in lieu of coupling first into X¹ and then diazotizing that initial coupling product and coupling into X², one may first form a monoazo compound corresponding to the azo coupling product of X¹ and X², and then couple into the X¹ portion of that monoazo compound in a manner analogous to that employed to prepare the compounds of Formula C above.

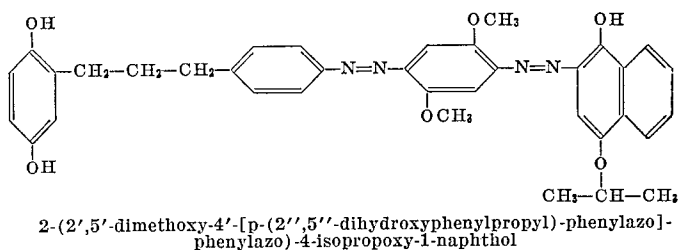
As examples of suitable dye developers within the scope of this invention, mention may be made of the following:



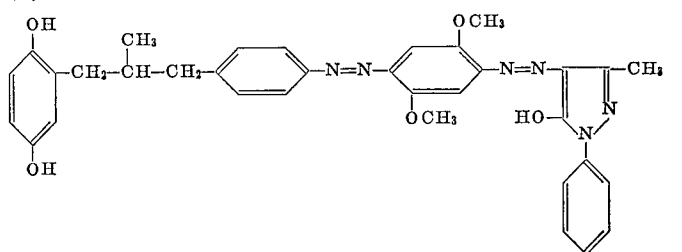
(VIII)



(IX)



(X)



(XI) 5-amino-4-(2',5'-dimethoxy-4'-[m-(2'',5''-dihydroxyphenethyl)-phenylazo]-phenylazo)-1-naphthol

(XII) 5-amino-4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxy-4'-methylphenethyl)-phenylazo]-phenylazo)-1-naphthol

(XIII) 1-phenyl-3-methyl-4-(2',5'-dimethoxy-4'-[p-(3'',4''-dihydroxyphenethyl)-phenylazo]-phenylazo)-5-pyrazolone

(XIV) 2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxy-4''-chloro-phenethyl)-phenylazo]-phenylazo)-4-β-hydroxyethoxy-1-naphthol

(XV) 2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenethyl)-o-methylphenylazo]-phenylazo)-4-n-propoxy-1-naphthol

As examples of additional coupling components which may be used to provide X², mention may be made of:

4-benzyl-1-naphthol
4-methyl-1-naphthol
4-methoxy-α-naphthylamine
4-acetamido-α-naphthylamine
Phenol
Aniline
1,5-naphthalenediamine
p-Cresol
1-hydroxyanthracene
1-hydroxy-2-naphthylamine
Diketohydrindene
Malononitrile
Acetoacetanilide

The novel dye developers of this invention are to be distinguished from the compounds disclosed and claimed in the copending applications of Helen P. Husek and Myron S. Simon, Serial No. 197,283, and Serial No. 197,259 now U.S. Patent No. 3,134,763, both filed May 24, 1962, as

continuations in part of Serial No. 612,054, filed September 25, 1956 (now abandoned), by the presence of the alkylene group R. The presence of this alkylene group R insulates the dihydroxyphenyl group Y 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 R helps to avoid color changes in the transfer dye image should be transferred dye developer subsequently be oxidized. The dye developers of this invention are also unexpectedly superior to disazo dye developers such as those having the azo group directly attached to the hydroquinone group 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.

The following examples of the preparation of dye developers within the scope of this invention are given for purposes of illustration only.

Example 1

2,5-dimethoxy-4-p-(2',5'-bis-acetoxyphenethyl)-phenylazoaniline hydrochloride (1 g.; 0.002 mol.) is dissolved in acetic acid and diazotized with 2 cc. of 1 N sodium nitrite at about 10° C. The resulting solution is added, with constant stirring, to a solution of 0.35 g. of 4-methoxy-1-naphthol dissolved in alcohol. Sufficient sodium acetate is added to give a pH of approximately 7.0. After coupling is completed, the reaction mixture is filtered. The precipitate is washed with water and purified by dissolving it in methyl Cellosolve and reprecipitating with water. The acetyl groups are removed by hydrolysis in vacuo with sodium hydroxide by heating for a few minutes on a steam bath. Precipitation with hydrochloric acid gives the desired 2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-phenylazo)-4-methoxy-1-naphthol [Formula VI]. A greenish-blue solution is obtained when the product is dissolved in alkali or inorganic solvents, such as dimethylformamide.

Example 2

2,5 - dimethoxy - 4 - p - (2',5' - bis - acetoxyphenethyl) - phenylazoaniline (2.05 g.) is diazotized in a manner similar to that described in Example 1 and coupled with 0.8 g. of 8-acetamido-2-naphthol. The reaction mixture is filtered and the precipitate washed with water and then dissolved in acetone. After reprecipitation with aqueous hydrochloric acid, the acetyl groups are removed by heating, in vacuo, with sodium hydroxide. The resulting 8 - acetamido - 1 - (2',5' - dimethoxy - 4' - [p - (2'',5'' - dihydroxyphenethyl) - phenylazo] - phenylazo) - 2-naphthol [Formula II] is soluble in alkali and organic solvents.

Example 3

4 - [p - (2',5' - diacetoxyphenethyl) - phenylazo] - 1-naphthylamine hydrochloride (1 g.) is suspended in 20 cc. of 1 N hydrochloric acid, cooled to about 10° C. and diazotized with sodium nitrite. The diazotized base is then added, with stirring, to an alcohol-acetone solution of N-phenyl-2-naphthylamine containing some sodium acetate. Sufficient additional sodium acetate is added to give a pH of about 7.0. The reaction mixture is filtered after coupling is complete, and the precipitate is washed with water and reprecipitated from methyl Cellosolve. The acetyl groups are removed by hydrolysis in a manner similar to that described in Examples 1 and 2 to give 2-(4'-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]- α -naphthylazo)-1-anilino-naphthalene which is soluble in alkali and organic solvents.

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 photographic use of the dye developers and should not be construed as limiting the invention in any way.

Example 4

A photosensitive element is prepared by coating a gelatin-coated film base with a solution containing 3% of 2 - (2',5' - dimethoxy - 4' - [p - (2'',5'' - dihydroxyphenethyl) - phenylazo] - phenylazo) - 4 - methoxy - 1 - naphthol [Formula VI 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	6.0
1-phenyl-3-pyrazolidone	0.2
Sodium hydroxide	5.0
Potassium bromide	0.5

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% nylon Type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for N-methoxymethyl polyhexamethylene adipamide) in 80% aqueous isopropanol. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a cyan positive dye image of the photographed subject.

Example 5

A photosensitive element is prepared similar to that described in Example 4 using 3% of 4-(2',5'-dimethoxy-4' - [p - (2'',5'' - dihydroxyphenethyl) - phenylazo]-phenylazo)-N,N-dimethylaniline [Formula III]. Exposure and processing with a liquid processing composition and image-receiving element similar to those described in Example 3 gives a positive dye image.

As will be readily understood by one skilled in the art, the dye developers not specifically described in the above specific examples may be prepared by diazotization and coupling procedures similar to those illustrated by Examples 1 through 3, substituting the desired azo couplers and diazotizable amino compound.

The quinones of the novel azo dye developers of this invention may be prepared by oxidizing under conditions which do not attach the azo bond, e.g., by oxidizing with benzoquinone, chloranil, or mercuric acetate. These azo quinones are useful in the photographic processes disclosed and claimed in the copending application of Howard G. Rogers, Serial No. 825,359, filed July 6, 1959, as a continuation-in-part of, and replacement for, Serial No. 599,122, filed July 20, 1956, now abandoned.

The dye developers of this invention are also useful in integral multilayer photosensitive elements for use in multicolor diffusion transfer process. As an example of such photosensitive elements, mention may be made of the photosensitive elements disclosed and claimed in the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956, 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 photosensitive elements within the scope of this invention may be used in roll film units which contain a plurality of photosensitive frames. The photosensitive elements of this invention are especially useful in composite roll film intended for use in a "Polaroid Land Camera," sold by Polaroid Corporation, Cambridge 39, Massachusetts, or a similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on February 10, 1948. In general, such composite roll films comprise a photosensitive roll, a roll of image-receiving material and a plurality of pods containing an aqueous alkaline processing solution. The rolls and pods are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pods may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of the pods used in such units are well known to the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

It will be noted that the liquid processing composition may contain one or more auxiliary or accelerating silver halide developing agents, such as p-methylaminophenol (Metol); 2,4-diaminophenol (Amidol); benzylaminophenol; hydroquinone; a substituted hydroquinone such as toluhydroquinone, phenylhydroquinone, or 4'-methylphenylhydroquinone; or a 3-pyrazolidone such as 1-phenyl-3-pyrazolidone. These silver halide developing agents are substantially colorless, at least in their unoxidized form. It is possible that some of the dye developer oxidized in exposed areas may be oxidized by an energy transfer reaction with oxidized auxiliary developing agent.

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed and claimed in the copending application of

Milton Green and Howard G. Rogers, Serial No. 50,851, filed August 22, 1960 now U.S. Patent No. 3,173,786.

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 1-2% 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 medium 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 between a "color former" or "coupler" and the oxidized developing agent, as well as so-called auto-coupling processes in which color is obtained by a reaction of the oxidized developing agent with unoxidized developing agent.

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-methoxymethylpolyhexamethylene 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 dye developers herein set forth are also useful in the formation of colored images in accordance with the photographic products and processes described and claimed in U.S. Patent No. 2,968,554, issued to Edwin H. Land on January 17, 1961.

The novel compounds herein disclosed are also suitable for use as dyes for textiles fibres, such as nylon.

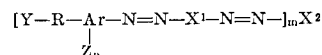
In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black.

Since certain changes may be made in the above 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 shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic developer composition comprising an aqueous solvent, an alkaline material soluble therein,

a silver halide developing agent which is substantially colorless in at least the unoxidized form, and an azo dye developer of the formula:



wherein Y is selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl radicals and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, said $-N=N-$ group being directly attached to a ring carbon of said aryl nucleus; R is a divalent alkylene group directly attached to said aryl nucleus Ar and to said phenyl ring of Y; each Z is selected from the group consisting of halogen, alkoxy and alkyl radicals; n is from 0 to 2, inclusive; m is 1; and each of X^1 and X^2 is the radical of an azo dye coupler linked to said $-N=N-$ groups and completing said azo dye developer, said azo dye developer containing only one said Y radical.

2. A photographic developer composition as defined in claim 1, wherein X^2 is a phenolic azo coupler radical.

3. A photographic developer composition as defined in claim 1, wherein X^2 is an aromatic amino azo coupler radical.

4. A photographic developer composition as defined in claim 1, wherein X^2 is a heterocyclic aromatic azo coupler radical.

5. A photographic developer composition as defined in claim 1, wherein X^2 is selected from the group consisting of aliphatic and alicyclic activated methylene azo coupler radicals.

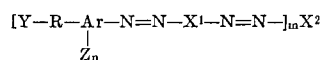
6. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is a 3-pyrazolidone.

7. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is a hydroquinone.

8. A photographic developer composition comprising an aqueous alkaline solution of 4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-phenylazo)-N,N-dimethylaniline and a silver halide developing agent which is substantially colorless in at least the unoxidized form.

9. A photographic developer composition comprising an aqueous alkaline solution of 2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-phenylazo)-4-methoxy-1 naphthol and a silver halide developing agent which is substantially colorless in at least the unoxidized form.

10. A photographic product comprising a support, a silver halide emulsion in a layer carried by said support and an azo dye developer in a layer carried by said support, said azo dye developer being a compound of the formula:



wherein Y is selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl radicals and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, said $-N=N-$ group being directly attached to a ring carbon of said aryl nucleus; R is a divalent alkylene group directly attached to said aryl nucleus Ar and to said phenyl ring of Y; each Z is selected from the group consisting of halogen, alkoxy and alkyl radicals; n is from 0 to 2, inclusive; m is 1; and each of X^1 and X^2 is the radical of an azo dye coupler linked to said $-N=N-$ groups and completing said azo dye developer, said azo dye developer containing only one said Y radical.

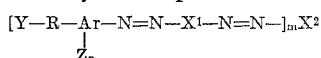
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11. A photographic product as defined in claim 10, wherein said azo dye developer is 4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-phenylazo)-N,N-dimethylaniline.

12. A photographic product as defined in claim 10, wherein said azo dye developer is 2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-phenylazo)-4-methoxy-1-naphthol.

13. A photographic product as defined in claim 10, wherein said azo dye developer is in a layer positioned between said support and said layer containing said silver halide emulsion.

14. In a process of forming a photographic image in color, the steps which comprise developing an exposed silver halide emulsion with an aqueous alkaline solution containing an azo dye developer of the formula:



wherein Y is selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl radicals and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, said —N=N— group being directly attached to a ring carbon of said aryl nucleus; R is a divalent alkylene group directly attached to said aryl nucleus Ar and to said phenyl ring of Y; each Z is selected from the group consisting of halogen, alkoxy, and alkyl radicals; n is from 0 to 2, inclusive; m is 1 and each of X^1 and X^2 is the radical of an azo dye coupler linked to said —N=N— groups and completing said azo dye developer, said azo dye developer containing only one said Y radical, to provide in said emulsion an imagewise distribution of unoxidized dye developer in undeveloped areas of said emulsion, and transferring at least part of said imagewise distribution of unoxidized dye developer by imbibition from said emulsion to an image-receiving layer in superposed relationship with said emulsion to impart a transfer image in color to said image-receiving layer.

15. The process as defined in claim 14, wherein said dye developer is disposed prior to exposure in a photosensitive element containing said emulsion and the solution containing said dye developer is formed by permeating said photosensitive element with an aqueous alkaline liquid capable of solubilizing said dye developer.

16. The process as defined in claim 15, wherein said liquid is introduced by being spread in a substantially uniform layer between said photosensitive element and an image-receiving element including said image-receiving layer as said elements are brought into superposed relationship.

17. The process as defined in claim 15, wherein said liquid contains a thickener for increasing viscosity and for facilitating the spreading thereof between said photosensitive element and said image-receiving element.

18. The process as defined in claim 14, wherein said dye developer is dissolved in an aqueous alkaline solution prior to application thereof to said exposed emulsion.

19. A process as defined in claim 14, wherein X^2 is a phenolic azo coupler radical.

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20. A process as defined in claim 14, wherein X^2 is an aromatic amino azo coupler radical.

21. A process as defined in claim 14, wherein X^2 is a heterocyclic aromatic azo coupler radical.

22. A process as defined in claim 14, wherein X^2 is an azo coupler radical selected from the group consisting of aliphatic and alicyclic activated methylene couplers.

23. The process as defined in claim 14, wherein said dye developer is 4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-phenylazo)-N,N-dimethylaniline.

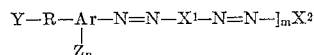
24. The process as defined in claim 14, wherein said dye developer is 2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-phenylazo)-4-methoxy-1-naphthol.

25. A process as defined in claim 14, wherein said aqueous alkaline solution includes a silver halide developer agent which is substantially colorless in at least its unoxidized form.

26. A process as defined in claim 25, wherein said silver halide developing agent is a 3-pyrazolidone.

27. A process as defined in claim 25, wherein said silver halide developing agent is a hydroquinone.

28. The process which comprises developing an exposed photosensitive silver halide emulsion with an aqueous alkaline solution of an azo dye developer of the formula:



wherein Y is selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl radicals and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, said —N=N— group being directly attached to a ring carbon of said aryl nucleus; R is a divalent alkylene group directly attached to said aryl nucleus Ar and to said phenyl ring of Y; each Z is selected from the group consisting of halogen, alkoxy and alkyl radicals; n is from 0 to 2, inclusive; m is 1; and each of X^1 and X^2 is the radical of an azo dye coupler linked to said —N=N— groups and completing said azo dye developer, said azo dye developer containing only one said Y radical.

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NORMAN G. TORCHIN, *Primary Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,236,643

February 22, 1966

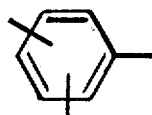
Helen P. Husek

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, for that portion of formula (A) reading

Y— read [Y—

line 33, for "benzene" read -- a benzene --; lines 46 to 51, the benzene ring should appear as shown below instead of as in the patent:



column 4, line 31, for "O,O" read -- O,O' --; lines 46 and 47, for "(4-aminophenyl)", each occurrence, read -- (4'-aminophenyl) --; column 8, line 46, for "be" read -- the --; line 72, for "phenylazo-4" read -- phenylazo)-4 --; column 10, line 18, for "process" read -- processes --; column 11, line 63, for "textiles" read -- textile --; column 13, line 30, for "m¹ is 1" read -- m is 1 ; --; column 14, lines 17 and 18, for "developer" read -- developing --; lines 28 to 31, for the left-hand portion of the formula reading

Y— read [Y—

Signed and sealed this 24th day of September 1968.

(SEAL)
Attest:

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Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents