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3,142,565

**PHOTOGRAPHIC PRODUCTS, PROCESSES  
AND COMPOSITIONS EMPLOYING AZO  
DYE DEVELOPERS**

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No Drawing. Filed Sept. 10, 1962, Ser. No. 222,656  
29 Claims. (Cl. 96—29)

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 developing agents are used.

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 an exposed silver halide emulsion and imparting a reversed or positive colored image of the developed 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.

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 images present in an exposed silver halide emulsion; thus they may be referred to as dye developers. These novel dyes or dye developers will be further described hereinafter.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

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 developers for 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 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 photo-

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sensitive 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 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. 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 stripping the image-receiving layer from the silver halide emulsion at the end of the imbibition period.

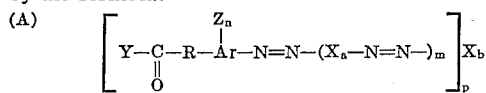
The dye developers of this invention may be utilized in the photosensitive element, for example in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer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

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increase viscosity is substantially unaffected when left in solution for a long period of time may also be used.

The dye developers of this invention may be represented by the formula:



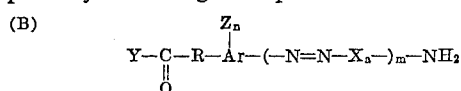
wherein Ar is an aryl nucleus, such as a benzene or naphthalene nucleus; each Z is an alkoxy group, preferably a lower alkoxy group such as methoxy, ethoxy, etc., an alkyl group, preferably a lower alkyl group such as methyl, ethyl, etc., a hydroxyl group, or a halogen group such as chlorine;  $m$  is 0 or 1;  $n$  is 0 or a positive integer from 1 to 4, inclusive;  $p$  is 1 or 2; R is an alkylene group, preferably containing no more than 5 carbon atoms; Y is a p-dihydroxyphenyl or o-dihydroxyphenyl group, and alkyl and halogen substituted derivatives thereof;  $X_a$  and  $X_b$  are each the radical of a coupling component, which coupling component may be the same or different. By the expression "coupling component," as used in the above formula and hereinafter, is meant a compound capable of being coupled into by a diazonium salt, i.e., an azo coupler.

In a preferred embodiment, the aryl nucleus is a benzene nucleus and  $p$  is 1.

As illustrations of suitable azo coupling components or couplers from which  $X_a$  and  $X_b$  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  $\beta$ -keto 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, carboxamido, sulfonamido, etc.

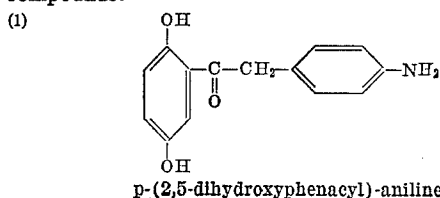
As used herein with reference to  $X_a$  and  $X_b$ , the expression "radical of a phenolic coupler" is intended to refer to hydroxyphenyl, hydroxynaphthyl, hydroxyanthryl, etc. radicals, and substituted derivatives thereof; the expression "radical of an aromatic amino coupler" is intended to refer to 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:

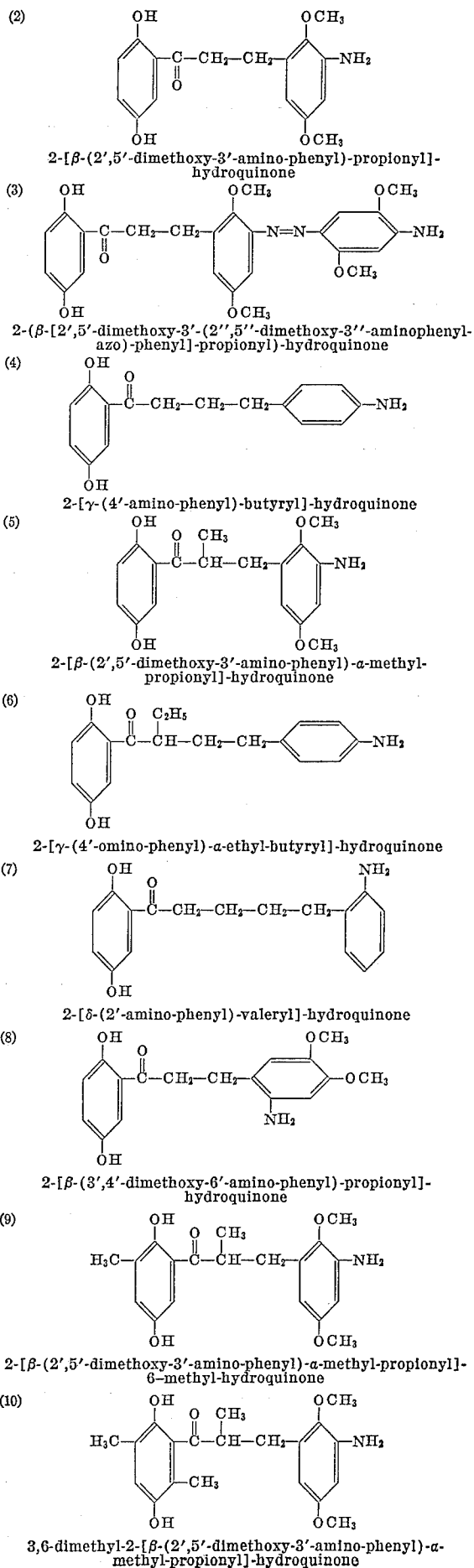


wherein Y, R, Ar, Z,  $n$ ,  $X_a$ , and  $m$  have the same meaning as above, and coupling diazotized compound (B) into the desired coupling component providing  $X_b$ .

As examples of useful intermediates within the scope of Formula B, mention may be made of the following compounds:

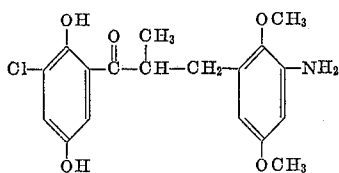


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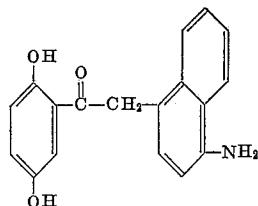
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(11)



6-chloro-2-[β-(2',5'-dimethoxy-3'-amino-phenyl)-α-methyl-propionyl]-hydroquinone

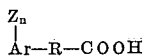
(12)



1-amino-4-(2',5'-dihydroxyphenacyl)-naphthalene

In general, the compounds of Formula B, wherein R is any desired homologue may be prepared by (a) nitrating a compound of the formula:

(C)



e.g., phenylacetic acid, naphthylacetic acid, their homologues and their analogues, to form the nitroaryl analogue; (b) forming the acid chloride of the said analogue; (c) forming the hydroquinone derivative by the Friedel-Crafts reaction; and (d) reducing the nitro group (preferably in an acid medium) to form the compound of Formula B.

The compounds of Formula B wherein *m* is 0 may also be prepared according to the procedure disclosed in the copending application of Elkan R. Blout and Myron S. Simon, Serial No. 165,006, filed January 8, 1962, and which is a continuation-in-part of Serial No. 685,066, filed September 20, 1957. If desired, the hydroxyl groups may be protected during reaction by the use of suitable protective derivatives, e.g., O-acetyl derivatives, according to the procedure disclosed in the aforementioned copending application. However, it is also contemplated to effect diazotization of the compounds of Formula B where the hydroxyl groups are free. Where desired, the monoazo intermediates may be employed for further diazotization without removal of the protective groups.

Where desired, the compounds of Formula B may be employed in the form of acid addition salts, e.g., the hydrochloride.

The coupling is generally performed at a pH which is preferably not greater than about 9. The hydroxy groups of Y may be protected during diazotization and coupling, as by the use of O-acetyl derivatives as mentioned above.

By the use of two mols of the diazonium salt to each mol of the coupling component, one may couple twice into certain of the coupling components which provide the residue X<sub>b</sub>, as, for example, hydroxy and amino aromatic compounds which have two directing groups and two free coupling positions as, for example, 1,5-dihydroxynaphthalene. It may be noted that such bis coupling may give rise to a mixture of dye developers, and such mixtures may be used in the processes of this invention.

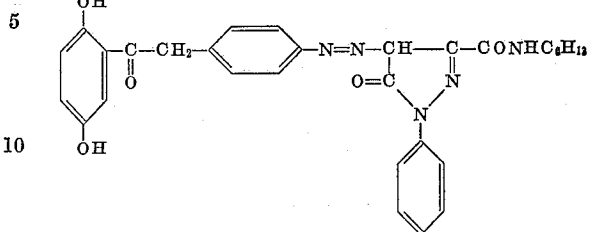
Where the coupling component is a phenolic coupler, and particularly a naphthol, it has been found that coupling ortho to the hydroxyl group gives a dye developer of superior color properties. It has also been found that such ortho-coupled dye developers exhibit essentially no pH sensitivity over a fairly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

As examples of suitable dye developers within the

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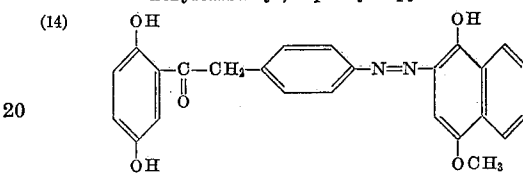
scope of this invention, mention may be made of the following:

(13)



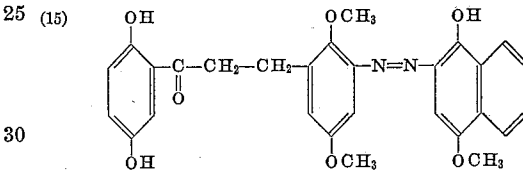
4-[p-(2',5'-dihydroxyphenacyl)-phenylazo]-3-(N-n-hexylcarbamyl)-1-phenyl-5-pyrazolone

(14)



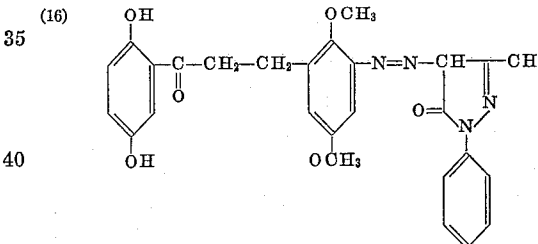
2-[p-(2',5'-dihydroxyphenacyl)-phenylazo]-4-methoxy-1-naphthol

(15)



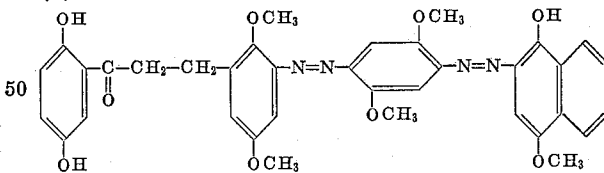
4-methoxy-2-(2',5'-dimethoxy-3'-[2''-(2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-1-naphthol

(16)



1-phenyl-3-methyl-4-(2',5'-dimethoxy-3'-[2''-(2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-5-pyrazolone

(17)



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

The coupling component employed to provide the residue X<sub>a</sub> 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 nucleus other than the one substituted by the azo grouping.

As examples of additional coupling components which may be used to provide X<sub>b</sub>, 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-naphthylidide

Diketohydrindene  
Malononitrile  
Acetoacetanilide

The novel dye developers of this invention are to be distinguished from the compounds disclosed and claimed in the copending application of Elkan R. Blout, Milton Green and Howard G. Rogers, Serial No. 144,816, filed October 18, 1961, as a continuation-in-part of Serial No. 612,045 filed September 25, 1956 (now abandoned), by the presence of the acyl group, i.e., the



group. The presence of the acyl group lowers the developing potential of the dye developer and the resulting dye developer, in the absence of an auxiliary or accelerating developing agent, is relatively unreactive, and thereby results in a useful synergistic developing agent which is essentially unreactive during storage, e.g., when the dye developer is disposed in the photosensitive element prior to exposure of said element.

The following examples of the preparation of dye developers within the scope of this invention by coupling compounds within Formula B are given for purposes of illustration only:

#### Example 1

(0.01 mol) of 2-[ $\gamma$ -2',5'-dimethoxy-3'-amino-phenyl]-propionyl]-hydroquinone hydrochloride was dissolved in 200 cc. of 6 N. hydrochloric acid and a solution of (0.01 mol) of sodium nitrite in 15 cc. of water. The mixture was stirred for approximately 15 minutes while being cooled to about 5° C., filtered through Celite, allowed to stand for approximately 30 minutes, and added to a solution of (0.0086 mol) of 4-methoxy-1-naphthol in 100 cc. of water and 120 cc. of pyridine. 20% sodium carbonate solution was added intermittently to retain the pH at 7 to 8. After approximately one hour the slurry was filtered, washed with aqueous acetic acid, then washed with water and purified by precipitation from methyl Cellosolve with 1% hydrochloric acid solution. The resultant 4-methoxy-2-(2',5'-dimethoxy-3'-[2''-(2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-1-naphthol [Formula 15], spectral absorption curves shows a  $\lambda_{\text{max}}$  at 530  $\mu$  in acetone,  $\epsilon=19,600$

#### Example 2

2-[ $\gamma$ -(2',5'-dimethoxy-3'-amino-phenyl)-propionyl]-hydroquinone hydrochloride was diazotized in a manner similar to that described in Example 2 and coupled with 1-phenyl-3-methyl-5-pyrazolone. The resultant product was 1-phenyl-3-methyl-4-(2',5'-dimethoxy-3'-[2''-(2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-5-pyrazolone [Formula 16]. The spectral absorption curve showed a  $\lambda_{\text{max}}$  at 410  $\mu$  in methyl Cellosolve,  $\epsilon=19,400$ .

#### Example 3

2-( $\gamma$ -[2',5'-dimethoxy-3'-(2'',5''-dimethoxy-3''-aminophenylazo)-phenyl]-propionyl)-hydroquinone hydrochloride was diazotized in a manner similar to that described in Example 2 and coupled with 4-methoxy-1-naphthol. The resultant product was 4-methoxy-2-[2',5'-dimethoxy-4'-(2'',5''-dimethoxy-3''-[2'''-(2''''',5''''-dihydroxybenzoyl)-ethyl]-phenylazo)-phenylazo]-1-naphthol [Formula 17]. The spectral absorption curve showed a  $\lambda_{\text{max}}$  at 590  $\mu$  in methyl Cellosolve,  $\epsilon=14,400$ .

In the same manner as described in the foregoing examples, 4-[p-(2',5'-dihydroxyphenacyl)-phenylazo]-3-(N-n-hexylcarbonyl)-1-phenyl-5-pyrazolone [Formula 13] and 2-[p-(2',5'-dihydroxyphenacyl)-phenylazo]-4-methoxy-1-naphthol [Formula 14] were prepared by coupling diazotized p-(2,5-dihydroxyphenacyl)-aniline with the azo coupler moiety of the compound.

#### Example 4

A photosensitive element was prepared by coating a gelatin-coated film base with a solution containing 3% of 4-methoxy-2-(2',5'-dimethoxy-3'-[2''-(2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-1-naphthol [Formula 15 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 had dried, a silver iodobromide emulsion was applied. This photosensitive element was 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 were brought into superposed relationship. The image-receiving element comprised a cellulose acetate-coated baryta paper which had 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 was separated and contained a magenta positive dye image of the photographed subject.

#### Example 5

A photosensitive element was prepared similar to that described in Example 4 using 3% of 1-phenyl-3-methyl-4-(2',5'-dimethoxy-3'-[2''-(2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-5-pyrazolone [Formula 16 as prepared in Example 2]. This photosensitive element was exposed and processed by spreading an aqueous liquid processing composition comprising:

	Percent
Sodium carboxymethyl cellulose-----	4.5
1-phenyl-3-pyrazolidone -----	0.2
Sodium hydroxide-----	3.0
Potassium bromide-----	0.2

between said photosensitive element and an image-receiving element as said elements were brought into superposed relationship. The image-receiving element comprised a cellulose-coated baryta paper which had been coated with a solution comprising 10% Nylon Type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware for N-methoxymethyl polyhexamethylene adipamide) in 80% aqueous ethanol. After an imbibition period of approximately one minute, the image-receiving element was separated and contained a yellow positive dye image of the photographed subject.

#### Example 6

A photosensitive element was prepared similar to that described in Example 4 using 3% of 4-methoxy-2-[2',5'-dimethoxy-4'-(2'',5''-dimethoxy-3''-[2'''-(2''''',5''''-dihydroxybenzoyl)-ethyl]-phenylazo)-phenylazo]-1-naphthol [Formula 17 as prepared in Example 3]. Exposure and processing with a liquid processing composition and image-receiving element similar to those described in Example 4 gave a tan positive dye image of the photographed subject.

#### Example 7

A photosensitive element was prepared similar to that described in Example 4 using 3% of 4-[p-(2',5'-dihydroxyphenacyl)-phenylazo]-3-(N-n-hexylcarbonyl)-1-phenyl-5-pyrazolone [Formula 13]. Exposure and processing with a liquid processing composition and image-receiving element similar to those described in Example 4 gave a yellow positive dye image.

## Example 8

A photosensitive element was prepared similar to that described in Example 4 using 3% of 2-[p-(2',5'-dihydroxyphenacyl) - phenylazo] - 4 - methoxy - 1 - naphthol [Formula 14]. Exposure and processing with a liquid processing composition and image-receiving element similar to those described in Example 4 gave a magenta positive dye image.

Repeating the procedures of Examples 4, 5 and 6 without the auxiliary developing agent results in positive dye images which exhibit poor contrast and colored highlights, thus indicating that the dye developer in the exposed areas of the light-sensitive element is not oxidized rapidly enough to control the transfer of said dye developer from the exposed areas to a superposed image-receiving layer.

The dye developers of this invention are also useful in integral multilayer photosensitive elements for use in multicolor diffusion transfer processes. 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.

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-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 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 textile 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.

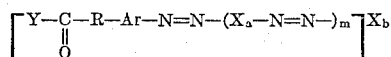
This application is in part a continuation of our copending application, Serial No. 685,081, filed September 20, 1957 (now abandoned).

Our copending U.S. application, Serial No. 222,702, filed concurrently herewith, claims the novel compounds of the present invention.

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 novel photographic developer composition comprising an aqueous alkaline solution of a colorless silver halide auxiliary developing agent and an azo dye of the formula:



wherein Ar is an aryl nucleus; R is an alkylene group; Y is a dihydroxyphenyl silver halide developing radical; X<sub>a</sub> and X<sub>b</sub> each represents the radical of an azo dye coupler linked to said —N=N— group and completing said azo dye; and *m* is an integer from 0 to 1, inclusive.

2. A novel photographic developer composition as defined in claim 1 wherein X<sub>b</sub> is a phenolic azo coupler radical.

3. A novel photographic developer composition as defined in claim 1 wherein X<sub>b</sub> is an aromatic amino azo coupler radical.

4. A novel photographic developer composition as defined in claim 1 wherein X<sub>b</sub> is a heterocyclic aromatic azo coupler radical.

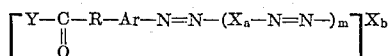
5. A novel photographic developer composition as defined in claim 1 wherein X<sub>b</sub> is selected from the group consisting of aliphatic and alicyclic activated methylene azo coupler radicals.

6. A novel photographic developer composition comprising an aqueous alkaline solution of 4-methoxy-2-(2',5' - dimethoxy-3' - [2'' - (2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-1-naphthol and a colorless silver halide auxiliary developing agent.

7. A novel photographic developer composition comprising an aqueous alkaline solution of 1-phenyl-3-methyl-4 - (2',5' - dimethoxy-3' - [2'' - (2''',5'''-dihydroxybenzoyl)-ethyl] - phenylazo) - 5 - pyrazolone and a colorless silver halide auxiliary developing agent.

8. A novel photographic developer composition comprising an aqueous alkaline solution of 4-methoxy-2-[2',5' - dimethoxy-4' - (2'',5''-dimethoxy-3'''-[2''''-(2''''',5'''''-dihydroxybenzoyl) - ethyl] - phenylazo) - phenylazo]-1-naphthol and a colorless silver halide auxiliary developing agent.

9. A novel photographic product comprising a support, a silver halide emulsion in a layer on said support, and a dye developer in a layer on the same side of said support as said emulsion, said dye developer comprising an azo dye of the formula:



wherein Ar is an aryl nucleus; R is an alkylene group; Y is a dihydroxyphenyl silver halide developing radical; X<sub>a</sub> and X<sub>b</sub> each represents the radical of an azo dye coupler linked to said —N=N— group and completing said azo dye; and *m* is an integer from 0 to 1, inclusive.

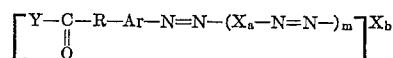
10. A novel photographic product as defined in claim 9 wherein said product contains a colorless silver halide auxiliary developing agent in a layer on the same side of said support as said emulsion.

11. A novel photographic product comprising a support, a silver halide emulsion in a layer on said support and 4-methoxy-2-(2',5' - dimethoxy-3' - [2'' - (2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-1-naphthol in a layer on the same side of said support as said emulsion.

12. A novel photographic product comprising a support, a silver halide emulsion in a layer on said support and 1-phenyl - 3 - methyl - 4 - (2',5'-dimethoxy-3' - [2'' - (2''',5'''-dihydroxybenzoyl) - ethyl] - phenylazo) - 5 - pyrazolone in a layer on the same side of said support as said emulsion.

13. A novel photographic product comprising a support, a silver halide emulsion in a layer on said support and 4 - methoxy-2-[2',5'-dimethoxy-4'-(2'',5''-dimethoxy-3'''-[2''''-(2''''',5'''''-dihydroxybenzoyl)-ethyl]-phenylazo)-phenylazo]-1-naphthol in a layer on the same side of said support as said emulsion.

14. In a process of forming a photographic image in color, the steps which comprise developing a latent image contained in an exposed silver halide emulsion by contacting said emulsion with an aqueous alkaline solution containing a colorless silver halide auxiliary developing agent and an azo dye developer of the formula:



wherein Ar is an aryl nucleus; R is an alkylene group; Y is a dihydroxyphenyl silver halide developing radical; X<sub>a</sub> and X<sub>b</sub> each represents the radical of an azo dye coupler linked to said —N=N— group and completing said azo dye developer; and *m* is an integer from 0 to 1, inclusive; oxidizing said dye developer in exposed areas to provide in said emulsion a predetermined distribution of unoxidized dye developer and transferring at least part of said distribution of said unoxidized dye developer by imbibition from said emulsion to an image-receiving element in superposed relationship with said emulsion to impart to said image-receiving element a reversed, positive dye image of the developed image.

15. A process as defined in claim 14 wherein X<sub>b</sub> is a phenolic azo coupler radical.

16. A process as defined in claim 14 wherein X<sub>b</sub> is an aromatic amino azo coupler radical.

17. A process as defined in claim 14 wherein X<sub>b</sub> is a heterocyclic aromatic azo coupler radical.

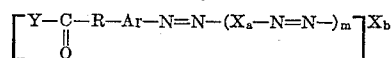
18. The process as defined in claim 14 wherein X<sub>b</sub> is selected from the group consisting of aliphatic and alicyclic activated methylene azo coupler radicals.

19. The process as defined in claim 14 wherein said compound is 1 - phenyl - 3-methyl-4-(2',5'-dimethoxy-3' - [2'' - (2''',5'''-dihydroxybenzoyl) - ethyl] - phenylazo) - 5-pyrazolone.

20. The process as defined in claim 14 wherein said compound is 4 - methoxy - 2 - (2',5' - dimethoxy-3' - [2'' - (2''',5''' - dihydroxybenzoyl) - ethyl] - phenylazo) - 1-naphthol.

21. The process as defined in claim 14 wherein said compound is 4 - methoxy - 2 - [2',5'-dimethoxy-4'-(2'',5''-dimethoxy - 3'''-[2''''-(2''''',5'''''-dihydroxybenzoyl)-ethyl]-phenylazo)-phenylazo]-1-naphthol.

22. A process of developing an exposed photosensitive silver halide emulsion which comprises contacting an exposed silver halide emulsion with an aqueous alkaline solution containing a colorless silver halide auxiliary developing agent and an azo dye of the formula:



wherein Ar is an aryl nucleus; R is an alkylene group; Y is a dihydroxyphenyl silver halide developing radical; X<sub>a</sub> and X<sub>b</sub> each represents the radical of an azo dye coupler linked to said —N=N— group and completing said azo dye; and *m* is an integer from 0 to 1, inclusive.

23. A process as defined in claim 22 wherein X<sub>b</sub> is a phenolic azo coupler radical.

24. A process as defined in claim 22 wherein X<sub>b</sub> is an aromatic amino azo coupler radical.

25. A process as defined in claim 22 wherein X<sub>b</sub> is a heterocyclic aromatic azo coupler radical.

26. The process as defined in claim 22 wherein X<sub>b</sub> is selected from the group consisting of aliphatic and alicyclic activated methylene azo coupler radicals.

27. The process as defined in claim 22 wherein said compound is 1-phenyl - 3 - methyl-4-(2',5'-dimethoxy-3' - [2'' - (2''',5''' - dihydroxybenzoyl)-ethyl]-phenylazo)-5-pyrazolone.

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28. The process as defined in claim 22 wherein said compound is 4-methoxy-2-(2',5'-dimethoxy-3'-[2''-(2''',5'''-dihydroxybenzoyl)-ethyl]-phenylazo)-1-naphthol.

29. The process as defined in claim 22 wherein said compound is 4-methoxy-2-[2',5'-dimethoxy-4'-(2'',5''-dimethoxy-3''-[2'''-(2''',5''''-dihydroxybenzoyl)-ethyl]phenylazo)-phenylazo]-1-naphthol. 5

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