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3,236,645

PHOTOGRAPHIC PROCESSES, COMPOSITIONS
AND PRODUCTS

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33 Claims. (Cl. 96—29)

This application is in part a continuation of our copend-
ing application, Serial No. 612,054, filed September 25,
1956 (now abandoned).

This invention relates to photography and more partic-
ularly 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 com-
positions for the development of silver halide emulsions,
in which the novel silver halide developing agent is cap-
able of developing an exposed silver halide emulsion and
imparting a reversed or positive colored image of the
developed image to a superposed image-receiving mat-
erial.

Further objects are to provide said novel silver halide
developing agents, and novel products, processes and
compositions suitable for use in preparing mono-
chromatic 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 in-
volving 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 disclo-
sure, 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 herein-
after.

The dye developers and the photographic processes and
compositions disclosed herein are particularly useful in
the treatment of an exposed silver halide emulsion, where-
by a positive dye image may be imparted to another el-
ement, 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 posi-
tive 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 con-
cepts herein set forth provide novel dye developers which
may be advantageously used in such processes.

In carrying out the process of this invention, a photo-
sensitive 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 super-
posed prior to, during or after wetting, on an image-

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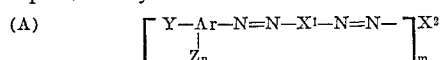
receiving element. In a preferred embodiment, the
photosensitive element contains a layer of dye developer,
and the liquid processing composition is applied to the
photosensitive element in a uniform layer as the photo-
sensitive element is brought into superposed position with
an image-receiving element. The liquid processing com-
position permeates the emulsion to provide a solution
of dye developer substantially uniformly distributed
therein. As the exposed silver halide emulsion is de-
veloped, 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 process-
ing composition. This immobilization is apparently due,
at least in part, to a change in the solubility characteris-
tics 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-receiv-
ing layer. The image-receiving layer receives a depth-
wise diffusion, from the emulsion, of unoxidized dye
developer, without appreciably disturbing the image-
wise distribution thereof, to provide a reversed or posi-
tive, 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 com-
pensate 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 be-
hind 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 sub-
ject 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 pre-
ferred embodiment, has the advantage of providing in-
creased 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 com-
position. 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, diethyl-
amine, 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 rela-
tively 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

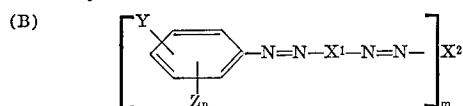
weight polymer such as a polymeric, water-soluble ether inert to an alkali solution, as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time may also be used.

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



wherein Ar is an aryl nucleus, such as a 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 paradihydroxyphenyl 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:

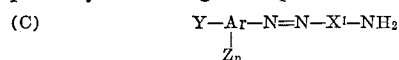


wherein Y, Z, n , X^1 , X^2 and m have the same meaning as above.

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 -keto acid arylamides; etc., and substituted derivatives thereof. Examples of groups which may be present in such substituted derivatives include alkyl, sulfo, alkoxy, aryl, aryl-oxy, amino, keto, alkylamino, arylamino, hydroxyl, cyano, alkylamido, arylamido, carbalkoxy, carboxamido, 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 a hydroxyphenyl, hydroxynaphthyl, hydroxy-anthryl, 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, 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 copending applications

of Myron S. Simon, Serial No. 612,053, filed September 25, 1956 (now abandoned), and in Serial Nos. 196,523, now U.S. Patent No. 3,183,089 and 196,524, now U.S. Patent No. 3,134,765, both filed May 21, 1962, as continuations-in-part of said Serial No. 612,053.

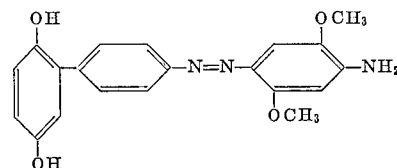
As examples of compounds which may be employed in the preparation of compounds within Formula C, e.g., by diazotizing the corresponding O,O'-diacetate and coupling into the desired azo coupler providing the radical X^1 , mention may be made of:

- 2-(p-aminophenyl)-hydroquinone
- 2-(m-aminophenyl)-hydroquinone
- 2-(p-aminophenyl)-5-methyl-hydroquinone
- 2-(p-aminophenyl)-5-chloro-hydroquinone
- 2-(3'-methyl-4'-aminophenyl)-hydroquinone
- 2-(p-aminophenyl)-5,6-dimethyl-hydroquinone
- 2-(4'-aminonaphthyl)-hydroquinone
- 2-(m-aminophenyl)-5-methyl-hydroquinone
- 2-(4'-amino-3'-methoxy-phenyl)-hydroquinone
- 2-(p-aminophenyl)-6-methyl-hydroquinone
- 2-(p-aminophenyl)-5-bromo-hydroquinone
- 2-(4'-amino-2',5'-dimethoxy-phenyl)-hydroquinone
- 2-(4'-amino-2'-chloro-phenyl)-hydroquinone
- 2-(4'-amino-2'-methyl-phenyl)-hydroquinone

These compounds are disclosed in the above-mentioned copending applications of Myron S. Simon.

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'-dihydroxyphenyl)-phenylazo]-aniline.

It will be understood that the selection of particular 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 applications of Myron S. Simon.

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 X^2 , 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.

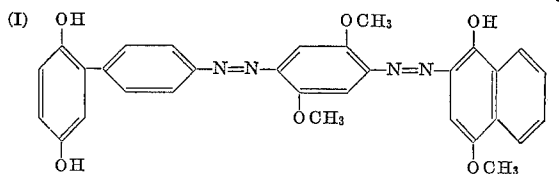
The coupling component employed to provide the residue X^1 is preferably a coupler containing a diazotizable amino group. It is to be understood, however, that one

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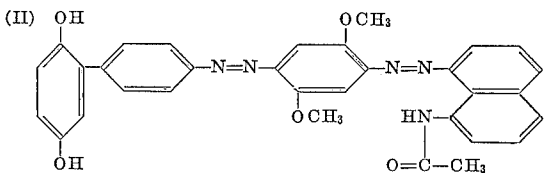
may employ a coupler having a group convertible to a diazotizable amino group, e.g., a nitro group. The diazotizable amino group may be on a ring or nucleus other than the one substituted by the azo grouping.

It will be noted that, in lieu of coupling first into X^1 and then diazotizing that initial coupling product and coupling into X^2 , one may first form a monoazo compound corresponding to the azo coupling product of X^1 and X^2 , and then couple into the X^1 portion of that monoazo compound in a manner analogous to that employed to prepare the compounds of Formula C above.

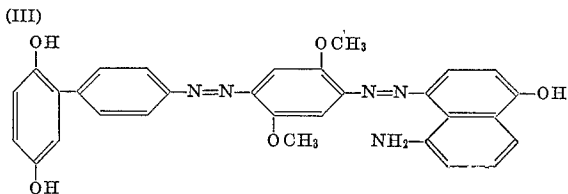
As examples of suitable dye developers within the scope of this invention, mention may be made of the following:



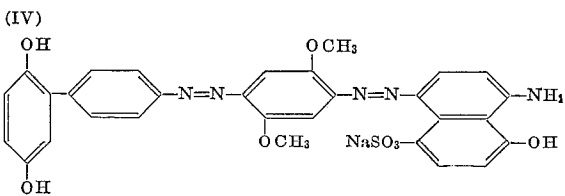
2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-4-methoxy-1-naphthol



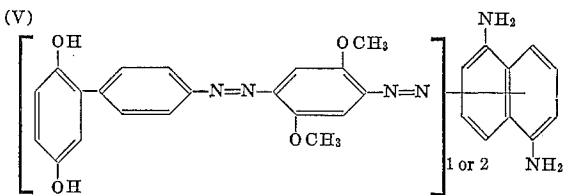
8-acetamido-1-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-2-naphthol



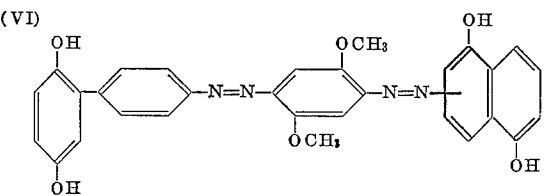
5-amino-4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-1-naphthol



8-hydroxy-4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-1-naphthylamine-5-sulfonate

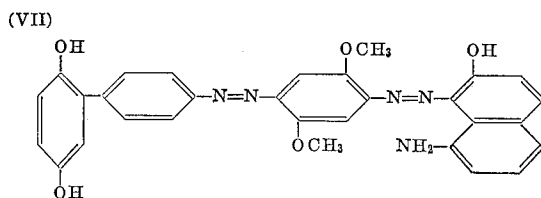


2- and 2,6-bis-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-1,5-naphthalene diamine

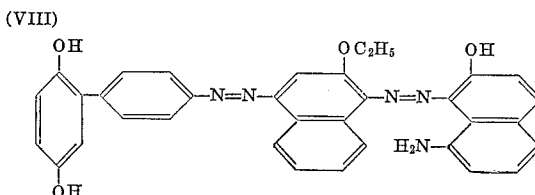


2- and 4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-1,5-dihydroxynaphthalene

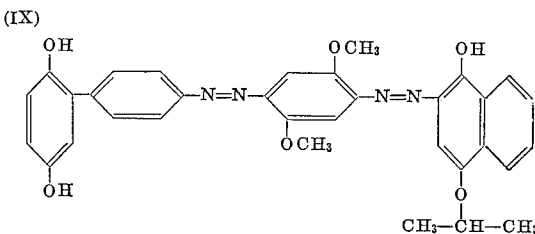
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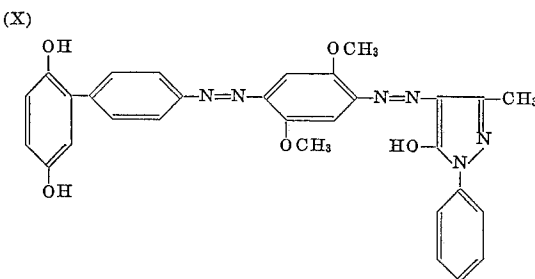
8-amino-2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-2-naphthol



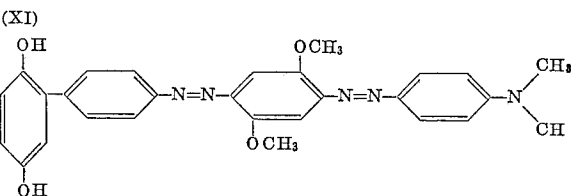
1-(4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-o-ethoxy-α-naphthylazo)-8-amino-2-naphthol



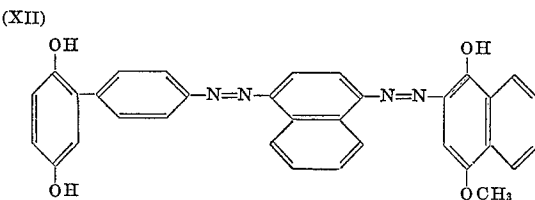
2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-4-isopropoxy-1-naphthol



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



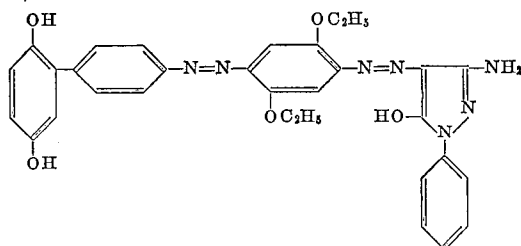
4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-N,N-dimethylaniline



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

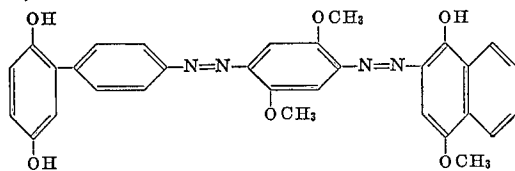
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(XIII)



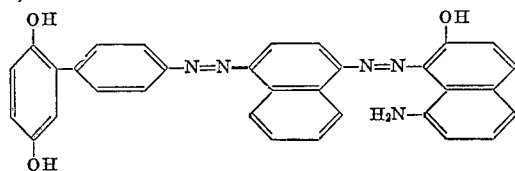
1-phenyl-3-amino-4-(4'-(p-(2'',5''-dihydroxyphenyl)-phenylazo)-2',5'-diethoxyphenylazo)-5-pyrazolone

(XIV)



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

(XV)



1-(4'-(p-(2'',5''-dihydroxyphenyl)-phenylazo)-8-amino-2-naphthol

As examples of additional coupling components which may be used to proxide 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-naphthanilide
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, Serial No. 192,354, now U.S. Patent No. 3,134,762, and Serial No. 192,355, both filed May 4, 1962, as continuations in part of Serial No. 612,055, filed September 25, 1956 (now abandoned), by the fact that the aryl nucleus Ar is directly attached to the phenyl ring of Y. The dye developers of this invention unexpectedly have been found to give higher film speed (exposure index), and better control or ratio between D_{max.} and D_{min.} when employed in diffusion transfer processes, as compared with similar dye developers of the just-mentioned Husek applications. 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.

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Example 1

2,5-dimethoxy-4-[4'-(2'',5''-bis-acetoxyphe-
nol)-phenylazo]-aniline (1.12 g., 0.0025 mole) in 10 cc. of glacial acetic acid is diazotized, at about 10–15° C., by the addition of 0.175 g. (0.0025 mole) of sodium nitrite in 2 cc. of water. The resulting solution is added, with stirring, to 0.43 g. of 4-methoxy-1-naphthol dissolved in 30 cc. of acetone, 20 cc. of water and 15 cc. of a 25% sodium carbonate solution. Sufficient sodium carbonate is added to keep the solution slightly basic. After stirring for an hour, the reaction mixture is filtered and the precipitate washed with water. The product is purified by twice dissolving in methyl cellosolve and precipitating in 1% hydrochloric acid. Hydrolysis by heating, under nitrogen, with 10% sodium hydroxide and methanol and precipitation with acetic acid yields 2-(2',5'-dimethoxy-4'-(p-(2'',5''-dihydroxyphenyl)-phenylazo)-phenylazo)-4-methoxy-1-naphthol [Formula I] in a 63% yield. Examination of the absorption spectrum of the product in methyl Cellosolve shows absorption maxima at 414 m μ (ϵ =21,000) and at 596 m μ (ϵ =48,000) with absorption above ϵ =10,000 from 400 to 670 m μ .

Example 2

1,5-dihydroxynaphthalene (0.4 g.) in a mixture of 30 cc. of acetone and 20 cc. of water is made slightly alkaline with 25% sodium carbonate solution. Diazotized 2,5-dimethoxy-4-[4'-(2'',5''-bis-acetoxyphe-
nol)-phenylazo]-aniline (prepared as described in Example 1) is added, with stirring, at about 10–15° C. The pH of the mixture is adjusted to about 7.5 by the addition of sodium carbonate. After an additional hour of stirring, the reaction mixture is filtered. The precipitate is washed with water and reprecipitated from methyl Cellosolve into 1% hydrochloric acid. The wet product is hydrolyzed by heating, under nitrogen, in 10% sodium hydroxide and methanol. After precipitation with glacial acetic acid and filtering, the precipitated product is reprecipitated from methyl Cellosolve into sodium chloride-sodium acetate solution, giving a 61.6% yield. The product is a mixture of the 2- and 4-coupled, and, in accordance with conventional azo dye nomenclature, may be referred to as 2,5-dimethoxy-4-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-aniline $\rightarrow$ 1,5-naphthalene diol [Formula VI]. It is believed that the product is predominantly the 4-coupled dye developer. The absorption spectrum of the product in methyl Cellosolve exhibits a maximum at 558 m μ , ϵ =31,000 with absorption above ϵ =14,000 from 400–630 m μ and ϵ >7,000 from 400–700 m μ .

Example 3

The procedures described in Examples 1 and 2 are repeated employing, as the coupling component, 0.4 g. of 5-amino-1-naphthol dissolved in 30 cc. of acetone and 30 cc. of water. The reaction mixture is maintained slightly basic by addition of sodium carbonate. The mixture is stirred for about 30 minutes after addition of the diazonium compound, after which the product is salted out with sodium acetate solution. The precipitate is collected, washed in water, dissolved in methyl Cellosolve, filtered and precipitated with sodium acetate solution. The product is reprecipitated, suspended in ethanol and hydrolyzed by heating, under nitrogen, in 10% sodium hydroxide for a few minutes in a steam bath. Precipitation with sodium acetate solution followed by reprecipitation from methyl Cellosolve with sodium acetate gives 5-amino-4-(2',5'-dimethoxy-4'-(p-(2'',5''-dihydroxyphenyl)-phenylazo)-phenylazo)-1-naphthol [Formula III] as a blue-black solid. The spectral absorption curve of the dye developer in methyl Cellosolve exhibits maxima at 535–540 m μ , ϵ >17,000 and at 581 m μ , ϵ >23,400 and an absorption above 15,000 from 400 to about 640 m μ .

Example 4

The procedure described in Example 3 is repeated using 0.0025 mole of 8-amino-2-naphthol to give 8-amino-2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl) - phenylazo]-phenylazo)-2-naphthol [Formula VII]. The absorption spectrum in methyl Cellosolve exhibits a maximum at 570 m μ , ϵ =18,600 and an absorption above 13,000 from 400 to about 640 m μ .

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 5

A photosensitive element is prepared by coating a gelatin-coated film base with a solution containing 3% of 8-acetamido-2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-4-methoxy - 1 - 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 -----	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 6% aqueous polyvinyl alcohol. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a navy blue positive dye image of the photographed subject.

Example 6

A photosensitive element similar to that described in Example 5 is prepared using 3% of 5-amino-4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl) - phenylazo]-phenylazo)-1-naphthol [Formula III] prepared as described in Example 3. Processing of the exposed photosensitive element with an aqueous processing composition comprising:

	Percent
Sodium carboxymethyl cellulose -----	5.0
Potassium bromide -----	0.2
1-phenyl-3-pyrazolidone -----	0.2
Sodium hydroxide -----	3.0

using, as the image-receiving element, a layer of polyvinyl alcohol (cast from a 6% aqueous polyvinyl alcohol solution) on a cellulose acetate-coated baryta paper support, gives a dark grey, positive image.

Example 7

A navy positive transfer image is obtained using a photosensitive element prepared and processed similar to that described in Example 5 using 3% of 2,5-dimethoxy-4-[p-(2',5'-dihydroxyphenyl) - phenylazo]-aniline $\rightarrow$ 1,5-naphthalene diol as prepared in Example 2 [Formula VI].

Example 8

Use of a photosensitive element prepared and processed similar to that described in Example 5 using 3% of 8-hydroxy - 4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl) - phenylazo] - phenylazo)-1-naphthylamine-5-sodium sulfonate gives a green positive transfer image.

As previously noted, it is also contemplated to utilize the dye developers of this invention in the processing composition. In this connection, it is sometimes desirable to place the silver halide emulsion layer over the image-receiving layer so that the dye developer must permeate through the emulsion before it can dye the image-receiving material. A suitable stripping layer is provided between the image-receiving and emulsion layers. Upon stripping, after imbibition, the emulsion layer and the layer of processing composition adhere to a backing or spreading layer or element provided to facilitate spreading of the processing composition. A suitable film structure of this type is described in U.S. Patent No. 2,698,244, issued December 28, 1954, to Edwin H. Land, and in particular, FIGURE 7 of said patent. The following examples are given to illustrate the use of such a film arrangement as well as the use of a dye developer in the processing composition, and are intended to be illustrative only.

Example 9

A photosensitive element is prepared in the following manner: A polyvinyl butyral coating is applied to a cellulose acetate-coated baryta paper, followed by coating with a solution comprising 15 g. of N-methoxymethyl polyhexamethylene adipamide in 80 cc. of isopropanol and 20 cc. of water to provide the image-receiving layer. The sheet is then coated with a 4% aqueous gelatin solution, followed by coating with a solution comprising 4 g. of cellulose acetate hydrogen phthalate in 80 cc. of acetone and 20 cc. of methanol. A silver halide emulsion is then applied and the photosensitive element exposed. Processing is effected by an aqueous composition comprising:

	Percent
Sodium carboxymethyl cellulose -----	4.5
Sodium hydroxide -----	4.0
Potassium bromide -----	0.2
Sodium carbonate -----	4.0
1-phenyl-3-pyrazolidone -----	0.2
5 - amino-4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-1 - naphthol [Formula III, prepared as described in Example 3] -----	5.0

spread between the exposed photosensitive element and a backing or spreading element comprising a polyvinyl butyral-coated baryta paper. After an imbibition period of approximately 2 minutes, the image-receiving layer is separated and contains a dark grey positive dye image of the photographed subject.

Example 10

The procedure described in Example 9 is repeated employing an aqueous processing composition comprising:

	Percent
Sodium carboxymethyl cellulose -----	4.5
Sodium hydroxide -----	2.0
Potassium bromide -----	0.2
Sodium carbonate -----	2.0
1-phenyl-3-pyrazolidone -----	0.2
8 - amino-2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl) - phenylazo]-phenylazo)-2-naphthol [Formula VII, prepared as described in Example 4] -----	4.0

After an imbibition period of approximately two minutes, the image-receiving layer is separated and contains a navy blue, positive dye image.

It should be noted that dye developers in which a hydroquinonyl group becomes a part of the conjugated system may be sensitive to pH changes. Since the dye developer is rendered effective by solution in an aqueous alkaline liquid processing composition, it accordingly is necessary to assure that the environment in which the transferred and unreacted dye developer is deposited has or is capable of attaining the requisite pH value affording the desired color to the diffused dye developer. This may be accomplished by use of a volatile basic compound such as diethylamine in the liquid processing composition. If so-

dium hydroxide is utilized in the processing liquid, it becomes carbonated after processing and by contact with the air and this is effective to provide the desired pH change. Further control of the pH of the transferred and unreacted dye developer may be had by utilizing an image-receiving element which is difficultly penetrable by alkali, for example an appropriate nylon such as N-methoxymethyl polyhexamethylene adipamide, or by the use of a receiving element in which an acid or an acid-forming compound, e.g., oleic acid, has been incorporated.

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, now U.S. Patent No. 3,185,567, 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 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, now U.S. Patent 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-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.

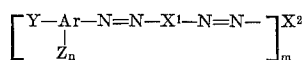
In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black.

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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 directly attached to said phenyl ring of Y and 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; 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 X¹ and X² 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 Ar is phenyl, n is 0, m is 1, and Y is 2,5-dihydroxyphenyl.

3. A photographic developer composition as defined in claim 1, wherein X² is a phenolic azo coupler radical.

4. A photographic developer composition as defined in claim 1, wherein X² is an aromatic amino azo coupler radical.

5. A photographic developer composition as defined in claim 1, wherein X² is a heterocyclic aromatic azo coupler radical.

6. A photographic developer composition as defined in claim 1, wherein X² is selected from the group consisting of aliphatic and alicyclic activated methylene azo coupler radicals.

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

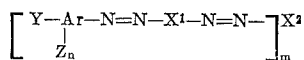
8. A photographic developer composition as defined in claim 1, wherein said silver halide developing agent is a hydroquinone.

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

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

12. 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-

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dihydroxyphenyl, o-dihydroxyphenyl radicals and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus directly attached to said phenyl ring of Y and 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; 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 X¹ and X² 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.

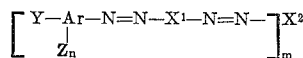
13. A photographic product as defined in claim 12, wherein said azo dye developer is 2-(2',5'-dimethoxy-4'-[p - (2'',5'' - dihydroxyphenyl) - phenylazo] - phenylazo)-4-methoxy-1-naphthol.

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

15. A photographic product as defined in claim 12, wherein said azo dye developer is 2,5-dimethoxy-4-[p-(2',5' - dihydroxyphenyl) - phenylazo] - aniline→1,5-naphthalene diol.

16. A photographic product as defined in claim 12, wherein said azo dye developer is in a layer positioned between said support and said layer containing said silver halide emulsion.

17. 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 directly attached to said phenyl ring of Y and 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; 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 X¹ and X² 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.

18. The process as defined in claim 17, wherein Ar is phenyl, n is 0, m is 1, and Y is 2,5-dihydroxyphenyl.

19. The process as defined in claim 17, 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.

20. The process as defined in claim 19, 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.

21. The process as defined in claim 19, wherein said liquid contains a thickener for increasing viscosity and for facilitating the spreading thereof between said photosensitive element and said image-receiving element.

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22. The process as defined in claim 17, wherein said dye developer is dissolved in an aqueous alkaline solution prior to application thereof to said exposed emulsion.

23. A process as defined in claim 17, wherein X^2 is a phenolic azo coupler radical.

24. A process as defined in claim 17, wherein X^2 is an aromatic amino azo coupler radical.

25. A process as defined in claim 17, wherein X^2 is a heterocyclic aromatic azo coupler radical.

26. A process as defined in claim 17, wherein X^2 is an azo coupler radical selected from the group consisting of aliphatic and alicyclic activated methylene couplers.

27. The process as defined in claim 17, wherein said dye developer is 2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-4-methoxy-1-naphthol.

28. The process as defined in claim 17, wherein said dye developer is 5-amino-4-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenyl)-phenylazo]-phenylazo)-1-naphthol.

29. The process as defined in claim 17, wherein said dye developer is 2,5-dimethoxy-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-aniline→1,5-naphthalene diol.

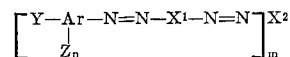
30. A process as defined in claim 17, wherein said aqueous alkaline solution includes a silver halide developing agent which is substantially colorless in at least the unoxidized form.

31. A process as defined in claim 30, wherein said silver halide developing agent is a 3-pyrazolidone.

32. A process as defined in claim 30, wherein said silver halide developing agent is a hydroquinone.

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33. 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 directly attached to said phenyl ring of Y and 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; 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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