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AZO DYE DEVELOPERS

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5 Claims. (Cl. 260—162)

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 developers which may be advantageously used in such processes.

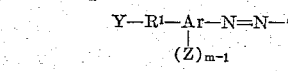
In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed prior to, during or 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 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 separating the image-receiving layer from the silver halide emulsion at the end of the imbibition period.

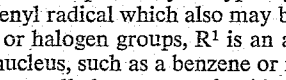
The dye developers of this invention may be utilized in the photosensitive element, for example in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer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

(A) 

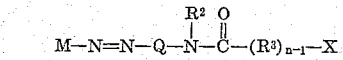
wherein Y is a para-dihydroxyphenyl or an ortho-dihydroxyphenyl radical which also may be nuclear substituted by alkyl or halogen groups, R^1 is an alkylene group, Ar is an aryl nucleus, such as a benzene or naphthalene nucleus, each Z is an alkyl group, preferably a lower alkyl group such as methyl or ethyl, an alkoxy group, preferably a lower alkoxy group such as methoxy, or a halogen, such as chlorine, m is 1, 2 or 3, and Q is the radical of an azo coupling component. Dye developers of the formula:

(B) 

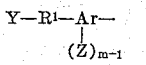
wherein Y, Ar, Z, m and Q have the same meanings as above, are disclosed in the copending application of Myron S. Simon, Serial No. 612,053, filed September 25, 1956 (now abandoned, and replaced by Serial No. 196,523, filed May 21, 1962).

We have now discovered highly useful dye developers which are related to the above-mentioned dye developers and which have improved properties.

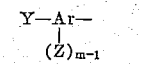
The novel azo dye developers of this invention may be represented by the formula:

(C) 

wherein M is

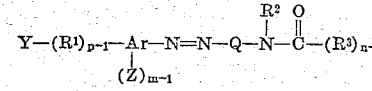


or



R^1 is an alkylene group, preferably an alkylene group containing no more than five carbon atoms and more preferably an ethylene ($-CH_2CH_2-$) or trimethylene ($-CH_2-CH_2-CH_2-$) group; 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 a methyl or ethyl, or a halogen, such as chlorine, or an alkoxy group, preferably a lower alkoxy group such as methoxy or ethoxy; m is 1, 2 or 3; Y is a para-dihydroxyphenyl or ortho-dihydroxyphenyl radical which also may be nuclear substituted by alkyl or halogen groups; Q is the radical of an azo coupler (coupling component); R^2 is hydrogen or an alkyl group, preferably a lower alkyl group such as methyl or ethyl; R^3 is an alkylene group, and preferably an alkylene group containing less than six carbons; n is 1 or 2; and X is a benzene nucleus substituted by at least two hydroxyl and/or amino groups, substituted in the ortho or para positions with respect to each other, and also may be substituted by halogen, alkyl, or additional hydroxyl or amino groups, insofar as the silver halide developing ability possessed by X is not destroyed by such further substitution. The amino groups in X may be substituted by alkyl groups.

Alternatively, the novel dye developers of this invention may be represented by the formula:

(CC) 

wherein Y, R^1, Ar, Z, m, Q, R^2, R^3, n and X have the same meaning as above, and p is 1 or 2.

One method of preparing the dye developers of this invention is by reacting dye developers of the above Formulae A and B, wherein Q contains a reactive amino

group, with a suitable derivative of a compound of the formula:

(D) 

such as, for example, the corresponding lactone or acid chloride, wherein R^3 is an alkylene group, preferably an alkylene group containing less than six carbons, X is a phenyl radical the benzene nucleus of which is substituted, in the ortho or para positions with respect to each other, by members of the group consisting of hydroxyl and amino radicals, and X also may be nuclear substituted by other groups, e.g., alkyl, alkoxy, and halogen, and n is 1 or 2.

It will be noted that Q may contain substituents such as alkyl, sulfo, alkoxy, aryl, aryloxy, amino, alkylamino, arylamino, hydroxyl, cyano, keto, alkylamido, arylamido, carbalkoxy, carboxamido, sulfonamido, etc.

In a preferred embodiment, Ar is a benzene nucleus, and X and Y are hydroquinonyl groups.

Compounds of Formulae A and B useful in preparing the novel dye developers of this invention may be synthesized as described in the aforementioned copending applications, i.e., by diazotizing a compound of the formula:

(E) 

or

(F) 

wherein Z, m, Ar, R^1 and Y have the same meaning as above, and particularly a derivative thereof wherein the hydroxyl groups of Y are protected, e.g., an O-acylated derivative, and coupling the diazotized compound E or F into an aryl or an aromatic or a heterocyclic azo coupler possessing an amino group (or a group readily convertible into an amino group), which amino group should not enter into the coupling reaction. The preparation of amino compounds within the Formula E is disclosed in the copending application of Elkan R. Blout, Milton Green, Howard G. Rogers, Myron S. Simon and Robert B. Woodward, Serial No. 612,051, filed September 25, 1956 (now U.S. Patent No. 3,019,107, issued January 30, 1962), and disclosed and claimed in a continuation-in-part thereof, Serial No. 98,287, filed March 27, 1961. The preparation of protected derivatives of these amino compounds for use in the diazotization procedure, such as the bis-acetoxy derivatives, is disclosed and claimed in the copending application of Milton Green and Helen P. Husek, Serial No. 612,063, filed September 25, 1956, which application has been abandoned in favor of a continuation-in-part thereof, Serial No. 805,673, filed April 13, 1959 (now U.S. Patent No. 3,019,254, issued January 30, 1962).

As illustrations of suitable azo coupling components or couplers from which Q 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, naphthylamines, anthrols, 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 arylamines; etc. and substituted derivatives thereof; which couplers possess an amino group which will not enter into the coupling reaction. 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 respect to Q, the expression

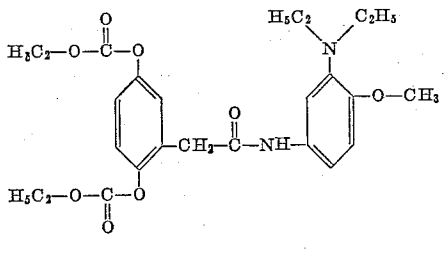
"radical of a phenolic coupler" is intended to refer to hydroxyphenyl, hydroxynaphthyl, hydroxyanthryl, etc., radicals, and substituted derivatives thereof; the expression "radical of an aromatic amino coupler" is intended to refer to aminophenyl, aminonaphthyl, etc., radicals, and substituted derivatives 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.

It is to be understood that the reactive amino group may be in a portion of the azo coupler radical other than that to which the azo group is attached. In certain instances, as where it may be desired to direct the azo coupling into a particular portion of the coupler, one may employ a nitro-substituted coupler and selectively reduce the nitro group to an amino group after azo coupling has been effected. Thus, one may azo couple into a nitrophenyl-substituted pyrazolone and subsequently selectively reduce the nitro to an amino group for further reaction.

The amino-substituted, azo intermediate is reacted with a suitable derivative of a compound of the above-mentioned Formula D, such as, for example, the lactone or acid chloride, according to the synthetic procedures disclosed and claimed in the copending application of Elkan R. Blout et al., Serial No. 471,542, filed November 26, 1954 [now abandoned in favor of a continuation-in-part application, Serial No. 1,443, filed January 11, 1960]. Suitable compounds for this purpose include homogentisic acid lactone, homogentisic acid chloride and gentisic acid chloride. When employing such compounds, it is preferred to protect the hydroxyl or amino groups in X which provide the developing function in order to avoid undesirable side reactions; this may be accomplished by acylation or by reaction with an alkyl chloroformate to form carboalkoxy derivatives. After reaction, and prior to photographic use, the protective groups are removed, as by hydrolysis. Examples of such protected compounds include homogentisic acid chloride dibenzoate and dicarbomethoxy gentisyl chloride. It will be apparent that one advantage of using a lactone, e.g., homogentisic acid lactone, is that it is unnecessary to further protect the hydroxyl groups and hence no hydrolysis step is necessary.

Additional lactones include 2,5-dihydroxy-β-methyl-dihydrocinnamic acid lactone, 2,4,5-trihydroxy-β-dihydrocinnamic acid lactone, 2,5-dihydroxy-4-methoxy-β-methyl-dihydrocinnamic acid lactone, 2-hydroxy-5-amino-β-methyl-dihydrocinnamic acid lactone, and 2,5-dihydroxy-3,6-dimethyl-β-methyl-dihydrocinnamic acid lactone, which lactones may be prepared as disclosed and claimed in the copending application of Samuel Dershowitz, Serial No. 147,761, filed October 26, 1961.

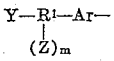
An alternative method of synthesizing dye developers within the scope of this invention is to diazotize a compound of the Formula E or F, e.g., an O-acylated derivative as described above, and couple the resulting diazotised compound into the compounds disclosed and claimed in the copending application of Milton Green, Helen P. Husek and Sidney Kasman, Serial No. 709,001, filed January 15, 1958 (now abandoned and replaced by Serial No. 200,639, filed June 7, 1962), e.g.,



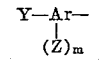
and hydrolyze the coupling product to regenerate the

hydroquinonyl groups. Diazotization of non-developer amines, e.g., aniline and 2,5-dimethoxy-aniline, into the compounds of Serial No. 709,001 (now abandoned) is disclosed and claimed in the copending application of Milton Green, Helen P. Husek and Sidney Kasman, Serial No. 75,127, filed December 12, 1960, as a continuation-in-part of Serial No. 709,005, filed January 15, 1958 (now abandoned).

In the preferred embodiment, M is a



group, since the resulting products do not exhibit the pH sensitivity of the dye developers wherein M is



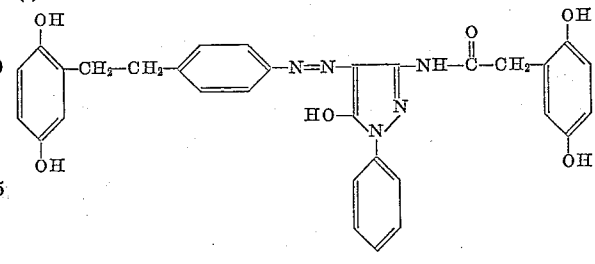
i.e., where *p* in Formula CC is 1.

The novel and unobvious dye developers of this invention possess superior photographic properties as compared with many dye developers of the aforementioned copending applications, e.g., the dye developer of Formula I below gave a lower $D_{min.}$ and greater density contrast when employed in the diffusion transfer process of the aforementioned U.S. Patent No. 2,983,606, as compared with the closely related 1-phenyl-3-homogentisamido-4-phenylazo-5-pyrazolone dye developer disclosed in Serial No. 471,542 (now abandoned in favor of Serial No. 1,443, as noted above). Similarly, the dye developer of Formula I below, when used in the processing composition, gave transfer images of improved contrast as compared with the closely related 1-phenyl-3-amino-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone or 1-phenyl-3-N-n-hexylcarboxamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone of said Serial No. 612,045 (now abandoned in favor of Serial No. 144,816, as noted above).

In addition, many of the novel dye developers of this invention, e.g., the compound of Formula I below, crystallize to yield polarizing crystals and thus are useful in the processes and products of U.S. Patent No. 2,997,390 issued to Edwin H. Land on August 22, 1961.

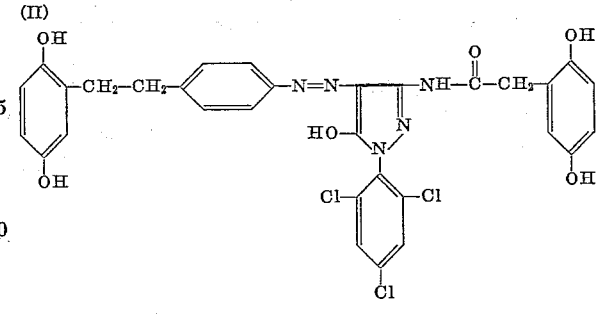
As examples of dye developers within the scope of this invention, mention may be made of the following:

(I)



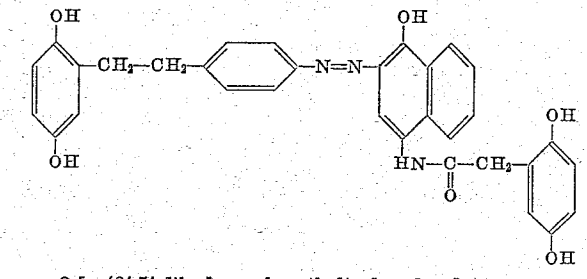
1-phenyl-3-homogentisamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone

(II)



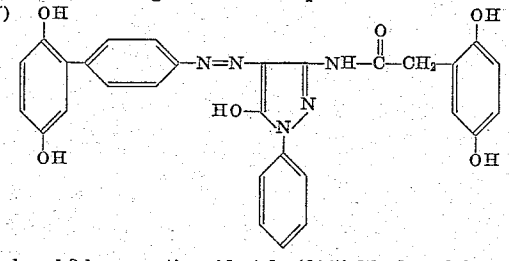
1-(2',4',6'-trichlorophenyl)-3-homogentisamido-4-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-5-pyrazolone

(III)



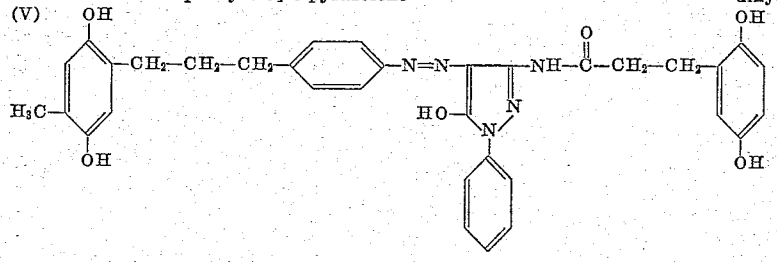
2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-homogentisamido-1-naphthol

(IV)



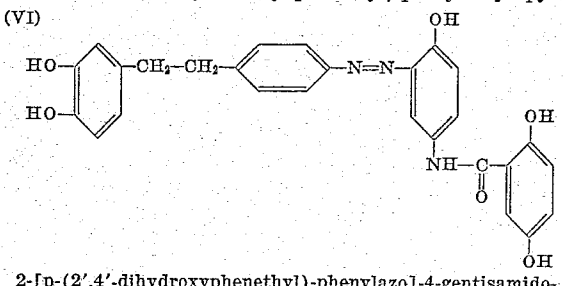
1-phenyl-3-homogentisamido-4-[p-(2',5'-dihydroxylphenyl)-phenylazo]-5-pyrazolone

(V)



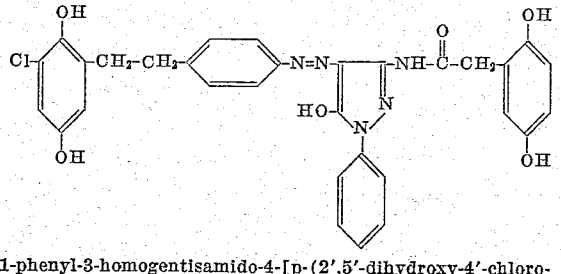
1-phenyl-3-(2',5'-dihydroxy-dihydrocinnamido)-4-[p-(2',5'-dihydroxy-4-methyl-phenethyl)-phenylazo]-5-pyrazolone

(VI)



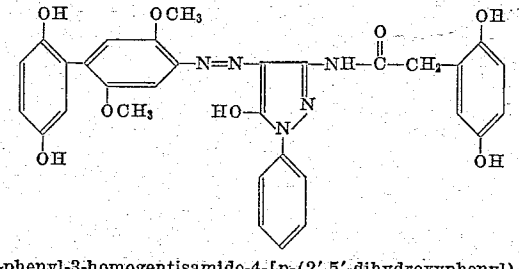
2-[p-(2',4'-dihydroxyphenethyl)-phenylazo]-4-gentisamido-1-phenol

(VII)



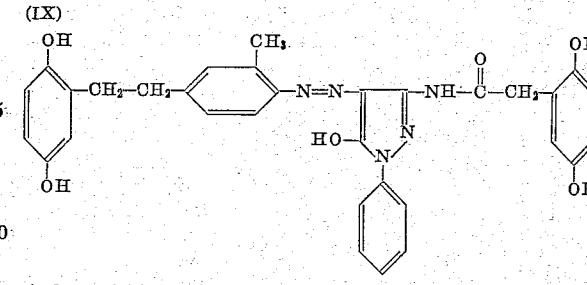
1-phenyl-3-homogentisamido-4-[p-(2',5'-dihydroxy-4'-chlorophenethyl)-phenylazo]-5-pyrazolone

(VIII)



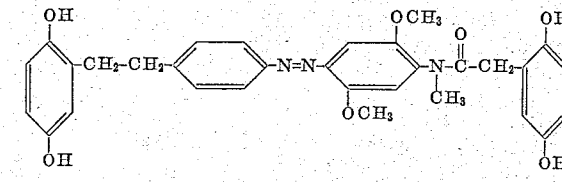
1-phenyl-3-homogentisamido-4-[p-(2',5'-dihydroxyphenyl)-2,5-dimethoxyphenylazo]-5-pyrazolone

(IX)



1-phenyl-3-homogentisamido-4-[p-(2',5'-dihydroxyphenethyl)-o-methylphenylazo]-5-pyrazolone

(X)



1-N-methyl-homogentisamido-2,5-dimethoxy-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-benzene

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

Example 1

Aminophenethyl hydroquinone O,O-diacetate hydrochloride (7.9 g.; 0.02 mol) is dissolved in 150 cc. of water containing 4 cc. of concentrated HCl (0.05 mol), and diazotized at 0–5° C. by the addition of 1.4 g. $NaNO_2$ (0.02 mol) in 15 cc. of water. After ten minutes, the solution is clarified after which the pH is raised to 5–6 with sodium acetate. The clear diazo solution is then added at room temperature over a period of half an hour to a solution of 3.15 g. (0.018 mol) of 1-phenyl-3-amino-5-pyrazolone in 300 cc. of ethanol and 300 cc. of 10% $NaHCO_3$. The resulting yellow-brown slurry is stirred at room temperature for two hours, filtered, and the filter cake washed thoroughly with 10% $NaHCO_3$. The filter cake is reslurried in dilute acetic acid solution, filtered, and washed thoroughly with water. The product is dried in vacuo over sulfuric acid yielding 8 g. (89%).

To 115 cc. of dry benzene is added 6 g. (0.012 mol) of the preceding product, and 6 g. (0.018 mol) of bis-carbethoxy homogentisyl chloride, followed by 20 drops of pyridine. The solution is refluxed for four hours, cooled and precipitated by addition of hexane. A somewhat gummy orange solid precipitates and is filtered and washed with hexane.

The filter cake is immediately dissolved in a solution of 160 cc. of ethanol after which 40 cc. of water and 18 g. of potassium hydroxide are added and the flask immediately evacuated. It is shaken for five minutes with intermittent heating on a steam bath, then cooled and acidified directly with hydrochloric acid and diluted with water to complete the precipitation. After filtering the solid is washed with water.

The filter cake is dissolved in a minimum amount of ethanol under nitrogen and the hot solution treated with

activated charcoal. The product is reprecipitated from the filtrate by a 1% NaCl solution containing a trace of HCl, the solid filtered and the procedure repeated. The resulting orange-brown solid is filtered, washed with water and dried to give 6 g. (88% yield) of the dye developer 1-phenyl-3-homogentisamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone [Formula I] melting at 190° C. Analysis of the product shows:

	C	H	N
Calculated	65.8	4.8	12.4
Found	65.7	5.1	12.2

The absorption spectrum of this dye developer exhibits a $\lambda_{max.}$ at 407 mμ, ϵ=32,000.

Example 2

The procedure described in Example 1 is repeated using 1-(2',4',6-trichlorophenyl)-3-amino-5-pyrazolone in lieu of 1-phenyl-3-amino-5-pyrazolone. Nitrogen analysis of the 1 - (2',4',6' - trichlorophenyl) - 3 - homogentisamido-4 - [p - (2'',5'' - dihydroxyphenethyl) - phenylazo] - 5-pyrazolone [Formula II] (M.P. 160–165° C.) shows a value of 10.2% as compared to a calculated value of 10.5%.

Example 3

Aminophenethyl hydroquinone O,O-diacetate hydrochloride (6.7 g.) is dissolved in 100 cc. of water containing 3.6 cc. of concentrated hydrochloric acid, and diazotized at 5° C. by the addition of 1.2 g. of $NaNO_2$ in 20 cc. of water. After about ten minutes the solution is clarified and the pH raised to 5–6 with sodium acetate. The diazonium salt is added at 10° C. to 3.02 g. of 4-acetamido-1-naphthol in 20° C., the mixture is acidified with acetic acid, washed with water, filtered and dried.

The above product is hydrolyzed by dissolving 16.4 g. thereof in a solution of 10 g. of potassium hydroxide in 100 cc. of 50% ethanol, and refluxed under nitrogen for three and one-half hours. The solution is cooled, made barely acidic with concentrated hydrochloric acid, filtered, washed with water and dried.

A mixture of 3 g. of the thus prepared 2-[p-(2',5'-dihydroxyphenethyl) - phenylazo] - 4 - amino - 1 - naphthol, 3.1 g. of biscarbethoxy homogentisyl chloride and 60 cc. of o-dichlorobenzene is refluxed for two and one-half hours under a slow stream of nitrogen. The reaction mixture is then cooled, diluted with an equal amount of hexane and filtered. The wet filter cake is dissolved in a solution of 3 g. of potassium hydroxide in 50 cc. of ethanol and 10 cc. of water, and shaken in vacuo for ten minutes with intermittent warming on a steam bath. This mixture is then cooled and filtered into hydrochloric acid. The resulting slurry is filtered, washed well with water and then dried in vacuo over sulfuric acid. This product is dissolved in ethanol, filtered, clarified with Norite and Celite, and precipitated with water to give 0.65 g. (36% yield) of 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-homogentisamido-1-naphthol [Formula III], melting at 215–220° C. with decomposition. The spectral absorption curve of the product exhibits a $\lambda_{max.}$=514 mμ.

The following examples of the photographic use of the dye developers of this invention are given for purposes of illustration only.

Example 4

A photosensitive element is prepared by coating a gelatin-coated film base with a solution comprising 3% of 1 - phenyl-3-homogentisamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone [Formula I] in a solution comprising 4% cellulose acetate hydrogen phthalate in an 80:20 mixture of acetone and methanol. A silver iodobromide emulsion is applied over the layer of dye developer. After exposure, the photosensitive element is processed by an aqueous composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Potassium bromide	0.2
Sodium hydroxide	1.5
1-phenyl-3-pyrazolidone	0.2

while in superposed relationship with an image-receiving element prepared by coating a cellulose acetate - coated baryta sheet with a solution comprising 4 g. N-methoxymethyl polyhexamethylene adipamide in 80 cc. of isopropanol and 20 cc. of water. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a yellow, positive dye image of the photographed subjected matter.

Example 5

The procedure described in Example 4 is repeated employing, as the dye developer, 3% of 1 - (2',4',6' - trichlorophenyl) - 3 - homogentisamido - 4-[p-(2'',5''-dihydroxyphenethyl) - phenylazo]-5-pyrazolone [Formula II]. A yellow positive image is obtained at the end of the imbibition period.

Example 6

A magenta, positive dye image is obtained when the procedure described in Example 4 is repeated employing, as the dye developer, 3% of 2-[p-(2',5'-dihydroxyphenethyl) - phenylazo] - 4 - homogentisamido - 1 - naphthol [Formula III].

The quinones of the novel azo dye developers of this invention may be prepared by oxidizing under conditions which do not attack 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 processes. As an example of such photosenstive elements, mention may be made of the photosensitive elements disclosed and claimed in the copending U.S. applicataion 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-pheny-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 "monochromomatic" 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.

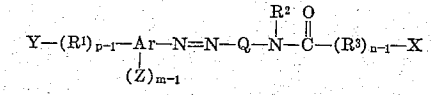
In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black.

This application is in part a continuation of our copending application, Serial No. 612,052, filed September 25, 1956 (now abandoned).

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. Azo dyes of the formula:



wherein Ar is an 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; each Z is selected from the group consisting of lower alkyl, halogen and lower alkoxy groups; *m* is an integer from 1 to 3, inclusive; Y is selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl radicals and lower alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; R^1 is a divalent lower alkylene group directly attached to said aryl nucleus Ar and to said phenyl ring of Y; Q is a divalent radical of an azo dye coupler linked to said —N=N— group and to said



R^2 is selected from the group consisting of hydrogen and lower alkyl groups; *n* is an integer from 1 to 2, inclusive; R^3 is a lower alkylene group; *p* is an integer from 1 to 2, inclusive; and X is selected from the group consisting of benzene nuclei substituted in the ortho and para positions, with respect to each other, by members of the group consisting of hydroxyl and amino radicals.

2. An azo dye as defined in claim 1, wherein Ar is benzene, R^1 is ethylene, *n* is 2, *m* is 1, *p* is 2, R^2 is hydrogen, R^3 is ethylene, and X and Y each is p-dihydroxyphenyl.

3. 1-phenyl-3-homogentisamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone.

4. 1-(2',4',6'-trichlorophenyl)-3-homogentisamido-4-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-5-pyrazolone.

5. 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-homogentisamido-1-naphthol.

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UNITED STATES PATENT OFFICE

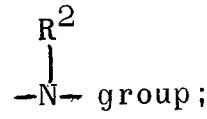
CERTIFICATE OF CORRECTION

Patent No. 3,135,734 June 2, 1964

Milton Green et al.

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 4, lines 67 and 68, for "arylamines" read -- arylamides --; column 5, lines 45 and 46, for "-β-dihydrocinnamic" read -- -β-methyl-dihydrocinnamic --; column 7, line 49, for "(2',4'-" read -- (3',4'- --; column 9, line 22, for (2',4',6-" read -- (2',4',6'- --; column 10, line 17, for "subjected" read -- subject --; column 11, lines 42 and 43, for '"monochromomatic"' read -- "monochromatic" --; column 12, lines 47 to 49, the formula should appear as shown below instead of as in the patent:



Signed and sealed this 9th day of March 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents