United States Patent Office 3,222,169
Patented Dec. 7, 1965

3,222,169

PHOTOGRAPHIC PRODUCTS, COMPOSITIONS AND PROCESSES EMPLOYING AZO DYE DEVELOPERS

Milton Green, Newton Center, and Howard G. Rogers, Weston, Mass., assignors to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Filed May 8, 1962, Ser. No. 193,326
39 Claims. (Cl. 96—29)

This application is in part a continuation of our copending application, Serial No. 663,905, filed June 6, 1957, now abandoned.

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

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

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

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

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

The invention accordingly comprises the processes involving the several steps and the relation and order of one or more of such steps with respect to each of the others, and the products and compositions possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

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

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

U.S. Patent No. 2,983,606, issued May 9, 1961 to Howard G. Rogers, discloses diffusion transfer processes wherein a photographic negative material, such as a photographic element comprising an exposed silver halide emulsion, is developed in the presence of a dye developer to impart to an image-receiving layer a reversed or positive dye image of the developed image by permeating into said emulsion a suitable liquid processing composition and bringing said emulsion into superposed relationship with an appropriate image-receiving layer. The inventive concepts herein set forth provide novel dye developers which may be advantageously used in such processes.

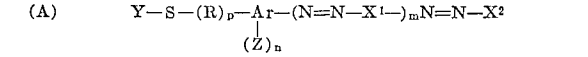
In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed prior to, during or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

ferred 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:

(A) 

wherein:

Y is a 2,5-dihydroxyphenyl group, which group also may be nuclear substituted by alkyl or halogen (such as chlorine) groups;

Ar is a divalent aryl nucleus, such as benzene or naphthalene nucleus, a ring carbon of said aryl nucleus being directly attached to an azo (—N=N—) group;

R is a divalent alkylene group, preferably an alkylene group containing no more than five (5) carbons, and more preferably an ethylene (—CH_2—CH_2—) or trimethylene (—CH_2—CH_2—CH_2—) group, directly attached to a ring carbon of said aryl nucleus Ar;

Each Z is an alkyl group, preferably a lower alkyl such as methyl or ethyl, an alkoxy group, preferably a lower alkoxy group much as methoxy or ethoxy, or a halogen such as chlorine;

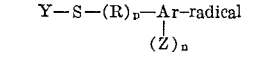
p is 0 or 1;

n is 0, 1 or 2;

m is 0 or 1;

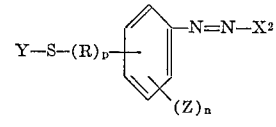
X^1 is the radical of an azo coupling component;

X^2 is the radical of an azo coupling component or a



And where X^2 is the radical of an azo coupling component or coupler, X^1 and X^2 may be the same or different, i.e., similar or dissimilar.

In a preferred embodiment, the compounds are monoazo and the aryl nucleus, Ar, is a benzene nucleus. Such compounds may be represented by the formula:

(B) 

wherein Y, R, *p*, Z, *n* and X^2 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 hydroxy or amino groups, such as pyrazolones or pyrroles; aliphatic or alicyclic activated methylene couplers, i.e., compounds having an aliphatic or alicyclic methylene group activated by two adjacent keto, aldehyde, ester or nitrile groups, which may be the same or different, or a keto, aldehyde, ester or nitrile group in combination with an amide group, e.g., 1,3-diketones or β-ketonic acid arylamides; etc., and substituted derivatives thereof. Examples of groups which may be present in such substituted derivatives include alkyl, sulfo, alkoxy, aryl, aryloxy, amino, keto, alkylamino, arylamino, hydroxyl, cyano, alkylamido, arylamido, carbalkoxy, carboxamido, sulfonamido, etc.

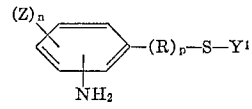
As used herein with reference to X^1 and X^2, the expression "radical of a phenolic coupler" is intended to refer to hydroxyphenyl, hydroxynaphthyl, hydoxyanthryl, etc. radicals, and substituted derivatives thereof; the expression "radical of an aromatic amino coupler" is intended to refer to aminophenyl, 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 compounds within Formulae A and B may be prepared from starting materials represented by the formula:

(C) 

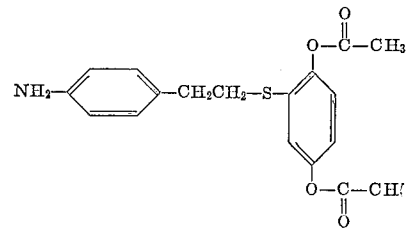
wherein Z, *n*, Ar, *p* and R have the same meaning as above and Y^1 is an O,O'-bis-acyl derivative of Y. The presence of the acyl radicals in the above starting materials is necessitated by the fact that free hydroquinone groups would effect decomposition of the intermediate diazonium compound required in preparation of the desired dye developers. Once the reactions are completed, the desired dihydroxyphenyl compounds may be readily obtained through hydrolysis. When using the above starting materials, the preparation may be carried out by diazotizing said starting materials; coupling the diazotized compound at a pH, preferably not greater than 9, into a coupling component which will provide the desired X^1 and/or X^2 coupler radical, and hydrolyzing the resulting bis-acyloxyphenyl azo compound to the desired dihydroxyphenyl derivative.

As indicated above, the aryl nucleus, Ar, is preferably a benzene nucleus and the preferred group of starting materials may be represented by the formula:

(D) 

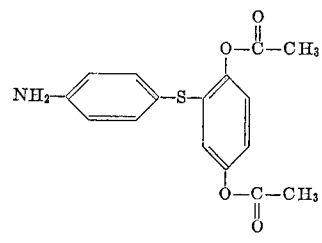
wherein Z, *n*, *p*, R and Y^1 have the same meaning as above. The preparation of starting materials within Formula C wherein *p* is 1 is disclosed in our copending application, Serial No. 663,866, filed June 6, 1957 (now U.S. Patent No. 3,009,958, issued November 21, 1961), and in a division thereof, Serial No. 93,303, filed March 6, 1961 (now U.S. Patent No. 3,081,339, issued March 12, 1963).

The preferred starting materials within the group represented by Formula C are:



p-aminophenethylthio-hydroquinone-O,O'-diacetate

and



p-aminophenylthio-hydroquinone-O,O'-diacetate

As examples of other compounds within Formula C, mention may be made of:

2-(p-aminophenethylthio)-5-methyl-hydroquinone-O,O'-diacetate

2-(p-aminophenethylthio)-5-chlorohydroquinone-O,O'-diacetate

2-(p-aminophenylthio)-3,6-dimethyl-hydroquinone-O,O'-diacetate
2-(p-aminophenethylthio)-3,5,6-trimethyl-hydroquinone-O,O'-diacetate
p-aminophenylmethylthio-hydroquinone-O,O'-diacetate
2-[γ-(4'-aminophenyl)-propylthio]-hydroquinone-O,O'-diacetate
2-(4'-amino-3'-methoxy-phenylthio)-hydroquinone-O,O'-diacetate
2-[4'-amino-3'-methylphenylthio]-hydroquinone-O,O'-diacetate
2-(α-4'-aminonaphthylthio)-hydroquinone-O,O'-diacetate
2-(4'-amino-3'-chlorophenylthio)-hydroquinone-O,O'-diacetate

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

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^1, and which have two available coupling positions, as, for example, phenols and aromatic amines such as 1,6-dihydroxy naphthalene and 1,5-diaminonaphthalene. In this connection, it should be noted that coupling may be effected in two steps using one mol of each of the desired diazotized developer groups.

Further by coupling the diazotized compounds of Formula C with coupling components which will provide the coupling residue X^1 with a diazotizable amino group, or a nitro group which may be reduced to a diazotizable amino group, the resulting monoazo compound represented by the formula:

(E) $Y^1—S—(R)_p—Ar(—(Z)_n)—N=N—X^1—NH_2$

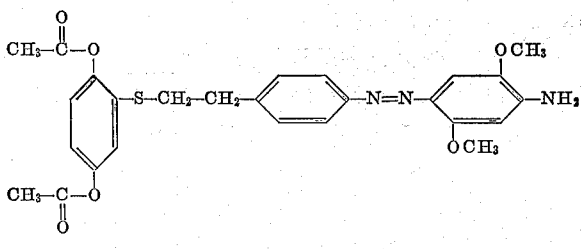
may in turn be diazotized and coupled with a coupling component which will provide the X^2 coupling residue and produce compounds represented by the formula:

(F) $Y—S—(R)_p—Ar(—(Z)_n)—N=N—X^1—N=N—X^2$

wherein both X^1 and X^2 are azo coupler radicals.

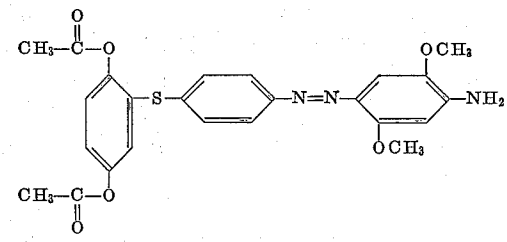
The preparation of diazo dye developers within the scope of this invention may give rise to a mixture containing both monoazo and diazo dye developers. It is to be understood that such mixtures may frequently be used without separation.

As examples of suitable monoazo compounds within Formula E which can be further diazotized and coupled, mention may be made of:



2,5-dimethoxy-4-[p-(2',5'-bis-acetoxyphenylthioethyl)-phenylazo]-aniline

and



2,5-dimethoxy-4-[p-(2',5'-bis-acetoxyphenylthio)-phenylazo]-aniline

and

Another method for preparing compounds within the scope of Formula A is to prepare a compound represented by the formula:

(G) $HS—(R)_p—Ar(—(Z)_n)—(N=N—X^1)_m—N=N—X^2$

wherein R, Ar, Z, *n*, *p*, X^1 and *m* have the same meaning as above; X^2 is a residue of a coupling component, a

$(HS—R—Ar(—(Z)_n)—)$

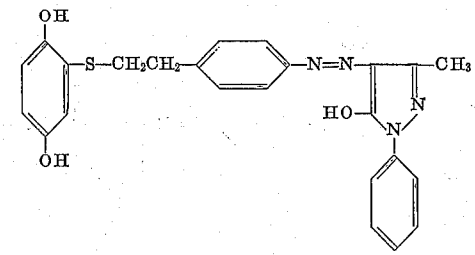
radical or a

$(HS—Ar(—(Z)_n)—)$

radical and reacting it with an appropriate p-benzoquinone compound to produce the desired dihydroxyphenyl compound. Thus, for example, one may diazotize p-acetylthioaniline, couple with 4-methoxy-1-naphthol to produce 2-[p-acetylthiophenylazo]-4-methoxy-1-naphthol, remove the acetyl group and then react the product with toluquinone to produce 2-[p-(2',5'-dihydroxy-6-methyl-phenylthio)-phenylazo]-4-methoxy-1-naphthol.

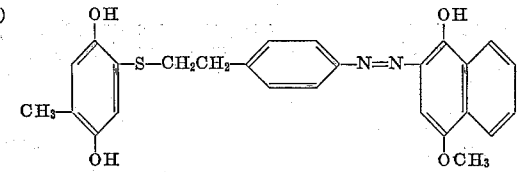
As examples of suitable dye developers within the scope of this invention, mention may be made of:

(I)



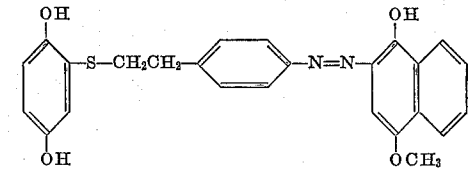
1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-5-pyrazolone

(II)



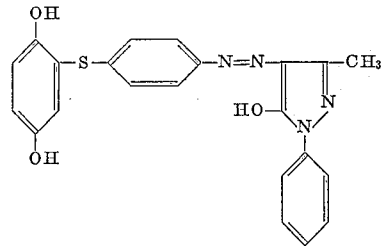
2-[p-(4'-methyl-2',5'-dihydroxyphenylthioethyl)-phenylazo]-4-methoxy-1-naphthol

(III)



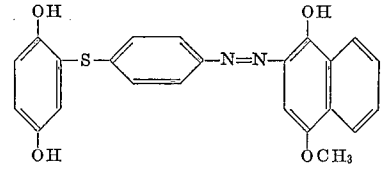
2-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-4-methoxy-1-naphthol

(IV)



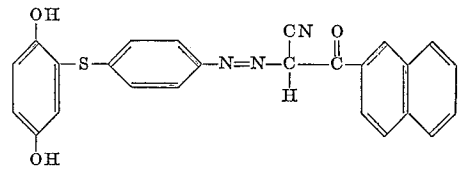
1-phenyl-3-methyl-4-[p-(2′,5′-dihydroxyphenylthio)-phenylazo]-5-pyrazolone

(V)



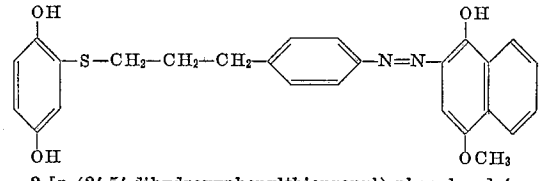
2-[p-(2′,5′-dihydroxyphenylthio)-phenylazo]-4-methoxy-1-naphthol

(VI)



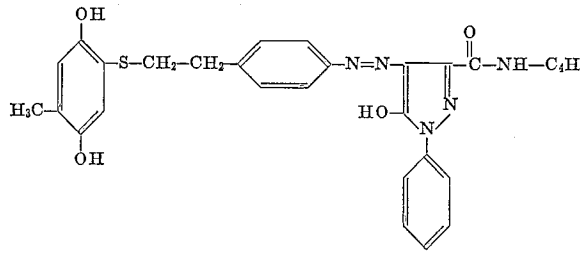
2-[α-cyano-α-(p-[2′,5′-dihydroxyphenylthio]-phenylazo)-acetyl]-naphthalene

(VII)



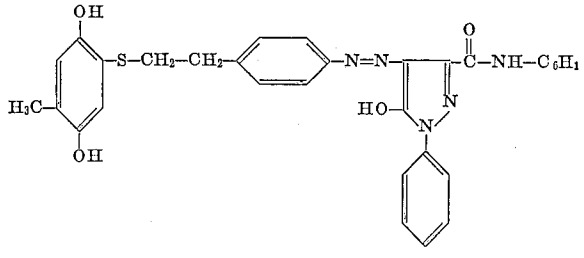
2-[p-(2′,5′-dihydroxyphenylthiopropyl)-phenylazo]-4-methoxy-1-naphthol

(VIII)



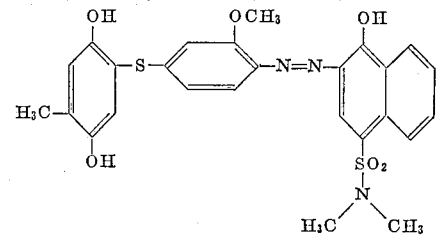
1-phenyl-3-N-n-butylcarbamyl-4-[p-(4′-methyl-2′5′-dihydroxyphenylthioethyl)-phenylazo]-5-pyrazolone

(IX)



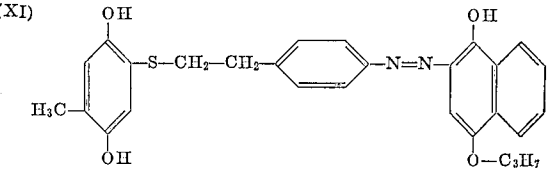
1-phenyl-3-N-n-hexylcarbamyl-4-[p-(4′-methyl-2′,5′-dihydroxyphenylthioethyl)-phenylazo]-5-pyrazolone

(X)



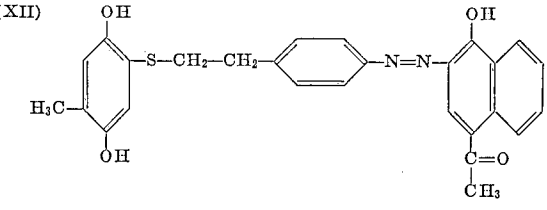
2-[p-(4″-methyl-2′,5′-dihydroxyphenylthio)-o-methoxy-phenylazo]-4-N,N-dimethylsulfonamido-1-naphthol

(XI)



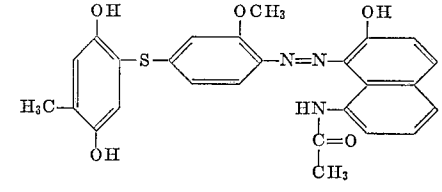
2-[p-(4′-methyl-2′,5′-dihydroxyphenylthioethyl)-phenylazo]-4-n-propoxy-1-naphthol

(XII)



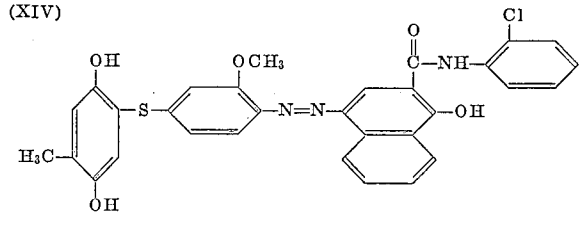
2-[p-(4′-methyl-2′,5′-dihydroxyphenylthioethyl)-phenylazo]-4-acetyl-1-naphthol

(XIII)



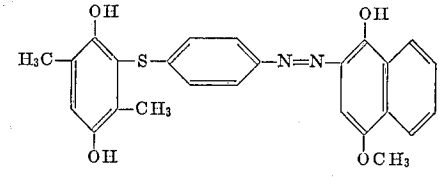
1-[p-(4′-methyl-2′,5′-dihydroxyphenylthio)-o-methoxy-phenylazo]-8-acetamido-2-naphthol

(XIV)



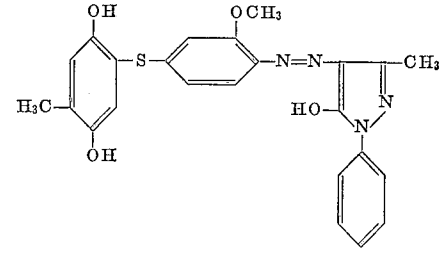
2-(N-o-chlorophenylcarboxamido)-4-[p-(4′-methyl-2′,5′-dihydroxyphenylthio)-o-methoxy-phenylazo]-1-naphthol

(XV)



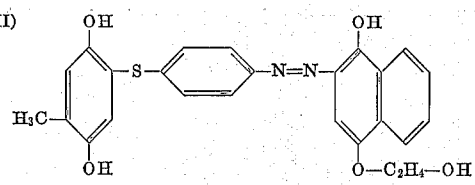
2-[p-(3′,6′-dimethyl-2′,5′-dihydroxyphenylthio)-phenylazo]-4-methoxy-1-naphthol

(XVI)



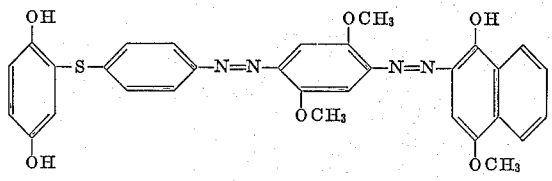
1-phenyl-3-methyl-4-[p-(4′-methyl-2′,5′-dihydroxyphenylthio)-o-methoxy-phenylazo]-5-pyrazolone

(XVII)



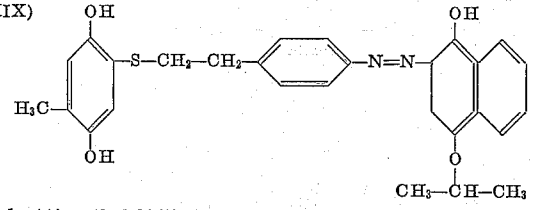
2-[p-(4'-methyl-2',5'-dihydroxyphenylthio)-phenylazo]-4-β-hydroxyethoxy-1-naphthol

(XVIII)



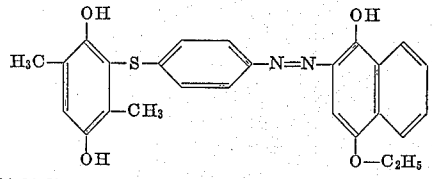
2-(2',5'-dimethoxy-4'-[p-(2'',5''-dihydroxyphenylthio)-phenylazo]-phenylazo)-4-methoxy-1-naphthol

(XIX)



2-[p-(4'-methyl-2',5'-dihydroxyphenylthioethyl)-phenylazo]-4-isopropoxy-1-naphthol

(XX)



2-[p-(3',6'-dimethyl-2',5'-dihydroxyphenylthio)-phenylazo]-4-ethoxy-1-naphthol

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 and reduced pH sensitivity over a fairly wide range on either side of neutral.

As examples of additional coupling components which may be used to provide X^1 and X^2, mention may be made of:

4-benzyl-1-naphthol
4-methyl-1-naphthol
4-methoxy-1-naphthylamine
4-acetamido-1-naphthylamine
5-amino-1-naphthol
Phenol
Aniline
1,5-naphthalene diamine
p-Cresol
1-hydroxyanthracene
2-hydroxyanthracene
1-hydroxy-2-naphthanilide
Diketohydrindene
Malononitrile
Acetoacetanilide
1-phenyl-3-amino-5-pyrazolone
1-phenyl-3-acetamido-5-pyrazolone
β-Naphthol
4-amino-1-naphthol
4-sulfo-1-naphthol
4-hexyloxy-1-naphthol
2-[α-cyanoacetyl]-coumarone

The novel dye developers of this invention are to be distinguished from the compounds disclosed and claimed in the copending application of Myron S. Simon, Serial No. 612,053, filed September 25, 1956 (now abandoned in favor of Serial Nos. 196,523 and 196,524, both filed May 21, 1962), and also the compounds disclosed and claimed in the copending applications of Elkan R. Blout, Milton Green and Howard G. Rogers, Serial No. 612,045, filed September 25, 1956 (now abandoned), and in Serial Nos. 144,816 (now U.S. Patent 3,134,672) and 145,978, both filed October 18, 1961 as continuations-in-part of said Serial No. 612,045, by the presence of the thio radical. The dye developers of this invention have unexpectedly been found to give diffusion transfer images of higher contrast than those of the above-mentioned copending applications, as well as faster film speeds than similar dye developers wherein the thio linkage is absent.

In general, starting materials within Formula C above, wherein p is 0, may be prepared by reacting the appropriate nitrophenylthiol or nitronaphthylthiol with the appropriate benzoquinone, followed by acylating the hydroxyl groups and reducing the nitro group. Starting materials within Formula C, wherein p is 1, generally may be prepared by reacting the appropriate 2-mercaptohydroquinone with the appropriate nitrophenylalkyl halide or nitronaphthylalkyl halide, preferably the bromide, followed by acylation and reduction.

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

Example 1

0.02 mol of 2,5-bis-acetoxyphenylthioethylaniline-hydrochloride (prepared by the procedure disclosed in our aforementioned copending application) is dissolved in 150 cc. of water containing 0.05 mol concentrated hydrochloric acid and diazotized at 0 to 5° C. by the addition of 0.02 mol sodium nitrite in 15 cc. of water. After ten minutes the solution is clarified and the pH 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 0.018 mol of 1-phenyl-3-methyl-5-pyrazolone in 300 cc. of ethanol, and 300 cc. of 10% sodium bicarbonate is added portionwise. The resulting yellowish slurry is stirred at room temperature for two hours, filtered, and the filter cake washed thoroughly with 10% sodium bicarbonate. 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.

The acetoxy radicals are hydrolyzed off by dissolving the above product in 160 cc. of ethanol, 40 cc. of water followed by 18 g. potassium hydroxide 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 filtration the solid is washed with water.

To purify, the filter cake is dissolved in a minimum amount of ethanol, under nitrogen, and the hot solution treated with activated charcoal. The material is reprecipitated from the filtrate by a 1% sodium chloride solution containing a trace of hydrogen chloride; the solid filtered and the procedure repeated. The resulting yellow solid is filtered, washed with water, and dried to give 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-5-pyrazolone, melting at 100 to 105° C. The visible spectrum exhibits a $\lambda_{max.}$ at 395 mμ, σ=25,300 in acetone.

Example 2

0.006 mol of 2,5-bis-acetoxyphenylthioethylaniline-hydrochloride, diazotized as in Example 1, is added at about 15° C. to a solution of 0.008 mol of 4-methoxy-1-naphthol in 100 cc. of acetone, and 100 cc. of saturated sodium bicarbonate is added portionwise. The slurry is stirred for four hours, filtered, and the filter cake washed well with water. The moist filter cake is dissolved in a solution of 3 g. of potassium hydroxide in 20 cc. of water and 40 cc. of ethanol and the flask is immediately evac-

uated. It is shaken for three minutes with intermittent warming on a steam bath, after which the solution is cooled briefly and then filtered rapidly into dilute hydrochloric acid. The resulting precipitate is filtered and washed well with water. The product is purified by recrystallization from aqueous methylcellosolve and dried to give 2-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-4-methoxy-1-naphthol, melting at 165 to 170° C. The visible spectrum exhibits a $\lambda_{max.}$ at 520 mμ, ε=22,700 in acetone.

Example 3

2,5-bis-acetoxyphenylthioaniline is prepared by dissolving 4.5 g. of p-nitro-thiophenol in 250 cc. of ethanol and adding slowly over a period of about one-half hour a solution of 10 g. of benzoquinone in 200 cc. ethanol. The resulting solution is poured into 2 liters of ice water and the precipitate is filtered and dried and recrystallized from a benzene-hexane solution. The product was refluxed with 150 cc. of acetyl chloride and 1 cc. of concentrated sulfuric acid for two hours, cooled, and poured into ice water to yield a gum which soon solidifies. The solid is triturated with water, filtered and dried over phosphorous pentoxide. The product is dissolved in ethanol and catalytically reduced over a palladium barium sulfate bed.

0.01 mol of the 2,5-bis-acetoxyphenylthioaniline, as prepared above, is dissolved in 20 cc. of water and 1.6 cc. of concentrated hydrochloric acid and diazotized by adding 0.7 g. of sodium nitrite dissolved in 10 cc. of water at 5° C.

The diazo product is added, dropwise with stirring, to a solution of 0.01 mol of 1-phenyl-3-methyl-5-pyrazolone in 50 cc. of water, 4.2 g. of sodium bicarbonate and 10 cc. of ethanol, the solution having previously been cooled to 5° C. The resulting yellow precipitate is filtered and then treated, under nitrogen, with 25 cc. of ethanol and 25 cc. of 20% sodium hydroxide solution for five minutes at 90 to 100° C. The product is precipitated by adding dilute hydrochloric acid and is recrystallized from ethanol to yield the desired 1-phenyl-3-methyl-4-[p-(2',5' - dihydroxyphenylthio) - phenylazo]-5-pyrazolone, melting at 202 to 204° C. The visible spectrum exhibits a $\lambda_{max.}$ at 420 mμ, ε=24,500 in 95% ethanol.

Example 4

0.005 mol of 2,5-bis-acetoxyphenylthioaniline is diazotized in a manner similar to that described in Example 3.

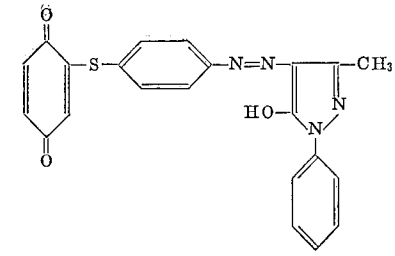
0.005 mol of 4-methoxy-1-naphthol is added to 25 cc. of acetone and 2.1 g. of sodium bicarbonate in 10 cc. of water and the suspension cooled to 5° C. The diazo solution is added dropwise and the suspension is stirred for five minutes. A red precipitate is filtered out and dissolved in ethanol. The solution is then filtered and the product precipitated with water. The precipitate is filtered and the wet filter cake hydrolyzed by heating, under nitrogen, with 20 cc. of ethanol and 20 cc. of 10% sodium hydroxide for four minutes. Precipitation with dilute hydrochloric acid gives 2-[p-(2',5'-dihydroxyphenylthio)-phenylazo]-4-methoxy-1-naphthol, melting at 146–149° C. The visible spectrum exhibits a $\lambda_{max.}$ at 530 mμ, ε=19,000 in acetone.

It is to be understood that the O,O'-bis-acyl compounds of Formula C may also be prepared by selective acylation of the hydroxyl groups of the corresponding p-dihydroxyphenyl compound in a manner similar to that described in U.S. Patent No. 3,019,254, issued January 30, 1962 to Milton Green and Helen P. Husek.

Other compounds which are also novel and are closely related to the compounds within Formula A may be prepared by oxidizing the dihydroxyphenyl groups of said compounds within Formula A to the corresponding quinone or dioxophenyl compounds under conditions which do not attack the azo bond. As examples of useful oxidizing agents for carrying out this oxidation, mention may be made of mercuric acetate and p-benzoquinone. These azo quinones may be used 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 preferred compounds of this class are the monoquinones which may be represented by the formula:

(H) $Y^2-(R)_p-S-Ar-(N=N-X^1)_m-N=N-X^2$ with $(Z)_n$ on Ar

wherein R, Ar, Z, *n*, *p* and *m* have the same meaning as above; X^1 and X^2 are radicals of azo coupling components; and Y^2 is a 2,5-dioxophenyl group which may also be substituted by alkyl and halogen groups. As an example of such compounds, mention may be made of:



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

These compounds are useful as color-providing materials and intermediates.

The following example of the preparation of a novel compound within the scope of Formula H is given for purposes of illustration only:

Example 5

0.10 mol of 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthio) - phenylazo] - 5 - pyrazolone, as prepared in Example 3, and 0.12 mol of mercuric acetate are dissolved in dimethylformamide and reacted while open to the air over a steam bath for three to four hours. Upon cooling, the insoluble mercurous acetate is filtered out and the product is precipitated by adding water. By crystallization of the product from a chloroform-methylcellosolve solution 1-phenyl-3-methyl-4-[p-(2',5'-dioxophenylthio)-phenylazo]-5-pyrazolone is obtained.

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 6

A photosensitive element is prepared by coating a gelatin-coated film base with a solution comprising 3% of 1-phenyl - 3 - methyl-4-[p - (2',5'-dihydroxyphenylthioethyl)-phenylazo]-5-pyrazolone (Formula I, as prepared in Example 1) in a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of tetrahydrofuran and acetone. After this coating has dried, a silver iodobromide emulsion is applied. An image-receiving element is prepared by coating a cellulose acetate-coated baryta paper with a solution comprising 4% N-methoxymethyl polyhexamethylene adipamide in ethanol. The photosensitive element is exposed and brought into superposed relationship with said image-receiving element as an aqueous liquid composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Potassium bromide	0.2
Sodium hydroxide	2.0
1-phenyl-3-pyrazolidone	0.2

is spread between said elements. After an inbibition period of approximately one minute, the image-receiving element is separated and contains a yellow positive image.

Example 7

When the procedure of Example 6 is repeated, using as the dye developer 4% of 2-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-4-methoxy - 1 - naphthol (Formula III, as prepared in Example 2) and using as the image-receiving element a cellulose acetate-coated baryta paper, which is coated with an aqueous solution containing 4% of polyvinyl alcohol, a magenta positive image is obtained.

Example 8

A photosensitive element is prepared similar to that described in Example 6 using 4% of 2-[p-(4'-methyl-2',5'-dihydroxyphenylthioethyl) - phenylazo]-4-methoxy - 1-naphthol (Formula II). Exposure and processing with a liquid processing composition and image-receiving element similar to those described in Example 6 give a magenta positive image.

Example 9

The process described in Example 6 is repeated using as the dye developer 3% of 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthio)-phenylazo] - 5-pyrazolone (Formula IV). The image-receiving element, prepared as described in said Example 6 except that a 10% N-methoxymethyl polyhexamethylene adipamide solution is used, contains a yellow positive dye image when separated from the photosensitive element after an imbibition period of approximately one minute.

Example 10

Use of a photographic element prepared and processed in a manner similar to that described in Example 6 using 3% of 2-[p-(2',5'-dihydroxyphenylthio) - phenylazo]-4-methoxy-1-naphthol (Formula V) gives a magenta positive image.

Example 11

The process described in Example 6 is repeated using a 2.5% of 2-[α-cyano-α-(p - [2',5'-dihydroxyphenylthio]-phenylazo)-acetyl]-naphthalene (Formula VI) as the dye developer and an aqueous processing composition comprising:

	Percent
Sodium carboxymethylcellulose	4.5
Potassium bromide	0.2
Sodium hydroxide	1.5
1-phenyl-3-pyrazolidone	.2

The image-receiving element, prepared as described in Example 6, contains a yellow positive dye image when separated from the photosensitive element after an imbibition period of one minute.

Example 12

A photosensitive element was prepared in a manner similar to the above examples, except that the dye developer was 2-[p-(2',5'-dihydroxyphenylpropylthio)-phenylazo]-4-methoxy-1-naphthol. After the coating containing the dye developer dried, a green-sensitive silver iodobromide emulsion was applied and allowed to dry. This photosensitive element was exposed, and brought into superposed relationship with an image-receiving element as an aqueous liquid composition comprising:

Water	cc	100
NaOH	g	5.17
Hydroxyethyl cellulose (high viscosity) (commercially available from Hercules Powder Co., Wilmington 99, Delaware, under the trade name Natrosol 250)	g	4.03
Sodium thiosulfate	g	1.15
Benzotriazole	g	2.3
N-benzyl-α-picolinium bromide	g	2.3

was spread between said elements. The image-receiving element comprised a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine on a baryta paper support. After an imbibition period of approximately one minute, the image-receiving element was separated and contained a magenta positive image.

As will be readily understood by one skilled in the art, the dye developers not specifically described in the above specific examples may be prepared by diazotization and coupling procedures similar to those illustrated by Examples 1 through 4, substituting the desired azo coupler and amino compound within the aforementioned Formula C.

Although the above examples have employed the dye developer in a layer of cellulose acetate hydrogen phthalate, it will be understood that the dye developer may be dissolved in a water-immiscible solvent, the resulting solution dispersed in gelatin, and the dispersion coated to provide the dye developer layer.

It should be noted that certain dye developers 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 sodium 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.

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-receiv-

ing 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 wells known to the art. See, for example, U.S. Patent 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.

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:

$$Y-S-(R)_p-Ar-(N=N-X^1-)_mN=N-X^2$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad (Z)_n$$

wherein Y is selected from the group consisting of 2,5-dihydroxylphenyl and alkyl and halogen nuclear substituted 2,5-dihydroxyphenyl groups; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, a ring carbon of said aryl nucleus being directly attached to an —N=N— group; R is a divalent alkylene group directly attached to a ring carbon of said aryl nucleus Ar; each Z is selected from the group consisting of alkyl and halogen groups; p is an integer from 0 to 1, inclusive; n is an integer from 0 to 2, inclusive; m is an integer from 0 to 1 inclusive; X^1 is the radical of an azo coupling component; and X^2 is selected from the group consisting of the radical of an azo coupling component and a

$$Y-S-(R)_p-Ar-$$
$$\qquad\qquad |$$
$$\qquad\quad (Z)_n$$

radical, provided that X^2 is the radical of an azo coupling component when m is 0; said azo coupler radicals completing said azo dye developer.

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

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

4. A photographic developer composition as defined in claim **1**, wherein said silver halide developing agent is a radical.

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

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

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

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

9. A photographic developer composition comprising an aqueous alkaline solution of 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthio)-phenylazo]-5-pyrazolone 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 2-[p-2',5'-dihydroxyphenylthio)-phenylazo]-4-methoxy-1-naphthol and a sil-

ver halide developing agent which is substantially colorless in at least the unoxidized form.

11. A photographic developer composition comprising an aqueous alkaline solution of 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-5-pyrazolone and a silver halide developing agent which is substantially colorless in at least the unoxidized form.

12. A photographic developer composition comprising an aqueous alkaline solution of 2-[α-cyano-α-(p-[2',5'-dihydroxyphenylthio]-phenylazo)-acetyl]-naphthalene and a silver halide developing agent which is substantially colorless in at least the unoxidized form.

13. 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 on the same side thereof as said silver halide emulsion, said azo dye developer being a compound of the formula:

$$Y-S-(R)_p-Ar-(N=N-X^1-)_mN=N-X^2$$
$$\qquad\qquad\quad (Z)_n$$

wherein Y is selected from the group consisting of 2,5-dihydroxyphenyl and alkyl and halogen nuclear substituted 2,5-dihydroxyphenyl groups; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, a ring carbon of said aryl nucleus being directly attached to an —N=N— group; R is a divalent alkylene group directly attached to a ring carbon of said aryl nucleus Ar; each Z is selected from the group consisting of alkyl and halogen groups; *p* is an integer from 0 to 1, inclusive; *n* is an integer from 0 to 2, inclusive; *m* is an integer from 0 to 1 inclusive; X^1 is the radical of an azo coupling component; and X^2 is selected from the group consisting of the radical of an azo coupling component and a

$$Y-S-(R)_p-Ar-$$
$$\qquad\quad (Z)_n$$

radical, provided that X^2 is the radical of an azo coupling component when *m* is 0; said azo coupler radicals completing said azo dye developer.

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

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

16. A photographic product as defined in claim **13**, wherein said azo dye developer is 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthio)-phenylazo]-5-pyrazolone.

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

18. A photographic product as defined in claim **13**, wherein said azo dye developer is 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-5 - pyrazolone.

19. A photographic product as defined in claim **13**, wherein said azo dye developer is 2-[α-cyano-α-(p-[2',5'-dihydroxyphenylthio]-phenylazo)-acetyl]-naphthalene.

20. 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:

$$Y-S-(R)_p-Ar-(N=N-X^1-)_mN=N-X^2$$
$$\qquad\qquad\quad (Z)_n$$

wherein Y is selected from the group consisting of 2,5-dihydroxyphenyl and alkyl and halogen nuclear substituted 2,5-dihydroxyphenyl groups; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, a ring carbon of said aryl nucleus being directly attached to an —N=N— group; R is a divalent alkylene group directly attached to a ring carbon of said aryl nucleus Ar; each Z is selected from the group consisting of alkyl and halogen groups; *p* is an integer from 0 to 1, inclusive; *n* is an integer from 0 to 2, inclusive; *m* is an integer from 0 to 1 inclusive; X^1 is the radical of an azo coupling component; and X^2 is selected from the group consisting of the radical of an azo coupling component and a

$$Y-S-(R)_p-Ar-$$
$$\qquad\quad (Z)_n$$

radical, provided that X^2 is the radical of an azo coupling component when *m* is 0; said azo coupler radicals completing said azo dye developer, 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.

21. The process as defined in claim **20**, 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.

22. The process as defined in claim **21**, 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.

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

24. The process as defined in claim **20**, wherein said dye developer is dissolved in an aqueous alkaline solution prior to application thereof to said exposed emulsion.

25. A process as defined in claim **20**, wherein X^2 is a phenolic azo coupler radical.

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

27. The process as defined in claim **20**, wherein X^2 is a heterocyclic aromatic azo coupler radical.

28. The process as defined in claim **20**, wherein X^2 is an azo coupler radical selected from the group consisting of aliphatic and alicyclic activated methylene couplers.

29. The process as defined in claim **20**, wherein said dye developer is 2-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-4-methoxy-1-naphthol.

30. The process as defined in claim **20**, wherein said dye developer is 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthio)-phenylazo]-5-pyrazolone.

31. The process as defined in claim **20**, wherein said dye developer is 2-[p-(2',5'-dihydroxyphenylthio)-phenylazo]-4-methoxy-1-naphthol.

32. The process as defined in claim **20**, wherein said dye developer is 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenylthioethyl)-phenylazo]-5-pyrazolone.

33. The process as defined in claim **20**, wherein said dye developer is 2-[α-cyano-α-(p-[2',5'-dihydroxyphenylthio]-phenylazo)-acetyl]-naphthalene.

34. The process as defined in claim **20**, wherein said aqueous alkaline solution includes a silver halide developing agent which is substantially colorless in at least the unoxidized form.

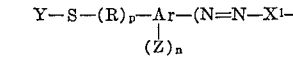
35. The process as defined in claim **34**, wherein said silver halide developing agent is a 3-pyrazolidone.

36. The process as defined in claim **34**, wherein said silver halide developing agent is a hydroquinone.

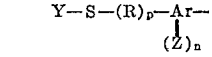
37. The process as defined in claim **20**, wherein Ar is phenyl, R is ethylene, Y is 2,5-dihydroxyphenyl, and *m* and *n* each are 0, and *p* is 1.

38. The process as defined in claim **20**, wherein Ar is phenyl, Y is 2,5-dihydroxyphenyl, and *m*, *n* and *p* each are 0.

39. 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 2,5-dihydroxyphenyl and alkyl and halogen nuclear substituted 2,5-dihydroxyphenyl groups; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, a ring carbon of said aryl nucleus being directly attached to an —N=N— group; R is a divalent alkylene group directly attached to a ring carbon of said aryl nucleus Ar; each Z is selected from the group consisting of alkyl and halogen groups; *p* is an integer from 0 to 1, inclusive; *n* is an integer from 0 to 2, inclusive; *m* is an integer from 0 to 1 inclusive; X^1 is the radical of an azo coupling component; and X^2 is selected from the group consisting of the radical of an azo coupling component and a



radical, provided that X^2 is the radical of an azo coupling component when *m* is 0; said azo coupler radicals completing said azo dye developer.

References Cited by the Examiner

UNITED STATES PATENTS

2,612,448	9/1952	Gaspar et al.	96—73
2,968,554	1/1961	Land	96—3
2,983,606	5/1961	Rogers	96—29
2,997,390	8/1961	Land	96—29
3,019,124	1/1962	Rogers	117—8
3,043,690	7/1962	Green et al.	96—66
3,134,672	5/1964	Blout et al.	96—29

FOREIGN PATENTS

682,665	11/1952	Great Britain.

OTHER REFERENCES

Venkataraman: Synthetic Dyes, Academic Press, New York (1952), pp. 358–359.

NORMAN G. TORCHIN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

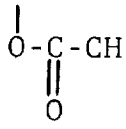
CERTIFICATE OF CORRECTION

Patent No. 3,222,169 December 7, 1965

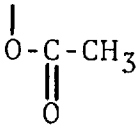
Milton Green et al.

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.

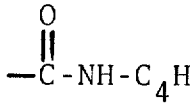
Column 3, line 17, after "as" insert -- a --; line 27, for "much" read -- such --; line 56, for "hydroxy" read -- hydroxyl --; column 4, lines 45 to 54, for that portion of the formula reading



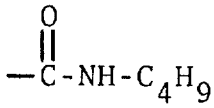
read



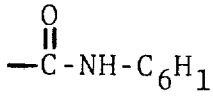
column 6, line 14, strike out "and"; column 7, lines 49 to 58, for that portion of the formula reading



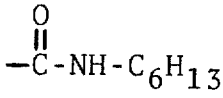
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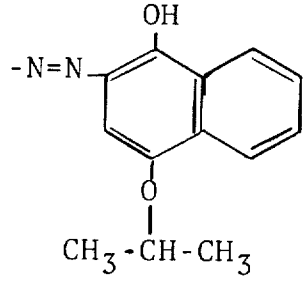
same column 7, lines 64 to 74, for that portion of the formula reading



read



column 9, lines 20 to 28, the extreme right-hand portion of the formula should appear as shown below instead of as in the patent:



column 10, line 63, for "σ=25,300" read -- ε =25,300 --; column 15, line 4, for "wells" read -- well --; column 16, line

51, for "said silver halide developing agent is a" read --

X^2 is a heterocyclic aromatic azo coupler --; line 58, for "in" read -- is --.

Signed and sealed this 20th day of August 1968.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents