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3,134,765
AZO DYES

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12 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

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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.

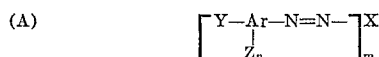
The dye developers of this invention may be utilized in the photosensitive element, for example in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer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

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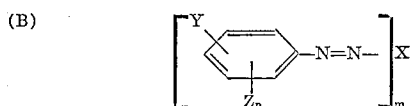
agents whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time may also be used.

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



wherein Y is a dihydroxyphenyl silver halide developing radical, i.e., para-dihydroxyphenyl or an ortho-dihydroxyphenyl group which also may be nuclear substituted by alkyl or halogen groups; Ar is a divalent aryl nucleus, such as a benzene or naphthalene nucleus, directly attached to the phenyl ring of Y; each Z is an alkyl group, preferably a lower alkyl group such as methyl or ethyl, an alkoxy group, preferably a lower alkoxy group such as methoxy, or a halogen, such as chlorine; n is 0, 1 or 2; m is 1 or 2; said aryl nucleus Ar being directly attached to the phenyl ring of Y, and the azo group —N=N— being directly attached to a ring carbon of said aryl nucleus Ar; and X is the radical of an azo coupling component.

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



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

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

As used herein with reference to X, the expression "radical of a phenolic coupler" is intended to refer to hydroxyphenyl, hydroxynaphthyl, hydroxyanthryl, etc. radicals, and substituted derivatives thereof, the expression "radical of an aromatic amino coupler" is intended to refer to aminophenyl, aminonaphthyl, etc. radicals, and substituted derivatives thereof; and the expressions "radical of a heterocyclic aromatic coupler," "radical of an aliphatic activated methylene coupler" and "radical of an alicyclic activated methylene coupler" are to be similarly construed.

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

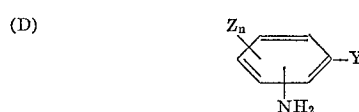


wherein Ar, Z, n and Y have the same meaning as above, and particularly a derivative wherein the hydroxyl groups of Y are protected, e.g., an O-acylated derivative, e.g., the O,O'-diacetate, and coupling the diazotized compound into the desired coupling component providing X. Preferably Ar is a benzene nucleus. The preparation of protected derivatives of these amino compounds, such as the bis-acetoxy derivatives, is described later in this ap-

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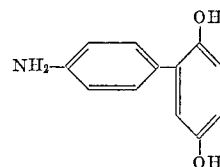
plication. Where N is 1 and at least one Z is alkoxy, such Z is preferably ortho to the amine group.

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



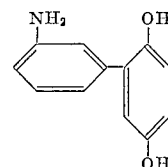
wherein Z, n and Y have the same meaning as above.

The preferred compounds within the group represented by Formula C are:



p-aminophenyl-hydroquinone

and



m-aminophenyl-hydroquinone

As examples of other compounds within Formula C useful in preparing the dye developers of Formula A, mention may be made of:

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

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

The azo coupling is generally performed at a pH which is preferably not greater than about 9. The hydroxy groups of Y are protected during diazotization and coupling, as by the formation of a bis-acetoxy derivative.

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, and which have two available coupling positions, as, for example, phenols and aromatic amines such as 1,6-dihydroxy naphthalene and 1,5-diaminonaphthalene.

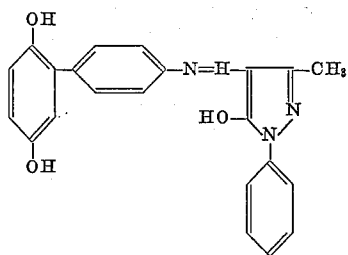
Where the azo coupling component is a phenolic coupler, and particularly an α -naphthol, it has been found that coupling ortho to the hydroxyl group gives a dye developer of superior color properties.

As examples of suitable dye developers within the

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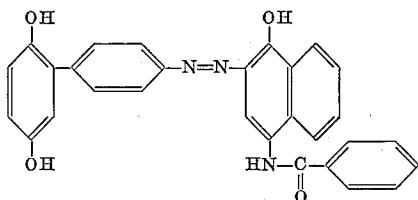
scope of this invention, mention may be made of the following:

(I)



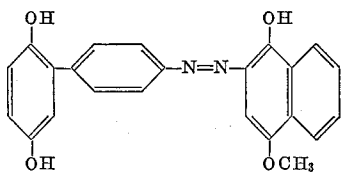
1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone

(II)



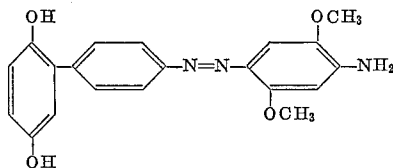
2-[p-(2',5'-dihydroxyphenyl)-phenylazo]-4-benzamido-1-naphthol

(III)



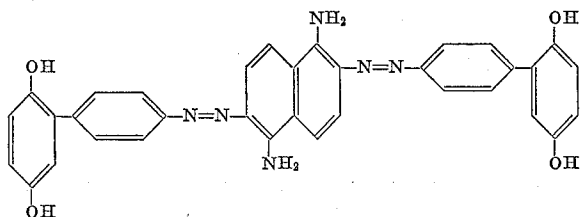
2-[p-(2',5'-dihydroxyphenyl)-phenylazo]-4-methoxy-1-naphthol

(IV)



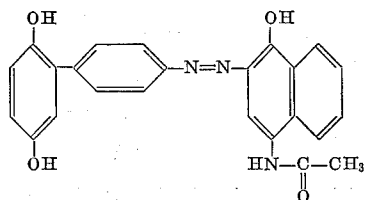
4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-2,5-dimethoxyaniline

(V)



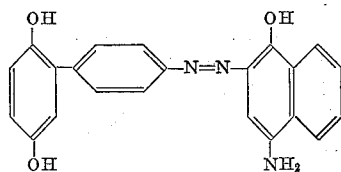
2,6-bis-[p-(2',5'-dihydroxyphenyl)-phenylazo]-1,5-naphthalene diamine

(VI)



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

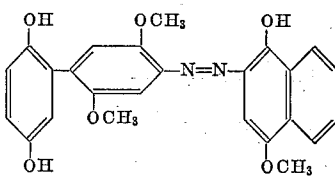
(VIII)



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

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(VIII)

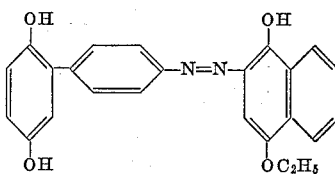


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2-[p-(2',5'-dihydroxyphenyl)-2,5-dimethoxy-phenylazo]-4-methoxy-1-naphthol

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(IX)

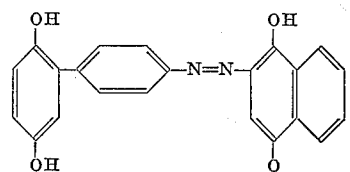


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2-[p-(2',5'-dihydroxyphenyl)-phenylazo]-4-ethoxy-1-naphthol

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(X)

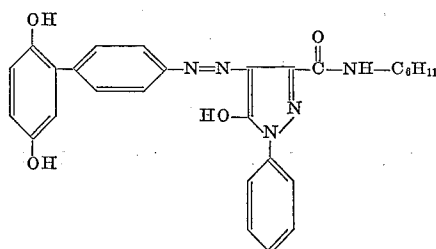


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2-[p-(2',5'-dihydroxyphenyl)-phenylazo]-4-isopropoxy-1-naphthol

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(XI)



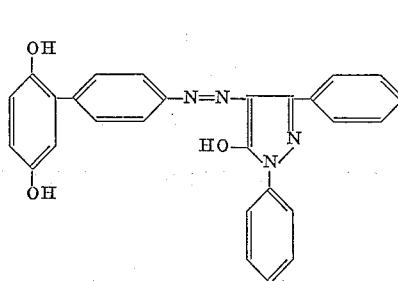
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1-phenyl-3-N-cyclohexylcarbamyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone

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(XII)



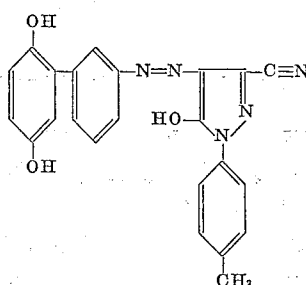
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1-phenyl-3-phenyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone

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(XIII)

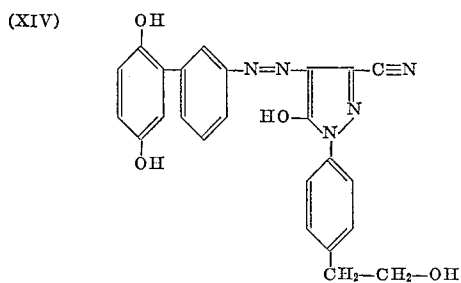


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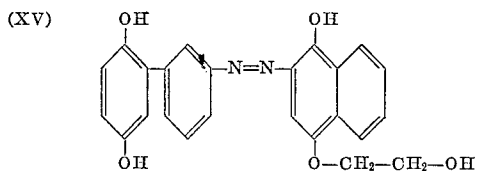
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1-(4'-methyl-phenyl)-3-cyano-4-[m-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone

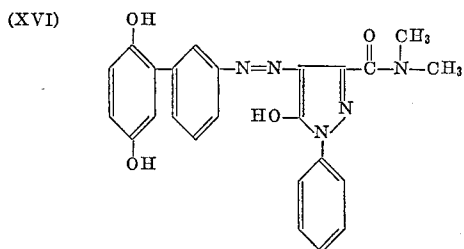
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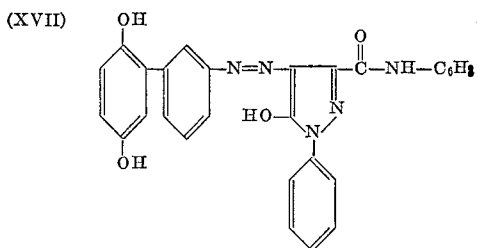
1-(4'-β-hydroxyethyl-phenyl)-3-cyano-4-[m-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone



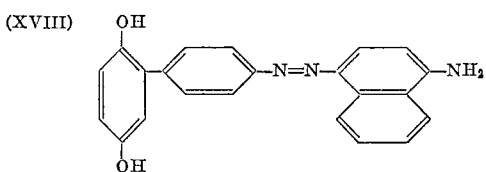
2-[m-(2',5'-dihydroxyphenyl)-phenylazo]-4-β-hydroxyethoxy-1-naphthol



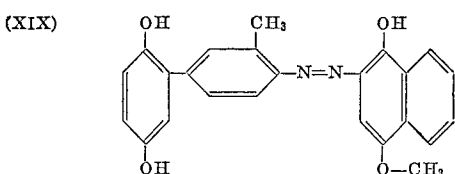
1-phenyl-3-N,N-dimethylcarbamyl-4-[m-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone



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

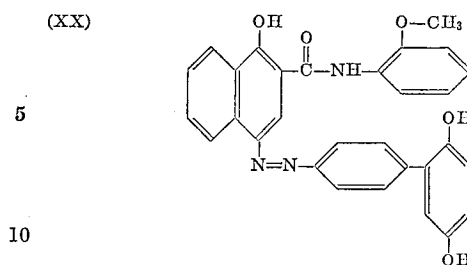


4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-1-naphthylamine

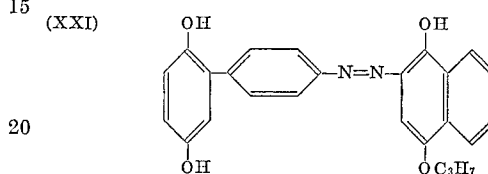


2-[p-(2',5'-dihydroxyphenyl)-o-methyl-phenylazo]-4-methoxy-1-naphthol

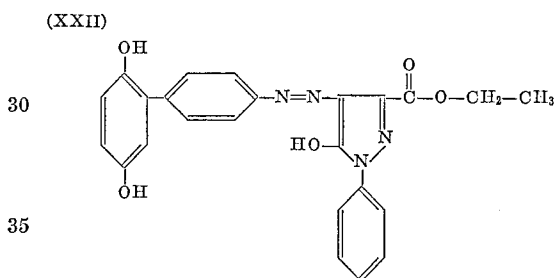
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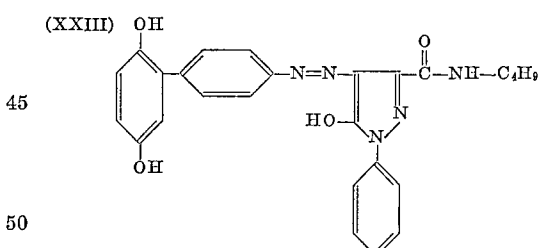
1-hydroxy-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-2-naphtho-o-anilide



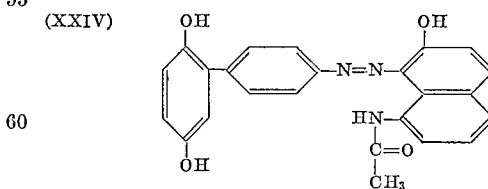
2-[p-(2',5'-dihydroxyphenyl)-phenylazo]-4-n-propoxy-1-naphthol



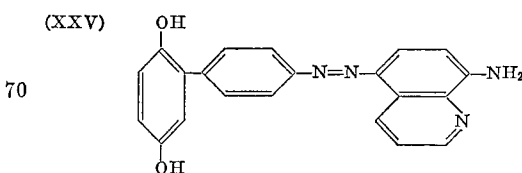
1-phenyl-3-carboxy-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone



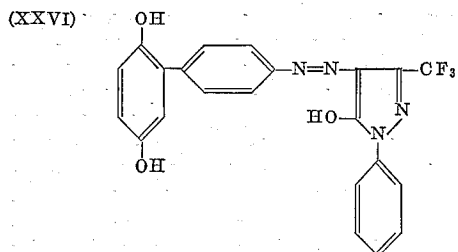
1-phenyl-3-N-n-butyl-carbamyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone



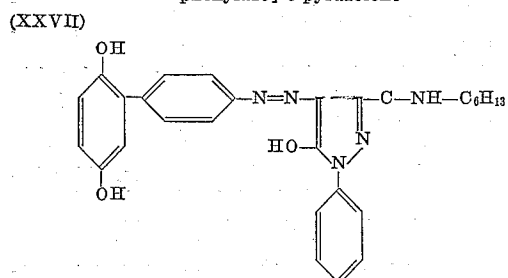
1-[p-(2',5'-dihydroxyphenyl)-phenylazo]-8-acetamido-2-naphthol



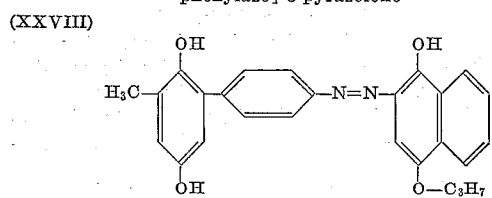
8-amino-5-[p-(2',5'-dihydroxyphenyl)-phenylazo]-quinoline



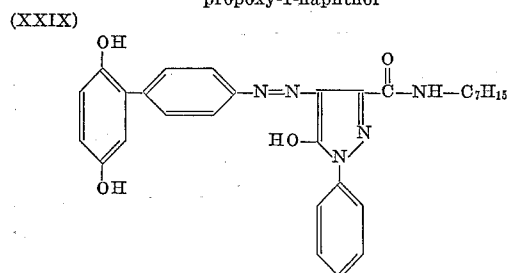
1-phenyl-3-trifluoromethyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone



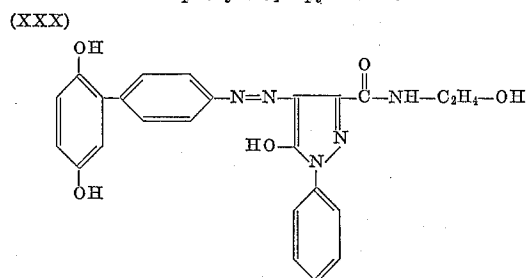
1-phenyl-3-N-n-hexyl-carbamyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone



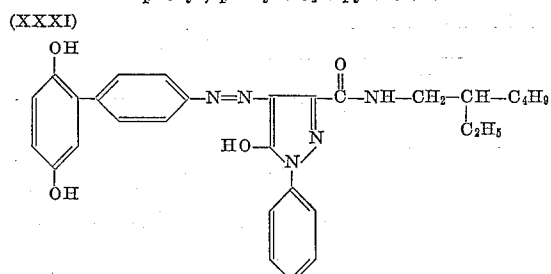
2-[p-(2',5'-dihydroxy-3'-methyl-phenyl)-phenylazo]-4-n-propoxy-1-naphthol



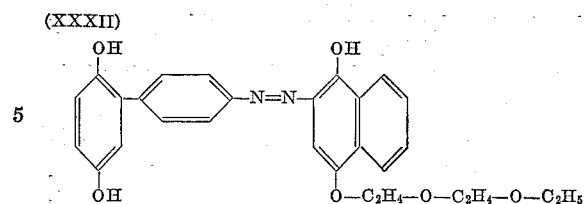
1-phenyl-3-N-n-heptylcarbamyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone



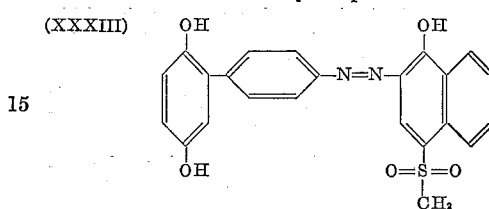
1-phenyl-3-N-beta-hydroxyethylcarbamyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone



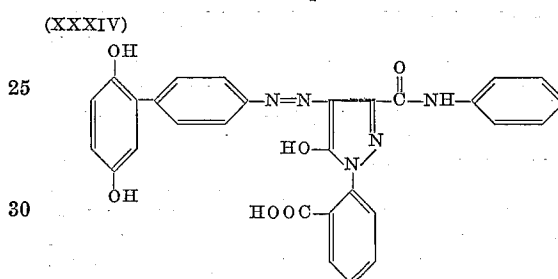
1-phenyl-3-(N-2'-ethylhexylcarbamyl)-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone



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



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



1-(o-carboxyphenyl)-3-carboxanilido-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone

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

- 4-benzyl-1-naphthol
 - 4-methyl-1-naphthol
 - 4-methoxy- α -naphthylamine
 - 4-methoxy-1-sulfonamido naphthalene
 - 4-acetamido- α -naphthylamine
 - Phenol
 - Aniline
 - 1,1'-dihydroxy-4,4'-biphenyl
 - 1,5-naphthalene diamine
 - p-Cresol
 - 3,6-bis-N,N-diethylsulfonamido-8-amino-1-naphthol
 - β -Naphthol
 - 4-sulfo-1-naphthol
 - py-3-hydroxytetrahydro-7-hydroxy-naphthoquinoline
 - 1-hydroxyanthracene
 - 1-hydroxy-2-naphthylamide
 - Diketohydrindene
 - 3-phenanthrol
 - Malononitrile
 - Acetoacetanilide
 - Brenthol
- 60 The novel dye developers of this invention are to be distinguished from 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 Serial Nos. 65 144,816 and 145,978, both filed October 18, 1961, as continuations-in-part of said Serial No. 612,045, by the fact that the aryl nucleus Ar is directly attached to the phenyl ring of Y. The dye developers of this invention unexpectedly have been found to give higher film speed 70 (exposure index), and better control or ratio between D_{min} and D_{max} when employed in diffusion transfer processes, as compared with similar dye developers of the just mentioned Blout et al. applications. The dye developers of this invention also are superior to dye developers such as phenylazo hydroquinone in that the re-

sulting dye transfer images are more stable, particularly as to heat and humidity.

One general method of preparing compounds within Formula C utilizes the Meerwein arylation reaction, in which benzoquinone or an alkyl or halogen substituted benzoquinone is reacted with the appropriate diazotized nitroaniline or nitronaphthylamine, and reducing the resulting nitroarylbenzoquinone product. The hydroquinonyl hydroxyl groups are acylated prior to diazotizing the amine group.

An alternative method of preparing compounds within Formula C is to react the desired diazotized nitroaniline or nitronaphthyl amine with, e.g., hydroquinone, followed by reduction to the desired amino product. The hydroquinonyl hydroxyl groups may be acylated before or after reduction of the nitro group.

The following examples of the preparation of compounds within Formula C are given for purposes of illustration only.

Example 1

27.6 g. of p-nitroaniline was dissolved in a hot solution of 60 cc. of water and 60 cc. of concentrated hydrochloric acid, and poured, with stirring, onto 500 g. of ice and 100 cc. of water in a flask shielded from light. A solution of 14 g. of sodium nitrite in 56 cc. of water was added rapidly below the surface of the suspension. 10 N sodium hydroxide solution was added until the solution was still acid but on longer turned Congo red paper blue. The reaction mixture was filtered into a funnel shielded from light, and added dropwise, at 10° C., to 24.2 g. of hydroquinone dissolved in 120 cc. of water. The resulting solution was stirred for an hour and then filtered. The precipitate was dissolved in 300 cc. of alcohol and precipitated into a salt and ice mixture to yield 29 g. of 2-(p-nitrophenyl)-hydroquinone as a light yellow precipitate, M.P. 214–220° C. Recrystallization from xylene raised the melting point to 219–221.5° C.

27.4 g. of 2-(p-nitrophenyl)-hydroquinone in 250 cc. of acetic anhydride and 2 cc. of sulfuric acid was heated on a steam bath for one half hour, and then poured onto excess ice. The mixture was stirred and slowly warmed on a steam bath until the excess anhydride was all decomposed. Water was added to completely precipitate the oil. The mixture was cooled in ice to crystallize the oil. After filtering, the precipitate was recrystallized from ethanol two times to give 13.4 g. of the diacetate, M.P. 114–116° C.

A solution of 13 g. of 2-(p-nitrophenyl)-hydroquinone-O,O'-diacetate in 130 cc. of ethyl acetate containing 6 g. of Raney nickel catalyst was hydrogenated at 32 p.s.i. overnight. The solvent was evaporated and the residue taken up in benzene and then precipitated with HCl. The precipitate was recrystallized from ethanol-ether to yield 9.9 g. of 2-(p-aminophenyl)-hydroquinone-O,O'-diacetate as tan glistening needles.

Example 2

The procedure of Example 1 was repeated, except that the reduction step was carried out as follows: 12.0 g. of 2-(p-nitrophenyl)-hydroquinone-O,O'-diacetate in 120 cc. of ethyl acetate containing 2 cc. of Raney nickel catalyst was hydrogenated at 88° C. for 5.5 hours, the initial hydrogen pressure being 19.5 p.s.i. The reaction mixture was filtered through Celite and alumina to obtain a clear yellow oil. This oil was washed three times with hexane, then covered with water and concentrated HCl added slowly with stirring. A white crystalline paste of the hydrochloride formed and was filtered to yield 8.3 g. Evaporation of the mother liquor yielded 0.4 g. additional product.

Example 3

80 cc. of concentrated HCl was added slowly to a stirred suspension of 27.6 g. of m-nitroaniline in 200 cc.

of water, and the mixture warmed on a steam bath. The resulting slurry of the hydrochloride was rapidly cooled to 0–5° C., and to this was added dropwise a solution of 13.8 g. of sodium nitrite in 25 cc. of water. Stirring was continued for one hour at 0–5° C., filtered and added all at once to a stirred suspension of 25.9 g. of purified benzoquinone in an aqueous solution of sodium acetate (100 g. sodium acetate in 1200 cc. water/ice mixture containing a small amount of antifoam agent) at a temperature below 15° C. The reaction mixture was stirred for 6 hours or overnight at room temperature, and the solid filtered, washed with water, and dried to yield 2-(m-nitrophenyl)-benzoquinone as a light brown powder, M.P. 106–109° C.

45 g. of 2-(m-nitrophenyl)-benzoquinone was placed in a hydrogenation flask with 500 cc. of ethanol and 1.4 g. of 10% palladium on charcoal catalyst. Hydrogenation was effected at room temperature, the theoretical amount of hydrogen being consumed within 4 hours. The hydrogenation product was isolated by filtration through Celite and evaporation of the solvent under vacuum.

The resulting 2-(m-aminophenyl)-hydroquinone (0.2 mole) was placed in a flask with 750 cc. of glacial acetic acid that had been presaturated with HCl gas. The resulting solution was stirred for 15 minutes with HCl gas continuously bubbled into the flask. Acetyl chloride (117 g.) was added dropwise with stirring. A warm water bath (45–50° C.) was placed under the reaction flask for 1 hour. The light brown solid which separated was filtered, washed, and dried in vacuum to yield 2-(m-aminophenyl) - hydroquinone-O,O'-diacetate hydrochloride.

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

Example 4

p-Aminophenyl hydroquinone-O,O'-diacetate hydrochloride is diazotized by adding 3.2 g. (0.01 mole) thereof to 20 cc. of water and 1.6 cc. of concentrated hydrochloric acid, and treating at 5° C. with 0.7 g. of sodium nitrite dissolved in 10 cc. of water.

The diazo product is added, dropwise with stirring, to a solution of 1.6 g. (0.01 mole) 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 a 20% sodium hydroxide solution for 5 minutes at 90–100° C. Acidification of the resulting solution with dilute hydrochloric acid yields the desired 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone [Formula I]. Recrystallization from ethanol gives 1.15 g. (32.2% yield) of the above product as a red solid, M.P. 195–199° C. The product is soluble in organic solvents such as acetone and ethanol, giving a yellow solution. The absorption spectrum of the dye developer exhibits a λ_{\max} at 420 m μ , $\epsilon > 22,400$, in ethanol. Analysis of the product shows:

	C	H	N
Calculated.....	68.4	4.7	14.5
Found.....	68.7	4.9	14.9

Example 5

p-Aminophenyl hydroquinone O,O'-diacetate hydrochloride (1.6 g.; 0.005 mole) is diazotized in a manner similar to that described in Example 1.

4-benzamido-1-naphthol (1.3 g.; 0.005 mole) 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 5 minutes. A brown-red precipitate is filtered

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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 4 minutes. Precipitation with dilute hydrochloric acid gives 2-[p-(2',5'-dihydroxyphenyl)-phenylazo]-4-benzamido-1-naphthol [Formula II], the absorption spectrum of which exhibits a λ_{\max} . at 505 μ in ethanol.

Example 6

p-Aminophenyl hydroquinone O,O'-diacetate hydrochloride (19.2 g.; 0.06 mole) is diazotized in a manner similar to that set forth in Example 1, and is poured into a solution of 9.2 g. of 2,5-dimethoxyaniline in 200 cc. of acetone and 100 cc. of water. Sodium acetate is added to bring the pH to about 6 and the mixture is stirred for half an hour. After filtering, the semi-solid precipitate is dissolved in acetone and precipitated by pouring onto 1% hydrochloric acid and ice. The oily precipitate is filtered, dissolved in methyl Cellosolve and precipitated into an ice solution saturated with sodium acetate and sodium chloride to give 22.5 g. of a yellow-orange product. Hydrolysis of this product gives 4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-2,5-dimethoxyaniline [Formula IV], the absorption spectrum of which exhibits a λ_{\max} . at 444-448 μ in methyl Cellosolve $\epsilon=26,000$.

Example 7

Diazotized p-aminophenyl hydroquinone O,O'-diacetate hydrochloride is coupled into 4-methoxy-1-naphthol in a manner similar to that set forth in the above examples. Hydrolysis of the hydroquinone diacetate gives 2-[p-(2',5'-dihydroxyphenyl)phenylazo]-4-methoxy-1-naphthol [Formula III], M.P. 201-203° C. The absorption spectrum of this product exhibits a λ_{\max} . of 540-542 μ in methyl Cellosolve, $\epsilon>23,000$. Analysis of the hydroquinone diacetate product shows:

	C	H	N
Calculated.....	68.9	4.7	5.95
Found.....	68.8	5.1	5.8

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 8

A photosensitive element is prepared by coating a gelatin-coated film base with a solution comprising 3% of 1-phenyl-3-[p-(2',5'-dihydroxyphenyl)-phenylazo]-4-methyl-5-pyrazolone (Formula I, as prepared in Example 4) 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 80% aqueous isopropanol. 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	1.5
1-phenyl-3-pyrazolidone	0.2

is spread between said elements. After an imbibition period of approximately 1 minute, the image-receiving element is separated and contains a yellow positive image.

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Example 9

The process described in Example 8 is repeated, using, as the dye developer, 3% of 2-[p-(2',5'-dihydroxyphenyl)-phenylazo]-4-methoxy-1-naphthol [Formula III]. The aqueous processing composition comprises:

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

The image-receiving element, prepared as described in Example 8, contains a magenta, positive dye image when separated from the photosensitive element after an imbibition period of approximately 1 minute.

Example 10

When the procedure of Example 9 is repeated employing, as the image-receiving element, a cellulose acetate-coated baryta paper which has been coated with a layer of polyvinyl alcohol (cast from a 6% aqueous polyvinyl alcohol solution), a purple, positive dye image is obtained.

Example 11

Use of 4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-2,5-dimethoxyaniline [Formula IV] in the process described in Example 9 results in a yellow, positive dye image on the image-receiving element.

Example 12

A photosensitive element is prepared as described in Example 8, using a solution of 2.5% of 2,6-bis-[p-(2',5'-dihydroxyphenyl)-phenylazo]-1,5-naphthalene [$\lambda_{\max}=440$, $\epsilon>13,000$; $\lambda_{\max}=610$, $\epsilon>39,000$; Formula V] in a methyl Cellosolve solution containing 4% cellulose acetate hydrogen phthalate. The photosensitive element is exposed and processed as described in Example 8, using an aqueous processing composition comprising:

	Percent
Sodium carboxymethyl cellulose	6.0
1-phenyl-3-pyrazolidone	0.2
Sodium hydroxide	5.0
Potassium bromide	0.5

After an imbibition period of approximately 1 minute, the image-receiving element is separated and contains a black, positive dye image.

Example 13

A photosensitive element is prepared in a manner similar to the above examples, except that the dye developer is dispersed in a layer of gelatin. The coating solution from which the dye developer layer is coated is prepared by dissolving 0.5 g. of 2-[m-(2',5'-dihydroxyphenyl)-phenylazo]-4- β -hydroxy-ethoxy-1-naphthol, 1 cc. of cyclohexanone, and 0.5 cc. of N-n-butylacetamide and diluting this solution at 40° C., with a solution comprising 5 g. of 10% gelatin solution, 1.67 cc. of water, and 0.67 cc. of Alkanol B. Emulsification is effected by high speed agitation in a Waring Blendor. 5 cc. of the resulting dye dispersion is added to 10 cc. of water containing small amounts of saponin and succinaldehyde, and then coated on the gelatin-subcoated cellulose acetate film base. After this coating has dried, a green-sensitive silver iodobromide emulsion is applied and allowed to dry. A photosensitive element prepared in this manner 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) [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

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

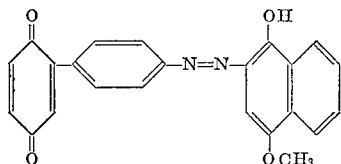
As will be readily understood by one skilled in the art, the dye developers not specifically described in the above specific examples may be prepared by diazotization and coupling procedures similar to those illustrated by Examples 4 through 7, substituting the desired azo coupler and amino compound within the aforementioned Formula C.

The dye developers of this invention which have, as part of the azo coupler radical X, a 1-o-carboxyphenyl-5-pyrazolone system, also are useful in the preparation of the pyrazolone lactones disclosed and claimed in the copending application of Samuel Dershowitz and Robert B. Woodward, Serial No. 101,264, filed April 6, 1961.

The use of 7-amino-1-naphthol as the azo coupler radical X has been found to give magenta dye developers having unexpectedly superior light stability and color characteristics. Dye developers of this type are disclosed and claimed in the copending application of Milton Green, Terry Milligan and Daniel L. Ross, Serial No. 174,248, filed February 19, 1962.

The use of 3-cyano-5-pyrazolones as the azo coupler radical X has been found to give yellow dye developers of unexpectedly superior light stability and color characteristics. Dye developers containing such 3-cyano-5-pyrazolone radicals are disclosed and claimed in the copending application of Daniel L. Ross, Serial No. 248,240, filed December 31, 1962.

The quinones of the novel azo dye developers of this invention, e.g.,



2-[p-(2',5'-dioxophenyl) - phenylazo] - 4 - methoxy-1-naphthol may be prepared by oxidizing under conditions which do not attach the azo bond, e.g., by oxidizing with benzoquinone, chloranil, or mercuric acetate. These azo quinones are useful in the photographic processes disclosed and claimed in the copending application of Howard G. Rogers, Serial No. 825,359, filed July 6, 1959, as a continuation-in-part of, and replacement for, Serial No. 599,122, filed July 20, 1956, now abandoned. One method of preparing such a quinone is to dissolve the azo dye developer and a 20% molar excess of mercuric acetate in e.g., dimethylformamide, and heat the mixture, while open to the air, on a steam bath for 3 to 4 hours. Upon cooling, the insoluble mercurous acetate is filtered out and the product is precipitated by adding water. Such oxidation procedures are described in the copending application of Richard S. Corley, Serial No. 700,276, filed December 3, 1957, now U.S. Patent No. 3,116,279.

It should be noted that dye developers in which a hydroquinonyl group becomes a part of the conjugated system are sensitive to pH changes in the absence of sulfo or carboxyl groups in the dye developer molecule. Thus 1-phenyl-3-[p-(2',5'-dihydroxyphenyl) - phenylazo] - 4-methyl-5-pyrazolone is yellow under neutral or acid conditions. Application of approximately 1.5% aqueous sodium hydroxide solution to a yellow image obtained using said dye developer results in a grayish-brownish color. 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" or a similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on February 10, 1948. In general, such composite roll films comprise a photosensitive roll, a roll of image-receiving material and a plurality of pods containing an aqueous alkaline processing solution. The rolls and pods are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pods may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of the pods used in such units are well known to the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

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

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed and claimed in the copending application of Milton Green and Howard G. Rogers, Serial No. 50,851, filed August 22, 1960.

The dye developers of this invention may be used also in conventional photographic processes, such as tray or tank development of conventional photosensitive films, plates or papers to obtain black and white, monochromatic or toned prints or negatives. By way of example, a developer composition suitable for such use may comprise an aqueous solution of approximately 1-2% of the dye developer, 1% sodium hydroxide, 2% sodium sulfite and 0.05% potassium bromide. After development is completed, any unreacted dye developer is washed out of the photosensitive element, preferably with an alkaline washing medium or other medium in which the unreacted dye developer is soluble. The expression "toned" is used to designate photographic images wherein the silver is retained with the precipitated dye, whereas "monochromatic" is intended to designate dye images free of silver.

It should be noted that the dye developers of this medium are self-sufficient to provide the desired color image and do not depend upon coupling reactions to produce the desired color. They thus provide a complete departure from conventional photographic color processes in which the color is produced by a coupling reaction between a "color former" or "coupler" and the oxidized developing agent, as well as so-called auto-coupling processes in which color is obtained by a reaction of the oxidized developing agent with unoxidized developing agent.

It will be apparent that, by appropriate selection of the image-receiving element from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency. Likewise, the inventive concepts herein set forth are adaptable for multicolor work by the use of special photographic materials, for example, film materials of the type containing two or more photosensitized elements associated with an appropriate number of image-receiving elements and adapted to be treated with one or more liquid processing compositions, appropriate dye developers suitable to impart the desired subtractive colors being incorporated in the photosensitized elements or in the liquid processing compositions. Examples of such photographic materials are disclosed in U.S. Patent No. 2,647,049 to Edwin H. Land.

As examples of useful image-receiving materials, mention may be made of nylon, e.g., N-methylolxymethyl-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 co-pending 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 fibers, such as nylon.

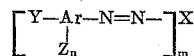
In the preceding portions of the specifications the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black.

This application is in part a continuation of my co-pending application Serial No. 612,053, 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 Y is a dihydroxyphenyl silver halide developing radical selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl, and lower alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus directly attached to said phenyl ring of Y and selected from the group consisting of benzene and naphthalene nuclei, said —N=N— group being directly attached to a ring carbon of said aryl nucleus; each Z is a member selected from the group consisting of lower alkyl, lower alkoxy and halogen radicals; n is from 0 to 2, inclusive; m is from 1 to 2, inclusive; and X is the radical of an azo dye coupler linked to said —N=N— group; said Y providing the only dihydroxyphenyl silver halide developing radicals in said azo dye.

2. An azo dye as defined in claim 1, wherein Ar is phenylene, n is 0, m is 1 and Y is p-dihydroxyphenyl.

3. 2 - [p - (2',5'-dihydroxyphenyl)-phenylazo] - 4 - methoxy-1-naphthol.

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

5. 1 - phenyl-3-N-n-hexyl-carboxamido-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone.

6. 2 - [p-(2',5'-dihydroxyphenyl)-phenylazo]-4-β-hydroxyethoxy-1-naphthol.

7. 2 - [p-(2',5'-dihydroxyphenyl)-phenylazo]-4-isopropoxy-1-naphthol.

8. 1 - phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenyl)-phenylazo]-5-pyrazolone.

9. 4 - [p-(2',5'-dihydroxyphenyl)-phenylazo]-2,5-dimethoxyaniline.

10. 2,6 - bis - [p-(2',5'-dihydroxyphenyl)-phenylazo]-1,5-naphthalene diamine.

11. A benzoquinone of an azo dye as defined in claim 1.

12. 2 - [p-(2',5'-dioxophenyl)-phenylazo]-4-methoxy-1-naphthol.

References Cited in the file of this patent

UNITED STATES PATENTS

2,997,390 Land _____ Aug. 22, 1961