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3,134,672

PHOTOGRAPHIC PRODUCTS, COMPOSITIONS AND PROCESSES EMPLOYING AZO DYE DEVELOPERS

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37 Claims. (Cl. 96—29)

This invention relates to photography and more particularly to products, compositions and processes for the development of photo-sensitive 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

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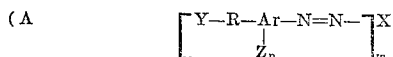
exposed and wetted with a liquid processing composition, for example by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed prior to, during or after wetting, on an image-receiving element. In a preferred embodiment, the photosensitive element contains 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, diethyl-

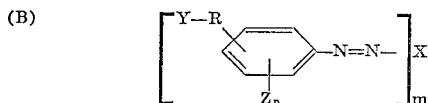
amine, sodium hydroxide or sodium carbonate, and may contain the dye developer. In some instances, it may contain an additional silver halide developing agent. If the liquid processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin, uniform layer, it may also include a viscosity-increasing compound constituting film-forming material of the type which, when spread over a water-absorbent base, will form a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric, water-soluble ether inert to an alkali solution, as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time may also be used.

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



wherein R is an alkylene group, preferably a lower alkylene group containing no more than five carbons and more preferably an ethylene ($-\text{CH}_2\text{CH}_2-$) or trimethylene ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) group; Ar is an aryl nucleus, such as a benzene or naphthalene nucleus; each Z is an alkyl group, preferably a lower alkyl group such as methyl or ethyl, an alkoxy group, preferably a lower alkoxy group such as methoxy, or a halogen, such as chlorine; n is 0, 1 or 2; Y is a para-dihydroxyphenyl or an ortho-dihydroxyphenyl group which also may be nuclear substituted by alkyl or halogen groups; m is 1 or 2; 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, R, 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 -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, alkyl-amino, arylamino, hydroxyl, cyano, alkylamido, aryl-amido, 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, R, 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, and coupling the diazotized compound into the desired coupling component providing X. Preferably Ar is a benzene nucleus. The preparation of amino compounds within the Formula C is disclosed and claimed in the copending application of Elkan R. Blout, Milton Green, Howard G. Rogers, Myron S. Simon and Robert B. Woodward, Serial No. 612,051, filed September 25, 1956 (now U.S. Patent No. 3,019,107, issued January 30, 1962), and in a continuation-in-part thereof, Serial No. 98,287, filed March 27, 1961. The preparation of protected derivatives of these amino compounds, such as the bis-acetoxy derivatives, is disclosed and claimed in the copending application of Molton Green and Helen P. Husek, Serial No. 612,063, filed September 25, 1956, which application has been abandoned in favor of a continuation-in-part, thereof, Serial No. 805,673, filed April 13, 1959 (now U.S. Patent No. 3,019,254 issued January 30, 1962).

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

p-Aminophenethyl-hydroquinone
2-(4'-aminonaphthylethyl)-hydroquinone
2-(p-aminophenethyl)-5-methyl-hydroquinone
2-(p-aminophenethyl)-5-chloro-hydroquinone
2-(3'-methyl-4'-aminophenethyl)-hydroquinone
2-(p-aminophenethyl)-5,6-dimethyl-hydroquinone
2-(p-aminophenethyl)-3,5,6-trimethyl-hydroquinone
2-m-aminophenethyl-hydroquinone
p-Aminophenylmethyl-hydroquinone
2-(m-aminophenethyl)-5-methyl-hydroquinone
1,2-dihydroxy-4-(p-aminophenethyl)-benzene
2-[γ -(4'-aminophenyl)- β -methyl-propyl]-hydroquinone
2-[γ -(4'-aminophenyl)-propyl]-hydroquinone
2-(4'-amino-3'-methoxy-phenethyl)-hydroquinone
2-[γ -(3'-amino-4'-methylphenyl)-propyl]-hydroquinone
2-(p-aminophenethyl)-6-methyl-hydroquinone
2-(p-aminophenethyl)-5-bromo-hydroquinone
2-(5'-aminonaphthylethyl)-hydroquinone

Particularly useful dye developers are those prepared from p-aminophenethyl-hydroquinone and 2-[γ -(4'-aminophenyl)-propyl]-hydroquinone.

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.

The azo coupling is generally performed at a pH which is preferably not greater than about 9. The hydroxy groups of Y are protected during diazotization and coupling, as by the formation of a bis-acetoxy derivative; such bis-acetoxy derivatives are described in the aforementioned application of Milton Green and Helen P. Husek.

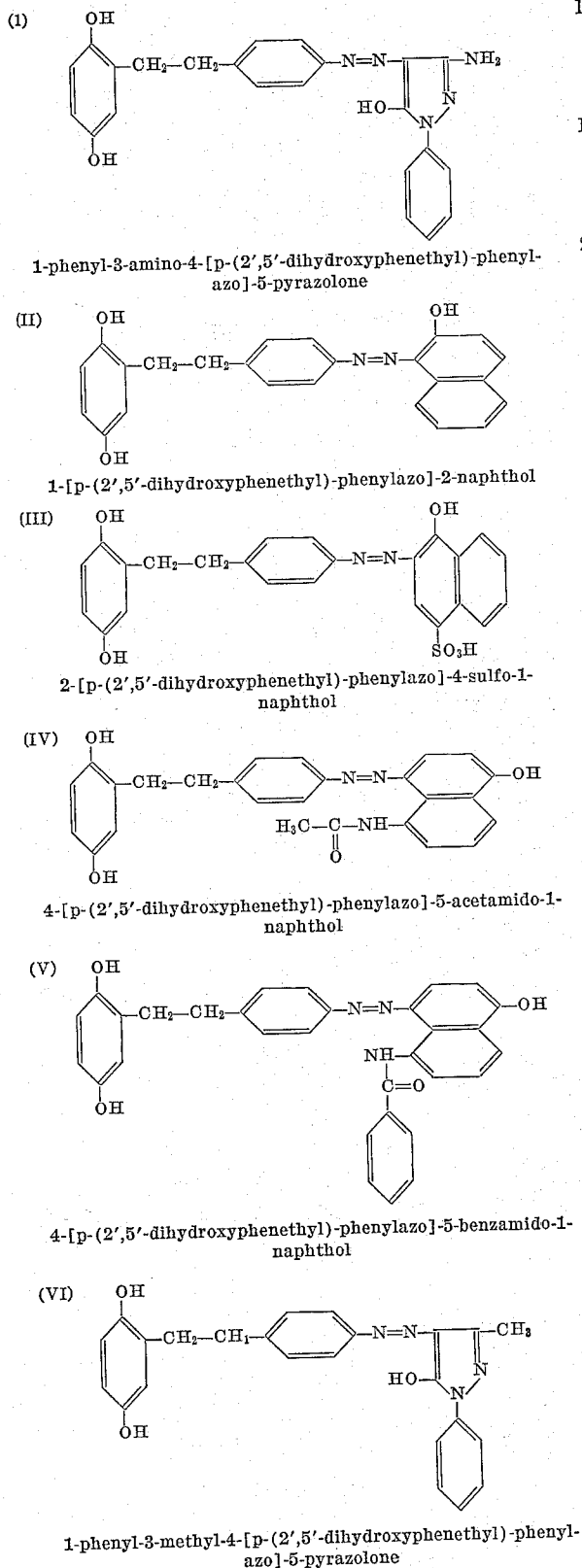
By the use of two moles of the diazonium salt to each mole of the coupling component, one may couple twice into certain of the azo coupling components which provide the azo coupling radical X, and which have two available coupling positions, as, for example, phenols and aromatic amines such as 1,6-dihydroxy naphthalene and 1,5-diamino-naphthalene.

Where the azo coupling component is a phenolic cou-

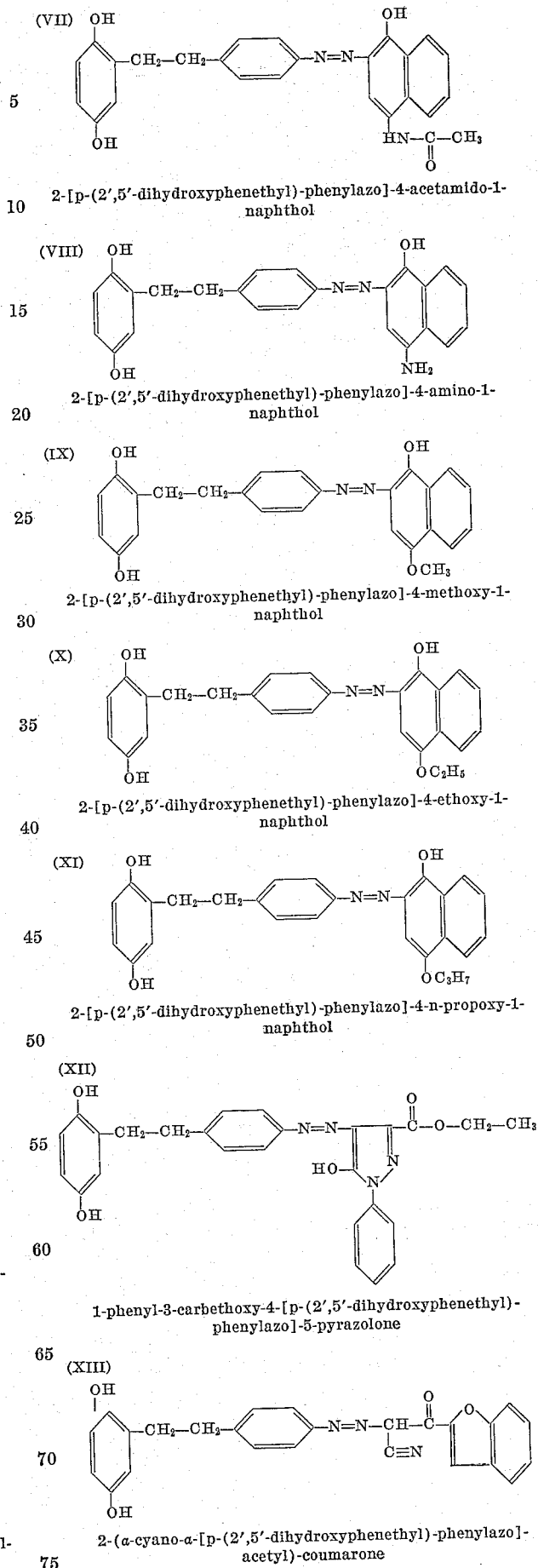
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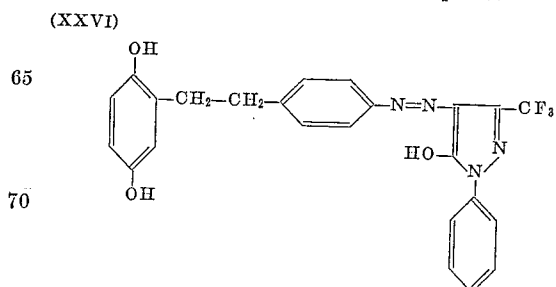
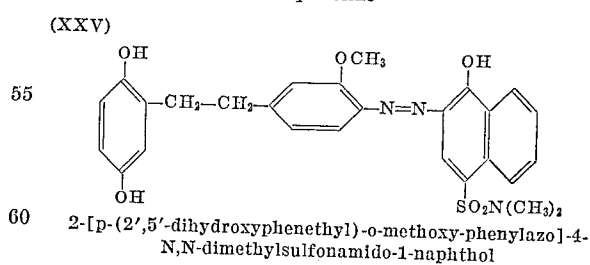
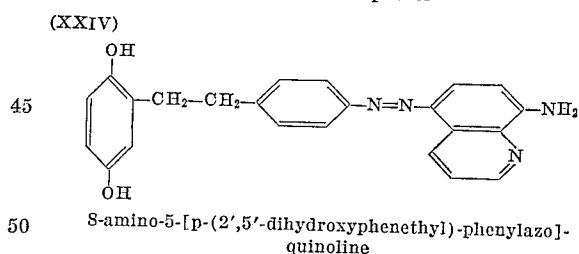
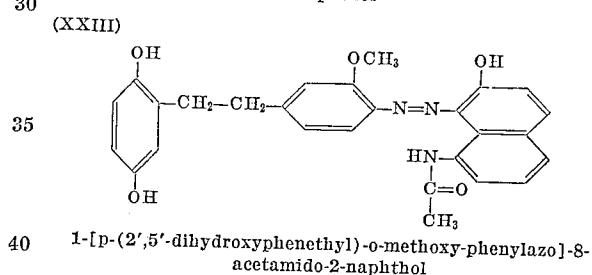
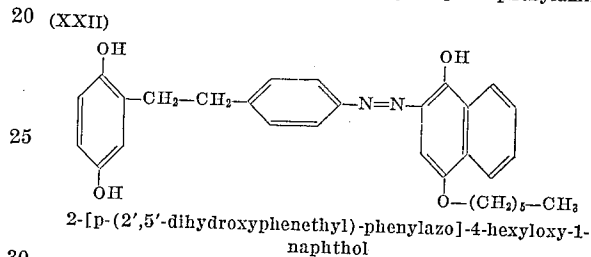
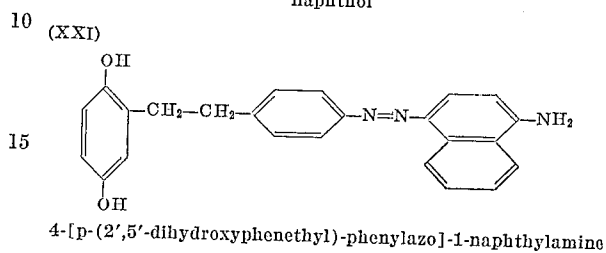
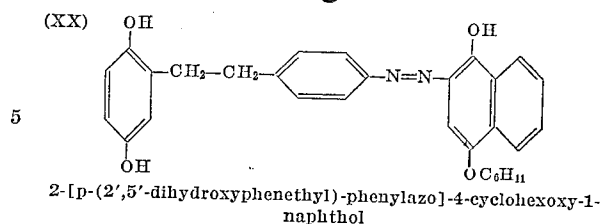
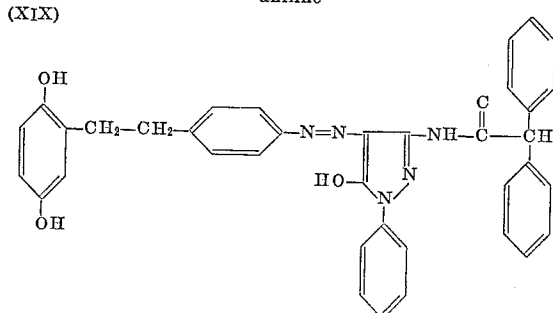
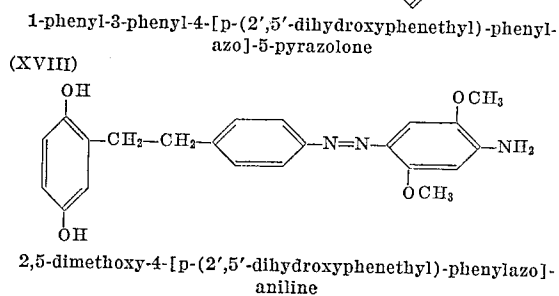
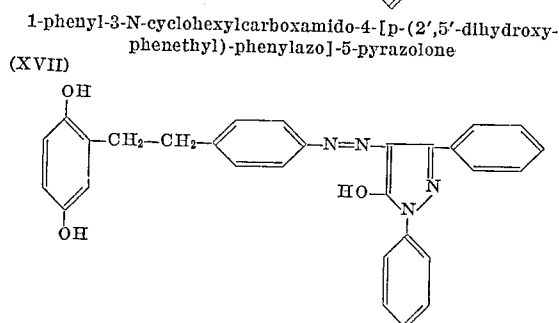
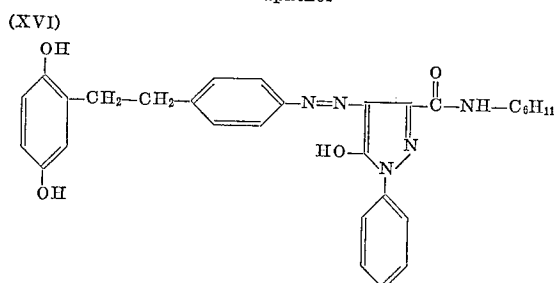
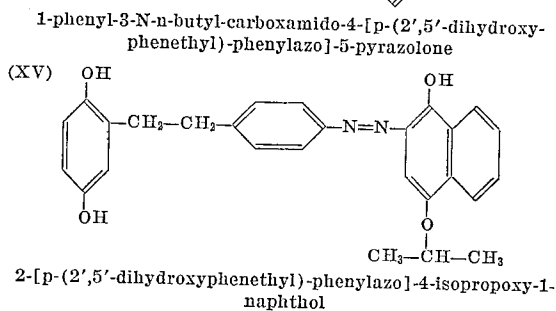
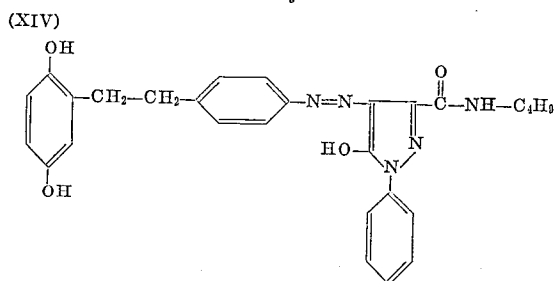
pler, and particularly in α -naphthol, it has been found that coupling ortho to the hydroxyl group gives a dye developer of superior color properties. It has also been found that such ortho-coupled dye developers exhibit essentially no pH sensitivity over a fairly wide range on either side of neutral.

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



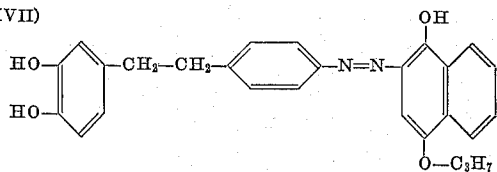
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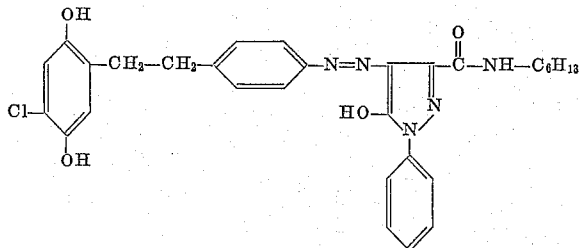
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(XXVII)



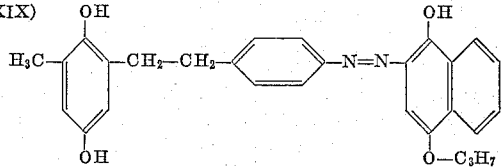
2-[p-(3',4'-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol

(XXVIII)



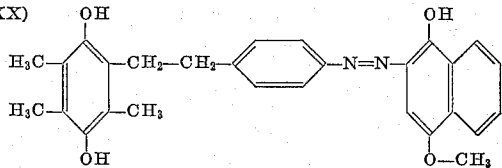
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(XXIX)



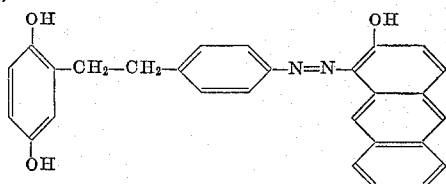
2-[p-(2',5'-dihydroxy-3'-methyl-phenethyl)-phenylazo]-4-n-propoxy-1-naphthol

(XXX)



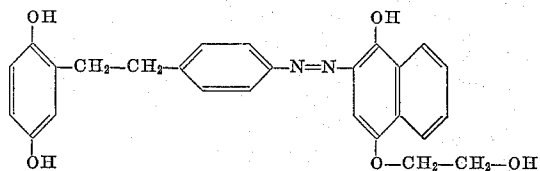
2-[p-(2',5'-dihydroxy-3',4',6'-trimethyl-phenethyl)-phenylazo]-4-methoxy-1-naphthol

(XXXI)



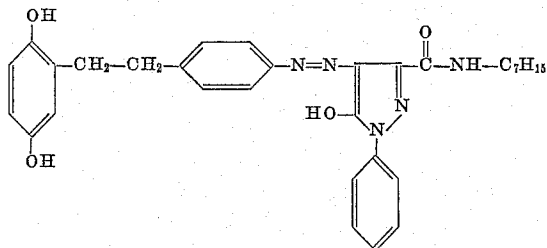
1-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-2-anthrol

(XXXII)



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

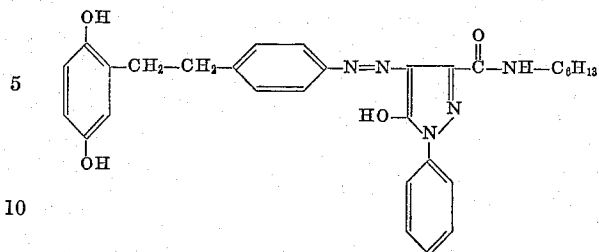
(XXXIII)



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

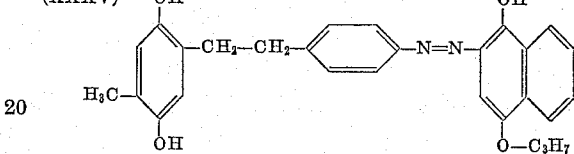
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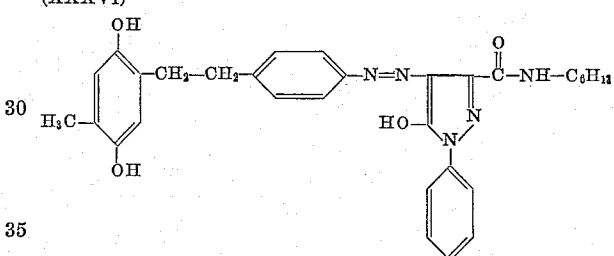
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(XXXV)



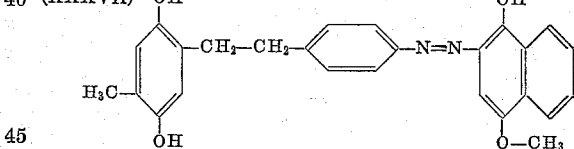
2-[p-(2',5'-dihydroxy-4'-methyl-phenethyl)-phenylazo]-4-n-propoxy-1-naphthol

(XXXVI)



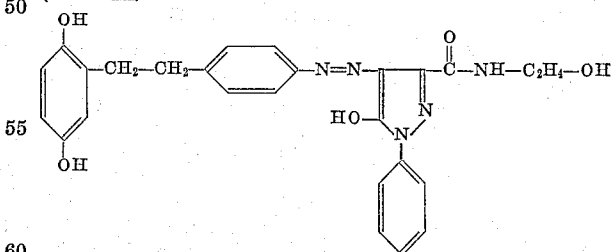
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(XXXVII)



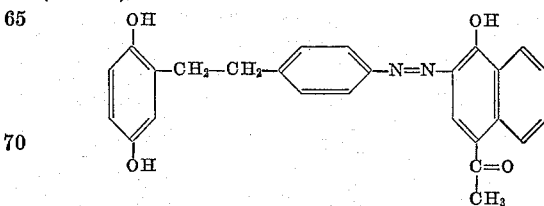
2-[p-(2',5'-dihydroxy-4'-methyl-phenethyl)-phenylazo]-4-methoxy-1-naphthol

(XXXVIII)



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

(XXXIX)

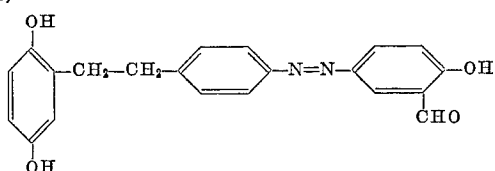


2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-acetyl-1-naphthol

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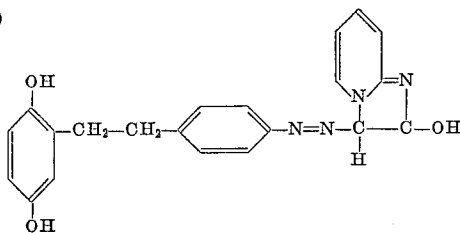
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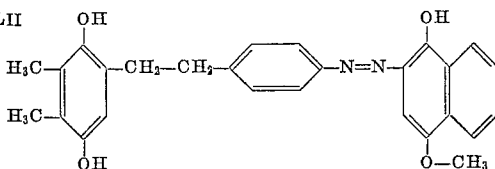
2-formyl-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-phenol

(XLI)



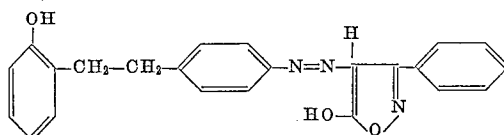
2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-pyrimidin-4-ol

(XLII)



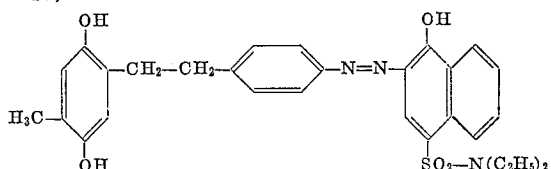
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(XLIII)



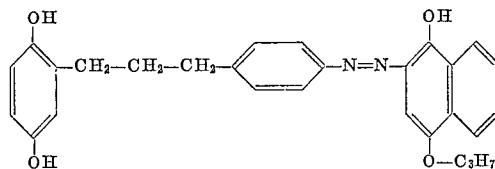
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(XLIV)



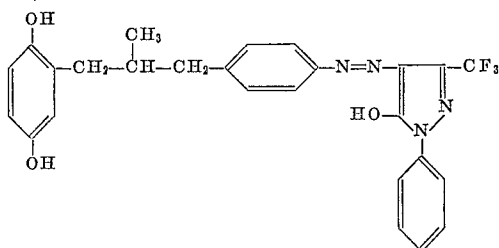
2-[p-(2',5'-dihydroxy-4'-methyl-phenethyl)-phenylazo]-4-N,N-diethylsulfonamido-1-naphthol

(XLV)



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

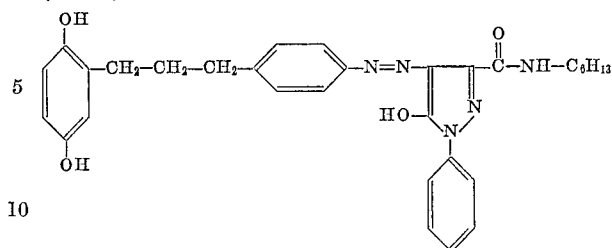
(XLVI)



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

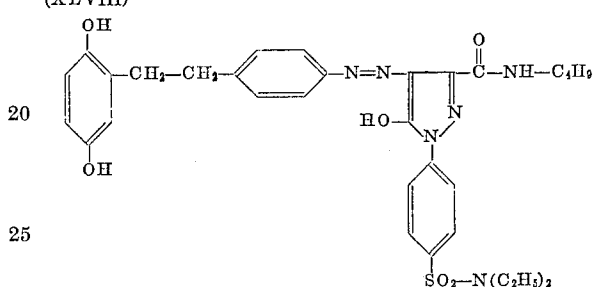
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(XLVII)



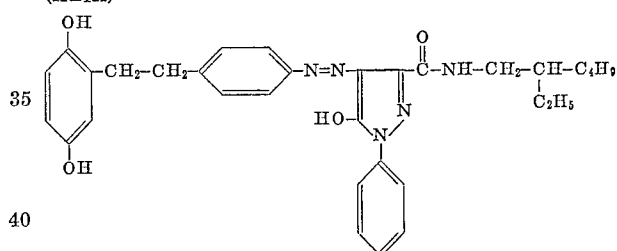
1-phenyl-3-N-n-hexylcarboxamido-4-[p-(2',5'-dihydroxyphenylpropyl)-phenylazo]-5-pyrazolone

(XLVIII)



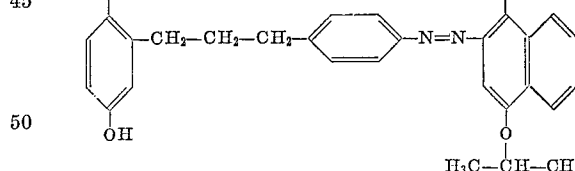
1-(p-N,N-diethylsulfonamidophenyl)-3-N-n-butylcarboxamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone

(XLIX)



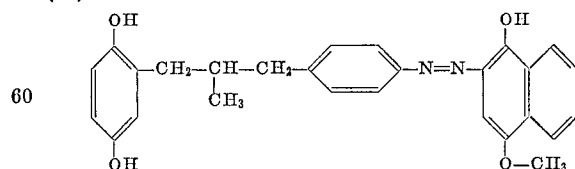
1-phenyl-3-(N-2'-ethylhexylcarboxamido)-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone

(L)



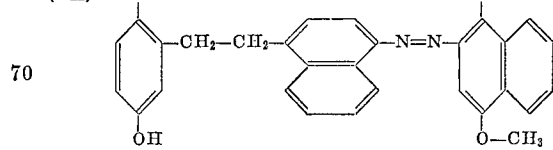
2-[p-(2',5'-dihydroxyphenylpropyl)-phenylazo]-4-isopropoxy-1-naphthol

(LI)



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

(LII)



2-[p'-(2',5'-dihydroxyphenethyl)-a-naphthylazo]-4-methoxy-1-naphthol

75

Oc1ccc(cc1)CCc2ccc(cc2)/N=N/c3c(O)ccc4ccccc34OCCCl

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

(LIV)

15

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

20

(LV)

5-β-hydroxyethylamino-8-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-1-naphthol

(LVI)

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

(LVII)

CCCC1=CC=C(C=C1C2=CC=CC=C2O)N=Nc3ccc(cc3CCc4cc(O)cc(O)cc4)O

2-[m-(2',5'-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol

(LVIII)

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

(LIX)

4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-hydroxy-acenaphthene

14

(LX)

5-amino-8-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-1-naphthol

(LXI)

2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-N-methyl-N-phenylisulfonamido-1-naphthol

25 (LXII)

30

35

2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-3,6-bis-N,N-diethylsulfonamido-S-N-p-tolylsulfonamido-1-naphthol

(LXIII)

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

(LXIV)

55 

60 4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-1-N-ethylamino-
naphthalene

(LXV)

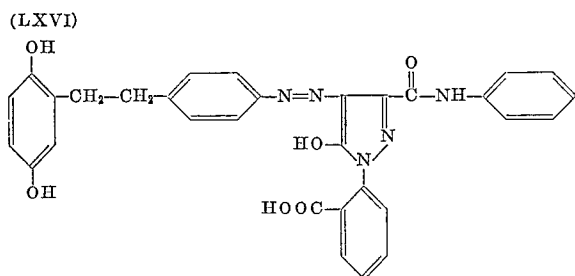
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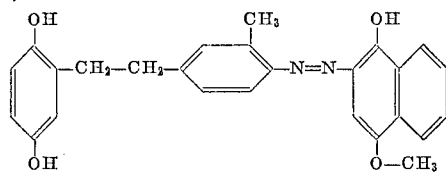
1-phenyl-3-n-carbobutoxy-4-[p-(2',5'-dihydroxyphenethyl)phenylazo]-5-pyrazolone

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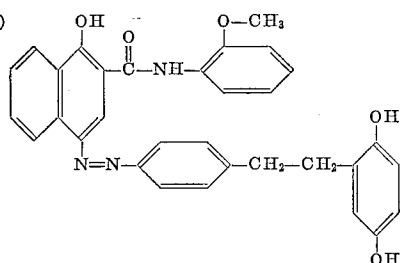
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(LXVII)



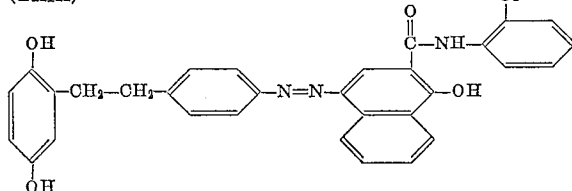
2-[p-(2',5'-dihydroxyphenethyl)-o-methyl-phenylazo]-4-methoxy-1-naphthol

(LXVIII)



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

(LXIX)



2-(N-o-chlorophenylcarboxamido)-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-1-naphthol

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

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

(LXXII) 1-p-tolyl-3-cyano-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone

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

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

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

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

(LXXVII) 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-chloro-1-phenol

(LXXVIII) 1-acetamido-8-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-7-naphthol

(LXXIX) 1-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-6-methoxy-2-naphthol

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

(LXXXI) 1-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-methoxy-2-naphthol

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

16

(LXXXIII) 1-phenyl-3-N-β-hydroxy-ethoxy - ethoxy - n-propyl-carboxamido-4-[p-(2',5' - dihydroxyphenethyl)-phenylazo]-5-pyrazolone

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

(LXXXV) 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-N,N-diethylsulfonamido-1-naphthol

(LXXXVI) 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-N,N-dimethylsulfonamido-1-naphthol

10 (LXXXVII) 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-sec. butoxy-1-naphthol

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

(LXXXIX) 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-butoxy-ethoxy-1-naphthol

15 (XC) 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-methoxy-triethoxy-1-naphthol

(XCI) 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-n-butoxy-1-naphthol

20 (XCII) 1-phenyl-3-N-n-butylcarboxamido-4-[p-(2',5'-dihydroxyphenylpropyl)-phenylazo]-5-pyrazolone

(XCIII) 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-γ-phenylpropoxy-1-naphthol

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

25 (XCV) 1-phenyl-3-N-n-butylcarboxamido-4-[p-(2',5'-dihydroxy-4'-methylphenethyl)-phenylazo]-5-pyrazolone

(XCVI) 1-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-2-naphthylamine

30 (XCVII) 1-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-methoxy-2-naphthylamine

(XCVIII) 1-m-trifluoromethyl-phenyl-3-carbethoxy-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone

35 (XCIX) 1-phenyl-3-N-n-amylicarboxamido-4-[p-(2',5'-dihydroxy-4'-methylphenethyl)-phenylazo]-5-pyrazolone

(C) 1-(o-carboxyphenyl)-3-phenyl-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-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

45 4-acetamido-α-naphthylamine

Phenol

Aniline

1,1'-dihydroxy-4,4'-biphenyl

1,5-naphthalene diamine

p-Cresol

50 3,6-bis-N,N-diethylsulfonamido-8-amino-1-naphthol

Py-3-hydroxytetrahydro-7-hydroxy-naphthoquinoline

1-hydroxyanthracene

1-hydroxy-2-naphthanilide

55 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 application of Myron S. Simon, Serial No. 612,053, filed September 25, 1956 (now abandoned in favor of a continuation-in-part thereof, Serial No. 196,523, filed May 21, 1962), by the presence of the alkylene group R. The presence of this alkylene group R insulates the dihydroxyphenyl group Y from conjugation with the chromophoric system of the rest of the molecule, and effectively avoids pH color sensitivity resulting from such conjugation.

65 In addition, the presence of the alkylene group R helps to avoid color changes in the transfer dye image should the transferred dye developer subsequently be oxidized. The dye developers of this invention are also superior to dye developers such as

70 phenylazohydroquinone in that the resulting dye transfer

images are more stable, particularly as to heat and humidity, and also to color changes from changes in pH.

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

Example 1

2,5-bis-acetoxy phenethylaniline hydrochloride (7.9 g.; 0.02 mol) is dissolved in 150 cc. of water containing 4 cc. of concentrated HCl (0.05 mol), and diazotized at 0-5° by the addition of 1.4 g. NaNO₂ (0.02 mol) 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 3.15 g. (0.018 mol) of 1-phenyl-3-amino-5-pyrazolone in 300 cc. of ethanol and 300 cc. of 10% NaHCO₃ is added portionwise. The resulting yellow-brown slurry is stirred at room temperature for two hours, filtered, and the filter cake washed thoroughly with 10% NaHCO₃. The filter cake is reslurried in dilute acetic acid solution, filtered, and washed thoroughly with water. The product is dried in vacuo over sulfuric acid, yielding 8 g. (89%).

The above product is dissolved in 160 cc. of ethanol, 40 cc. of water added followed by 18 g. of 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 filtering 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% NaCl solution containing a trace of HCl, the solid filtered, and the procedure repeated. The resulting yellow-orange solid is filtered, washed with water, and dried to give 4 g. (45% yield) of the dye developer 1-phenyl-3-amino-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone (Formula I) melting at 244-5° C. The spectral absorption curve shows a $\lambda_{\max}$ at 400 m μ in ethanol; $\epsilon=27,000$. Nitrogen analysis of the product gives a value of 15.9% as compared with a calculated value of 16.9%.

Example 2

2,5-bis-acetoxy phenethylaniline hydrochloride (2.1 g.; 0.006 mol) diazotized as described in Example 1 is added, at about 15° C., to a solution of 1.4 g. (0.008 mol) of 4-methoxy-1-naphthol in 100 cc. of acetone, and 100 cc. of saturated NaHCO₃ 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 evacuated. 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 methylcellulose and dried to give a 90% yield of 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-methoxy-1-naphthol, $\lambda_{\max}=530$ m μ in ethanol, $\epsilon=18,500$.

Example 3

2,5-bis-acetoxy phenethylaniline hydrochloride (3.5 g.) is diazotized and coupled into 5-acetamido-1-naphthol (1.4 g.) in a manner similar to that described in Example 1 to give 1 g. of 4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-acetamido-1-naphthol [Formula IV] as a reddish-brown solid. Nitrogen analysis of the product, which decomposes at 230° C., gives 9.3% as compared with the calculated 9.5%. The spectral absorption curve of this product in pyridine shows $\lambda_{\max}=474$ m μ .

Example 4

In a manner similar to that described in Example 1, 1 g. of 2,5-bis-acetoxy phenethylaniline hydrochloride is diazotized and coupled into 0.4 g. of β -naphthol to give 0.7 g. of 1-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-2-naphthol [Formula II] as an orange-brown solid which decomposes at 230° C. Nitrogen analysis of the product gives 5.4% as compared with the calculated 5.21%.

In the following examples all parts are given by weight except where otherwise noted, and all operations involving light sensitive materials are carried out in the absence of actinic radiation. These examples are intended to be illustrative only of the photographic use of the dye developers and should not be construed as limiting the invention in any way.

Example 5

A photosensitive element is prepared by coating a gelatin-coated-film base with a solution containing 3% of 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-methoxy-1-naphthol [Formula IX, as prepared in Example 2] in a 4% solution of cellulose acetate hydrogen phthalate in an 80:20 mixture, by volume, of acetone and methanol. After this coating has dried, a silver iodobromide emulsion is applied. This photosensitive element is exposed and processed by spreading an aqueous liquid processing composition comprising:

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

between said photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element comprises a cellulose acetate coated-baryta paper which has been coated with a solution comprising 4% Nylon Type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for N-methoxymethyl polyhexamethylene adipamide) in 80% aqueous isopropanol. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a magenta positive dye image of the photographed subject. Use of 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-ethoxy-1-naphthol [$\lambda_{\max}=530$ m μ in ethanol; Formula XI] also gives a magenta positive transfer image. Similarly, a magenta positive transfer image may be obtained by the use of 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-n-propoxy-1-naphthol [$\lambda_{\max}=532$ m μ in ethanol; Formula XI] or 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-isopropoxy-1-naphthol [$\lambda_{\max}=534$ m μ in ethanol; Formula XV].

Example 6

A photosensitive element is prepared similar to that described in Example 5 using 3% of 1-phenyl-3-amino-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone [Formula I, as prepared in Example 1]. Exposure and processing with a liquid processing composition and image-receiving element similar to those described in Example 5 gives a yellow positive dye image.

Example 7

A yellow positive transfer image is obtained using a photosensitive element prepared and processed similar to that described in Example 5 using 3% of 1-phenyl-3-methyl-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone [$\lambda_{\max}=404$ m μ in ethanol; Formula VI].

Example 8

Use of a photosensitive element prepared and processed similar to that described in Example 5 using 3% of 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-acetamido-1-naphthol [$\lambda_{\max}=521$ m μ in pyridine; Formula VII] gives a magenta positive transfer image.

Example 9

Repeating the process described in Example 5 using 3% of 4 - [p - β - (2',5' - dihydroxyphenyl) - ethylphenylazo]-5-benzamido-1-naphthol [$\lambda_{\max.}=476\text{ m}\mu$ in pyridine; Formula V] gives a magenta positive transfer image.

Example 10

A magenta positive transfer image is obtained by the use of a photosensitive element, prepared and processed similar to that described in Example 5, using 2.5% of 2 - [p - β - (2',5' - dihydroxyphenyl) - ethylphenylazo] 4-amino-1-naphthol [$\lambda_{\max.}=522\text{ m}\mu$ in pyridine; Formula VIII].

Example 11

A photosensitive element similar to that described in Example 5 is prepared using 2% of 2-[p- β -(2',5'-dihydroxyphenyl) - ethylphenylazo] - 4 - sulfo - 1 - naphthol [$\lambda_{\max.}=514\text{ m}\mu$ in pyridine; Formula III]. Processing of the exposed photosensitive element using as the image-receiving element, a layer of polyvinyl alcohol (cast from a 6% aqueous polyvinyl alcohol solution) on a cellulose acetate-coated baryta paper support, gives a red-orange positive image.

Example 12

A coating solution containing 3% of 1-phenyl-3-carbethoxy - 4 - [p - (2',5' - dihydroxyphenethyl) - phenylazo]-5-pyrazolone [$\lambda_{\max.}=422\text{ m}\mu$ in ethanol; Formula XII] is used to prepare a photosensitive element similar to that described in Example 5. After exposure, the photosensitive element is similarly processed and gives a yellow positive transfer image. Used in a similar manner, 1 - phenyl - 3 - N - n - butyl - carboxamido - 4 - [p - (2',5' - dihydroxyphenethyl) - phenylazo] - 5 - pyrazolone [$\lambda_{\max.}=455\text{ m}\mu$ in pyridine; Formula XIV] also gives a yellow positive transfer image.

Example 13

A photosensitive element is prepared similarly to that described in Example 5, using a coating solution containing 3% of 2-(α -cyano- α [p-2',5'-dihydroxyphenethyl]-phenylazo)-acetyl)-coumarone [Formula XIII;

$$\lambda_{\max.}=417\text{ m}\mu$$

in ethanol]. A yellow positive image is obtained when this photosensitive element is exposed and processed in a manner similar to that described in Example 5.

In certain embodiments it may be desirable to utilize the dye developer in the silver halide emulsion. The following example is given to illustrate this embodiment.

Example 14

A photosensitive element wherein the dye developer is incorporated in the silver halide emulsion is prepared by grinding to a paste 1.2 g. of 1-phenyl-3-N-n-butyl-carboxamido - 4 - [p - 2',5' - dihydroxy - phenethyl) - phenylazo] - 5 - pyrazolone [Formula XIV] in 3 cc. of water containing a few drops of a dispersing agent. The resulting paste is added to 30 cc. of a silver iodobromide emulsion, with stirring, and a layer of the emulsion containing the dye developer is cast on a gelatin-coated film base. Exposure and processing, in superposed relationship with an image-receiving element prepared as described in Example 5, with an aqueous processing composition comprising:

	Percent
Sodium carboxymethyl cellulose-----	4.5
Potassium bromide-----	0.2
Sodium hydroxide-----	1.2
1-phenyl-3-pyrazolidone -----	0.2

gives a yellow, positive dye image on the image-receiving element.

As mentioned above, it is also contemplated to employ the dye developers of this invention in the liquid process-

ing composition. The following example is given to illustrate this embodiment.

Example 15

An exposed silver iodobromide emulsion is processed, in superposed relationship with an image-receiving element prepared as described in Example 11, with an aqueous processing composition comprising

	Percent
Sodium carboxymethyl cellulose-----	4.5
Potassium bromide-----	0.2
1-phenyl-3-pyrazolidone -----	0.2
Sodium hydroxide-----	1.5
2 - [p - 2',5' - dihydroxyphenethyl) - phenylazo] - 4-methoxy-1-naphthol [Formula IX]-----	0.2

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

Example 16

A photosensitive element was prepared in a manner similar to the above examples, except that the dye developer was dispersed in a layer of gelatin. The coating solution from which the dye developer layer was coated was prepared by dissolving 0.5 g. of 2-[p-(2',5'-dihydroxyphenethyl) - phenylazo] - 4 - β - hydroxy - ethoxy-1-naphthol, 1 cc. of cyclohexanone, and 0.5 cc. of N-n-butylacetanilide 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 was effected by high speed agitation in a Waring Blendor. 5 cc. of the resulting dye dispersion was 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 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.

Substitution of the other dye developers described above in the procedures described in the above examples gave similar positive transfer images.

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.

The dye developers of this invention which have, as part of the azo coupler radical X, a 1-o-carboxyphenyl-5-pyrazolone system, e.g., compound LXVI, 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.

Dye developers within the scope of this invention which contain a 3-cyano-5-pyrazolone grouping as part of the

azo coupler radical X are disclosed and claimed in the copending application of Daniel L. Ross, Serial No. 248,240, filed December 31, 1962.

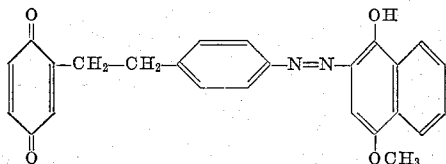
The use of 7-amino-1-naphthol as the azo coupler radical X has been found to give magenta dye developers having unexpectedly superior light stability and color characteristics. Dye developers of this type are disclosed and claimed in the copending application of Milton Green, Terry Milligan and Daniel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

The quinones of the novel azo dye developers of this invention may be prepared by oxidizing under conditions which do not attack the azo bond, e.g., by oxidizing with benzoquinone, chloranil, or mercuric acetate. These azo quinones are useful in the photographic processes disclosed and claimed in the copending application of Howard G. Rogers, Serial No. 825,359, filed July 6, 1959, as a continuation-in-part of, and replacement for, Serial No. 599,122, filed July 20, 1956, now abandoned.

The following example is illustrative of the preparation of the novel azo quinones:

Example 17

One mol of 2-[p-(2',5'-dihydroxyphenylethyl)-phenylazo]-4-methoxy-1-naphthol and a 20% molar excess of mercuric acetate are dissolved in dimethylformamide and reacted, while open to the air, on 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 from a chloroform-methyl cellosolve solution, 2-[p-(2',5'-dioxophenethyl)-phenylazo]-4-methoxy-1-naphthol



was produced melting at 180 to 182° C. The infrared absorption spectrum of this product exhibited typical quinone bands.

The dye developers of this invention are also useful in integral multilayer photosensitive elements for use in multicolor diffusion transfer processes. As an example of such photosensitive elements, mention may be made of the photosensitive elements disclosed and claimed in the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single common image-receiving element. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. In one of the preferred embodiments of photosensitive elements of this type, the dye developers are disposed in separate alkali-permeable layers behind the photosensitive silver halide emulsion stratum with which they are associated.

The photosensitive elements within the scope of this invention may be used in roll film units which contain a plurality of photosensitive frames. The photosensitive elements of this invention are especially useful in composite roll film intended for use in a "Polaroid Land Camera," sold by Polaroid Corporation, Cambridge 39, Massachusetts, or a similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on February 10, 1948. In general, such composite roll films

comprise a photosensitive roll, a roll of image-receiving material and a plurality of pods containing an aqueous alkaline processing solution. The rolls and pods are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pods may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of the pods used in such units are well known to the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

It will be noted that the liquid processing composition may contain one or more auxiliary or accelerating silver halide developing agents, such as p-methylaminophenol (Metol); 2,4-diaminophenol (Amidol); benzylaminophenol; hydroquinone; a substituted hydroquinone such as tolhydroquinone, 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-poly-

hexamethylene 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 fibres, such as nylon.

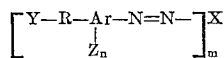
In the preceding portions of the specification the expression "color" has been frequently used. This expression is intended to include the use of a plurality of colors to obtain black.

This application is in part a continuation of our co-pending application, Serial No. 612,045, 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. A photographic developer composition comprising an aqueous solvent, an alkaline material soluble therein, a silver halide developing agent which is substantially colorless in at least the unoxidized form, and an azo dye developer of the formula:



wherein Y is selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl radicals and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, said $-\text{N}=\text{N}-$ group being directly attached to a ring carbon of said aryl nucleus; R is a divalent alkylene group directly attached to said aryl nucleus Ar and to said phenyl ring of Y; each Z is selected from the group consisting of halogen, alkoxy and alkyl 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 $-\text{N}=\text{N}-$ group and completing said azo dye developer.

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

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

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

5. A photographic developer composition as defined in claim 1, wherein X 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 is 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'-dihydroxyphenethyl)-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-amino-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone and

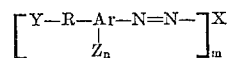
a silver halide developing agent which is substantially colorless in at least the unoxidized form.

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

11. A photographic developer composition comprising an aqueous alkaline solution of 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4- β -hydroxyethoxy-1-naphthol 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-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-isopropoxy-1-naphthol 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:



wherein Y is selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl radicals and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, said $-\text{N}=\text{N}-$ group being directly attached to a ring carbon of said aryl nucleus; R is a divalent alkylene group directly attached to said aryl nucleus Ar and to said phenyl ring of Y; each Z is selected from the group consisting of halogen, alkoxy and alkyl 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 $-\text{N}=\text{N}-$ group and 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'-dihydroxyphenethyl)-phenylazo]-4-methoxy-1-naphthol.

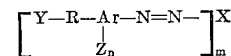
16. A photographic product as defined in claim 13, wherein said azo dye developer is 1-phenyl-3-amino-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone.

17. A photographic product as defined in claim 13, wherein said azo dye developer is 1-phenyl-3-N-n-hexylcarboxamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone.

18. A photographic product as defined in claim 13, wherein said azo dye developer is 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4- β -hydroxyethoxy-1-naphthol.

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

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:



wherein Y is selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl radicals and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus selected from the group consisting of benzene and naphthalene nuclei, said $-\text{N}=\text{N}-$ group being directly attached to a ring carbon of said aryl nucleus; R is a divalent alkylene group directly attached to said aryl nucleus Ar and to said phenyl ring of Y; each Z is selected from the

group consisting of halogen, alkoxy and alkyl 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 and 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 is a phenolic azo coupler radical.

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

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

28. The process as defined in claim 20, wherein X 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'-dihydroxyphenethyl)-phenylazo]-4-methoxy-1-naphthol.

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

31. The process as defined in claim 20, wherein said dye developer is 1-phenyl-3-N-n-hexyl-carboxamido-4-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-5-pyrazolone.

32. The process as defined in claim 20, wherein said dye developer is 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4- β -hydroxyethoxy-1-naphthol.

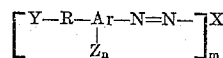
33. The process as defined in claim 20, wherein said dye developer is 2-[p-(2',5'-dihydroxyphenethyl)-phenylazo]-4-isopropoxy-1-naphthol.

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 which comprises developing an exposed photosensitive silver halide emulsion with an aqueous alkaline solution of an azo dye developer of the formula:



wherein Y is selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl radicals and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Ar is a divalent aryl nucleus 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; R is a divalent alkylene group directly attached to said aryl nucleus Ar and to said phenyl ring of Y ; each Z is selected from the group consisting of halogen, alkoxy and alkyl 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 and completing said azo dye developer.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

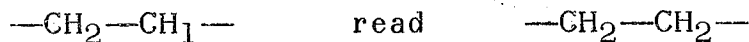
Patent No. 3,134,672

May 26, 1964

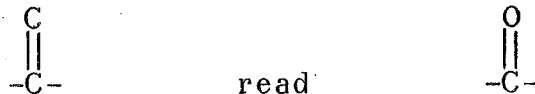
Elkan R. Blout et al.

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 2, lines 9 and 10, for "image-reeciving" read -- image-receiving --; line 58, for "liquiud" read -- liquid --; column 3, line 4, for "comopsition" read -- composition --; column 4, line 21, for "Molton Green" read -- Milton Green --; column 5, lines 63 to 73, for that portion of the formula reading:



column 7, lines 61 to 75, for that portion of the formula reading:



column 15, line 51, for "-dihydroxphenethyl)-" read -- -dihydroxyphenethyl)- --; column 16, line 73, for "by" read -- be --; column 19, line 56 and column 20, line 14, for "-[p-2',5'--", each occurrence, read -- -[p-(2',5'- --.

Signed and sealed this 20th day of October 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents