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3,241,963

NOVEL PHOTOGRAPHIC PRODUCTS, PROCESSES
AND COMPOSITIONS

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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 developing agents are used.

Another object is to provide novel processes and compositions for the development of silver halide emulsions, in which the novel 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.

A further object is to provide novel products, processes and compositions suitable for use in preparing monochromatic and multichromatic photographic images.

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 images present in an exposed silver halide emulsion; thus they may be referred to as dye developers. These novel dyes or dye developers will be further described hereinafter.

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 for use in such processes.

In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed prior to, during or after wetting, on an image-receiving element. In a preferred embodiment, the photosensitive element contains a layer of dye developer, and the liquid processing composition is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed position with an image-receiving element. The liquid processing com-

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position 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 depth-wise 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 stripping 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 a 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 about 0.5 to 8%, by weight, of the dye developer. Similar concentrations may be used if the dye developer is utilized as a component of the liquid processing composition. In an especially useful mode of disposing the dye developers in the photosensitive elements, the dye developer is dissolved in a water-immiscible solvent and then dispersed in a gelatin coating solution.

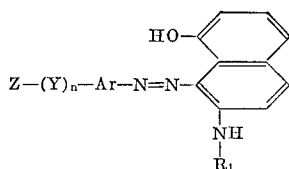
The liquid processing composition which is used in the processes herein disclosed comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate, and may contain the dye developer. In some instances, it may contain an additional silver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

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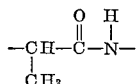
fectured when left in solution for a long period of time may also be used.

The dye developers of this invention are azo dyes having the formula:

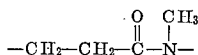
(1)



wherein Z is an ortho- or para-dihydroxyphenyl radical, Y is a lower alkylene radical, such as methylene, ethylene or isopropylene, a carboxamido or an alkylencarboxamido radical, n is 0 or 1, Ar is a phenyl or naphthyl radical and R_1 is hydrogen or an alkyl radical, preferably a lower alkyl radical. It should be understood that the term "alkylencarboxamido" is intended to include radicals wherein the alkylene group is branched, e.g.,



and wherein the carboxamido group is substituted, e.g.,

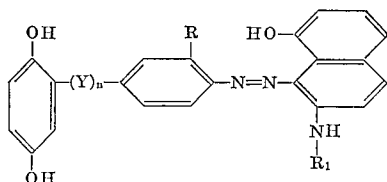


and combinations of radicals of both types. It should also be understood that the term "alkyl" is intended to include substituted alkyl radicals, for example, hydroxy-alkyl. Alkyl is also intended to include a branched as well as a straight chain, e.g.,



In a preferred embodiment, Z is a para-dihydroxyphenyl radical, and Ar is a phenyl radical. Such compounds may be represented by the formula:

(2)



wherein Y, n and R_1 have the same meaning as above and R is hydrogen or a halogen, methoxyl, methyl, or trifluoromethyl radical.

The dye developers of this invention may be prepared by coupling, in the 8-position, a 7-amino-1-naphthol coupler with a diazonium salt of an arylamine containing a silver halide developing radical. The dye developers prepared from this coupler exhibit an unexpected increase in light stability.

The dye developers of this invention wherein Ar is a naphthyl radical or a phenyl radical, wherein R, the substituent ortho to the azo group, is a halogen, methoxyl, methyl or trifluoromethyl group and R_1 is hydrogen, are also found to possess unexpected nondesensitizing properties in addition to the above-mentioned light stability properties. Because of these nondesensitizing properties, it is possible to incorporate such dye developers directly into the emulsion without any accompanying silver halide desensitization that would normally be expected to occur in compounds of this type. With the dye developers of this invention, the displacement of the optical sensitizing dyes on the silver halide grain is substantially decreased, thereby increasing the efficiency of the sensitizing agents.

Nondesensitizing properties are also found in compounds within Formula 2 wherein R is hydrogen and R_1 is an alkyl radical. By using the substituted amino-

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naphthol coupler, a greater choice of amine functions is available for coupling, thereby resulting in increased flexibility with regard to the synthesis of dye developers having desired color characteristics.

Substituted amino-naphthol couplers and their preparation are disclosed and claimed in the copending application of Daniel L. Ross, Serial No. 174,247, filed February 19, 1962.

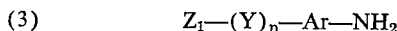
It should be understood that the group designated Ar may be substituted in positions other than the ortho position by, for example, halogen, lower alkyl and alkoxy radicals.

The ortho- or para-dihydroxyphenyl radical may also be substituted by, for example, alkyl and halogen substituents.

Certain of the dye developers of the present invention are subgeneric to certain specific classes of dye developers disclosed in the copending application of Elkan R. Blout, Saul G. Cohen, Milton Green, Howard G. Rogers, Myron S. Simon and Robert B. Woodward, Serial No. 1,443, filed January 11, 1960, the copending application of Elkan R. Blout, Milton Green and Howard G. Rogers, Serial No. 144,816, filed October 18, 1961, now U.S. Patent No. 3,134,672 as a continuation-in-part of Serial No. 612,045, filed September 25, 1956, (now abandoned), and the copending application of Myron S. Simon, Serial No. 612,053, filed September 25, 1956 (now abandoned). The dye developers of the present invention are distinguishable by the above-described, unobvious and unexpected properties that render them photographically superior to those set forth in the above-designated copending applications.

In addition, the dye developers disclosed herein exhibit a substantial increase in pH stability over the isomeric amino-naphthol dye developers of the above copending applications, that is, they are not subject to color change due to a change in pH. This property is highly desirable in the photographic employment of the dye developers of the present invention.

The dyes of Formula 1 may be prepared by diazotizing a compound of the formula:



wherein Y, n and Ar have the same significance as previously noted; and Z_1 represents the protected derivative of the ortho- or para-dihydroxyphenyl group, preferably the O-acylated derivative; coupling the diazotized compound into the desired 7-amino-1-naphthol coupler wherein the hydroxyl group of the coupler is also protected; and removing the protective groups prior to the photographic utilization of the compounds. Hydrolysis in the presence of alkali, for example, may be employed to remove the protecting groups.

The novel dye developers of this invention may also be prepared by coupling a diamine into the amino-naphthol coupler and adding the developer group as the lactone through amide condensation according to the method disclosed in the above-mentioned copending application Serial No. 1,443.

The compounds of Formula 1 may also be prepared by reacting a 1,7-dihydroxynaphthalene with an amine of the formula:



wherein R_1 has the same meaning as above, protecting the hydroxyl group of the coupler, coupling the resulting product with a diazotized compound of Formula 3, and removing the protective groups prior to photographic employment. This method of preparation is particularly useful in preparing compounds within Formula 1 wherein R_1 is an alkyl group.

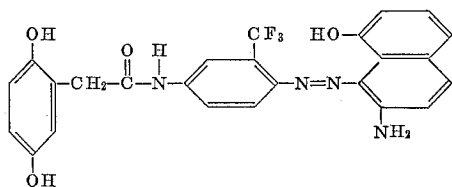
In addition to forming azo couplers for use in this invention by reacting a dihydroxynaphthalene with an amine, a two-step reaction of 7-hydroxy-1-naphthalene sulfonic acid with an amine and ammonium sulfate, fol-

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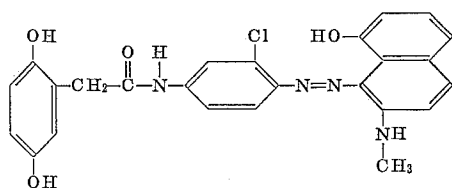
lowed by potassium hydroxide fusion, may also be used to produce azo couplers for this invention.

It should be noted that it is desirable to protect the hydroxyl groups, both on the dihydroxyphenyl radical and the amino-naphthol coupler, during synthesis, as by acylation, to avoid side reactions and to insure coupling in the desired position. If protecting groups were not employed, the position of coupling could not be controlled and an undesirable mixture of dyes of varying structure would result instead of compounds as shown by Formula 1.

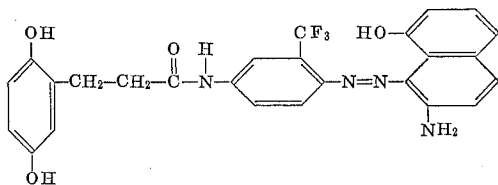
As examples of dye developers within the scope of this invention, mention may be made of:



(I) 8-(4'-(2,5-dihydroxyphenyl)-2'-trifluoromethyl)-phenylazo-7-amino-1-naphthol.

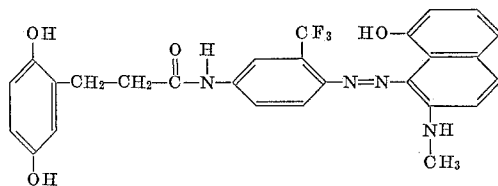


(II) 8-(4'-(2,5-dihydroxyphenyl)-2'-chloro)-phenylazo-7-methylamino-1-naphthol.

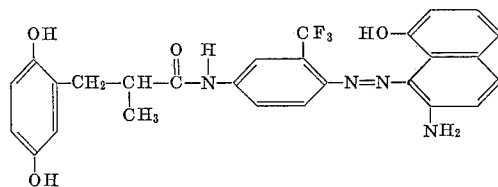


(III) 1-[2'-trifluoromethyl-4'-(2'',5'')-dihydroxyphenyl]-propionamido]-phenylazo-8-hydroxy-2-naphthylamine.

(IV) 1-(2'-chloro-4'-hydroquinonylpropionamido)-phenylazo-8-hydroxy-2-naphthylamine.



(V) 1-[2-trifluoromethyl-4-(2,5-dihydroxyphenyl)-propionamido]-phenylazo-2-methylamino-8-naphthol.



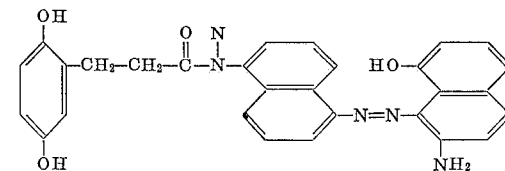
(VI) 1-[4'-(2'',5'')-dihydroxyphenylisobutyramido]-2'-trifluoromethyl]-phenylazo-8-hydroxy-2-naphthylamine.

(VII) 1-[2-trifluoromethyl-4-(2,5-dihydroxyphenyl)-isobutyramido]-phenylazo-2-methylamino-8-naphthol.

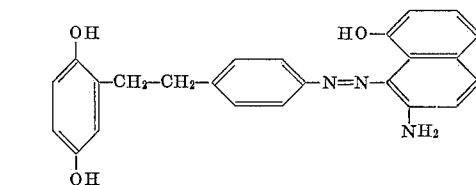
(VIII) 1-(2'-chloro-4'-hydroquinonylpropionamido)-phenylazo-8-hydroxy-2-N-methylnaphthylamine.

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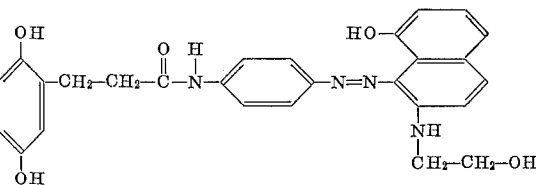
(IX) 1-[4-(2,5-dihydroxyphenyl)-propionamido]-phenylazo-2-ethylamino-8-naphthol.



(X) 1-[5-(2,5-dihydroxyphenylpropionamido)]-α-naphthylazo-2-amino-8-naphthol.

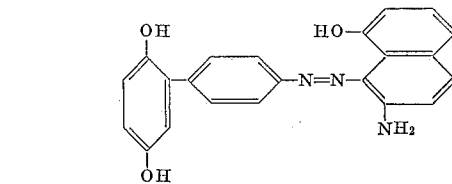


(XI) 1-[4-(2,5-dihydroxyphenethyl)]-phenylazo-2-amino-8-naphthol.

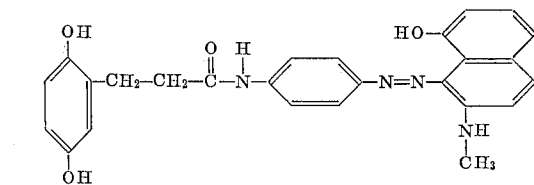


(XII) 1-[4'-(2'',5'')-dihydroxyphenyl]-propionamido]-phenylazo-8-hydroxy-2-(N-β-hydroxyethyl)-naphthylamine.

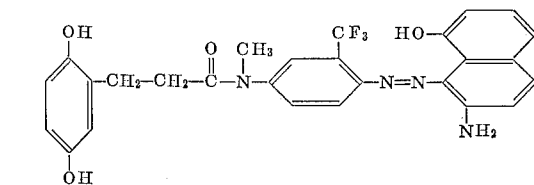
(XIII) 1-[4-(2,5-dihydroxyphenyl)-propionamido]-phenylazo-2-isopropylamino-8-naphthol.



(XIV) 1-(2,5-dihydroxyphenyl)-phenylazo-8-hydroxy-2-naphthylamine.



(XV) 1-[4-(2,5-dihydroxyphenylpropionamido)]-phenylazo-2-methylamino-8-naphthol.



(XVI) 1-[4'-(2'',5'')-dihydroxyphenyl-N-methylpropionamido]-2'-trifluoromethyl]-phenylazo-8-hydroxy-2-naphthylamine.

The following nonlimiting examples illustrate the preparation of intermediates within the scope of this invention:

Example A

A solution of 4.78 gm. (0.03 mole) of 8-hydroxy-2-naphthylamine in 50 ml. of acetic acid previously saturated with hydrogen chloride gas was placed in a 100 ml. flask equipped with a heating mantle, a thermometer,

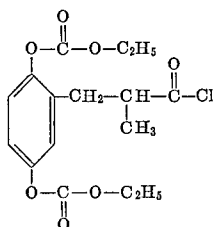
a mechanical stirrer, a pressure equalizing addition funnel open at the top, and a tube for introducing hydrogen chloride gas below the surface of the mixture. Dry hydrogen chloride gas was bubbled into the stirred mixture for 30 minutes. 10 ml. of acetyl chloride were then added. The addition funnel was then replaced with a reflux condenser. Stirring and the addition of hydrogen chloride gas was continued while the flask was heated to raise the temperature to 40° C. and maintained at 40–45° C. for 45 minutes. After that time, heating was discontinued while stirring was continued for another 15 minutes. The mixture was then diluted with 100 ml. of ether. The pale gray precipitate was collected by suction filtration and washed free of HCl and acetic acid with dry ether. 5.88 gm. of 8 - acetoxy - 2 - naphthylamine hydrochloride, melting at 184.5–185° C., were produced.

Analysis of the product shows:

	C	H	N
Calculated.....	60.63	5.09	5.89
Found.....	59.74	4.96	5.37

Example B

A mixture of 5.26 gm. of:



2,5 - bis-(cathyloxy)- α -methyl-dihydrocinnamoyl chloride (B.P. 180–185° C., at 0.7 mm. Hg) and 3.01 gm. of 2-nitro-5-amino-benzotrifluoride in 65 ml. of dry chlorobenzene were heated at reflux for 1.5 hours, after which time it was cooled and diluted with 300 ml. of hexane. The oil which separated was decanted and washed with hexane. The oil was then dissolved in 100 ml. of ethanol and hydrogenated in a Parr shaker with 0.5 gm. of 10% palladium-barium sulfate catalyst. Hydrogen uptake stopped at 82% of theoretical in less than 1 hour. The solution was filtered directly into 100 ml. of 6 N HCl and the resulting acidic solution was concentrated under reduced pressure to a volume of 150 ml. in the cold. After chilling overnight in a refrigerator, a white crystalline product appeared. The product was collected and washed with a small amount of ice water. The 4-[2',5'-bis - (cathyloxy)-phenyl]-isobutyramido-2-trifluoromethylaniline hydrochloride weighed 4.9 gm. and melted at 151.5–153° C.

Analysis of the product shows:

	C	H	N	Cl
Calculated.....	51.65	4.90	5.24	6.63
Found.....	51.78	4.93	5.16	6.91

Example C

40 gm. of 1,7-dihydroxynaphthalene, 43.5 cc. of 40% aqueous methylamine and 50 cc. of water were placed in a 200 cc. fusion bomb. The bomb was heated and rocked at 150° C. for 8 hours. The contents of the bomb were poured into a 1 liter beaker and 100 cc. of 50% sodium hydroxide and 300 cc. of water were added. After stirring, Celite was added and the mixture was filtered through a sintered glass funnel. 200 ml. of concentrated hydrochloric acid were added to the filtrate with stirring. The solution was cooled to room temperature and filtered

through a sintered glass funnel. The solid was stirred with 50 cc. of water and again filtered. The filtrates were collected and ammonium carbonate was added with stirring until no further white solid precipitated. The solid was separated and stirred with 200 cc. of water. The product was again collected and dried in a vacuum dessicator. The 2-methylamino-8-naphthol was a light gray powder and melted at 123–126° C. with decomposition.

7.28 gm. of 2-methylamino-8-naphthol and 72 cc. of acetic acid saturated with hydrogen chloride were placed in a 3-necked round-bottom flask fitted with magnetic stirrer, gas inlet tube, dropping tube, drying tube and thermometer. Hydrogen chloride gas was bubbled through the solution for 30 minutes. With the hydrogen chloride gas still being bubbled in, 145 cc. of acetyl chloride were added. The solution was then heated to 45–55° C. and maintained at that temperature for 1¾ hours. The solution was then poured slowly and with stirring into 1 liter of anhydrous ether. The resulting precipitate, 8-acetoxy-N-methyl-2-naphthylamine hydrochloride, was collected, washed with ether and dried in the vacuum dessicator. The product melted at 153–156° C. with decomposition.

Example D

40 gm. of 1,7-dihydroxynaphthalene, 14.78 gm. of isopropylamine, 25 gm. of ethanol and 75 cc. of water were placed in a 200 cc. fusion bomb. The bomb was heated to 180° C. and rocked for 8 hours. The contents were then removed, cooled to room temperature and mixed with 300 cc. of water and 500 cc. of 50% sodium hydroxide. Celite was added and the solution was filtered. 250 cc. of concentrated hydrochloric acid were added to the filtrate. After cooling the solution, the resulting aqueous layer was discarded. 500 cc. of 5% hydrochloric acid were added to the oily phase, heated and filtered. On cooling, a layer separated and solidified. The aqueous layer was neutralized with ammonium carbonate. The resulting thick gum was taken up in 110 cc. of hot 5% hydrochloric acid. Upon cooling, white crystals of 8-hydroxy-2-N-isopropyl-naphthylamine hydrochloride separates. Additional product was also obtained by extracting the above-solidified layer with two portions of ethyl acetate. The residue was then recrystallized from 250 ml. of hot 5% hydrochloric acid to give additional amine hydrochloride. The product melted at 196–200° C. with decomposition.

8.65 gm. of 8-hydroxy-2-N-isopropyl-naphthylamine hydrochloride and 83 cc. of acetic acid saturated with hydrogen chloride were placed in a 250 cc., 3-necked round-bottom flask fitted with magnetic stirrer, thermometer, reflux condenser, drying tube, and gas inlet tube. Hydrogen chloride gas was bubbled into the solution for 30 minutes, and, with the admission of the gas continued, 12.6 cc. of acetyl chloride were added. The solution was heated to 45–55° C. and maintained at that temperature for 1¾ hours. The solution was then poured slowly and with stirring into 1 liter of anhydrous ether. The resulting solid, 8-acetoxy-2-N-isopropyl-naphthylamine hydrochloride, was separated, washed with ether and dried in the vacuum dessicator.

The following nonlimiting examples illustrate the preparation of dye developers within the scope of this invention.

Example 1

5.35 gm. (0.01 mole) of 4-[2',5'-bis-(cathyloxy)-phenyl]-isobutyramido-2-trifluoromethyl aniline hydrochloride (prepared by the method of Example B) were diazotized in a mixture of 20 ml. of 6 N hydrochloric acid, 60 ml. of acetic acid, with aqueous NaNO₂ and ice for 30 minutes. The resulting disazo solution was poured into a solution of 2.38 gm. of 8-acetoxy-2-naphthylamine hydrochloride as prepared in Example A in 150 ml. of 80% acetic acid at 15° C. Saturated sodium acetate solution was added in small portions to raise the pH to about 4,

whereupon coupling proceeds rapidly. After stirring for one hour at 15–20° C., the mixture was diluted slowly with 350 ml. of water. The resulting sticky precipitate was separated, washed with water and then dissolved in 300 ml. of methyl Cellosolve for hydrolysis. The solution was placed in a 2 liter flask equipped with a stirrer, two dropping funnels, and a tube to pass nitrogen through the solution. After flushing the apparatus and solution with a rapid stream of nitrogen, a deaerated solution of sodium hydroxide (10 ml. of 50% NaOH) plus 90 ml. of water was run in. The solution, stirred for 30 minutes under nitrogen, turned from orange-brown to magenta. The solution was then acidified with a deaerated solution of 50 ml. of concentrated hydrochloric acid in 450 ml. of water. The precipitated dye was collected on a suction filter and washed with water. It was purified by dissolving in 250 ml. of methyl Cellosolve, filtering and then precipitated with 500 ml. of water containing a trace of hydrochloric acid. After drying at 70° C., the 4.1 gm. of 1 - [2' - trifluoromethyl-4'-(2'',5''-dihydroxyphenyl)-isobutyramido] - phenylazo-8-hydroxy-2-naphthylamine produced melted at 144–146° C.

Analysis:

	C	H	N
Calculated.....	59.77	4.64	10.35
Found.....	59.70	4.62	10.33

Example 2

2,5-bis-(cathyloxy)-phenylpropionyl chloride was reacted with 2-nitro-5-amino-benzotrifluoride and the product hydrogenated according to the procedure in Example B. The resulting 2-trifluoromethyl-4-(2,5-dicathyloxyphenyl)-propionamido-aniline hydrochloride (M.P. 169–173° C.) was diazotized and coupled according to the procedure in Example 1 with 8-acetoxy-2-naphthylamine hydrochloride, prepared as in Example A. The hydrolyzed product, 1-[2'-trifluoromethyl-4'-(2'',5''-dihydroxyphenyl) - propionamido] - phenylazo-8-hydroxy-2-naphthylamine, melted at 166–168° C. with decomposition and showed the following analysis:

	C	H
Calculated.....	59.08	4.39
Found.....	59.77	4.24

Example 3

2,5-bis-(cathyloxy)-phenylpropionyl chloride was reacted with 3-chloro-4-nitroaniline (J. Phys. Chem. [2], 102) and hydrogenated according to the procedure in Example B. The resulting 2-chloro-4-(2,5-bis-cathyloxyphenyl)-propionamido-aniline hydrochloride melted at 186–187° C. and showed the following analysis:

	C	H	Cl	N
Calculated.....	51.8	4.9	14.6	5.75
Found.....	51.9	5.1	14.3	5.9

The above product was then diazotized and coupled according to the procedure in Example 1 with 8-acetoxy-2-naphthylamine hydrochloride. The hydrolyzed product, 1 - (2' - chloro - 4' - hydroquinonylpropionamido) - phenylazo-8-hydroxy-2-naphthylamine melted at 160–165° C. with decomposition.

Example 4

2,5-bis-carbethoxy-homogentisic chloride was reacted, according to the method of Example B, with 2-nitro-5-amino-benzotrifluoride to produce 4-[2,5-bis-carbethoxy-homogentisamido]-2-trifluoromethyl-aniline hydrochloride which was then diazotized and coupled with 8-acetoxy-2-

naphthylamine hydrochloride. After hydrolysis, the resulting product, 8-(4'-homogentisamido-2'-trifluoromethyl)-phenylazo-7-amino-1-naphthol, melted at 214–215° C. with decomposition.

Example 5

p-Diacetoxy-phenethyl aniline, prepared according to the method disclosed in the copending application of Milton Green and Helen P. Husek, Serial No. 805,673, filed April 13, 1959, now U.S. Patent No. 3,019,254 issued January 30, 1962, was diazotized and coupled with 8-acetoxy-2-naphthylamine hydrochloride according to the procedure of Example 1. The resulting product, 1-[4-(2,5-dihydroxy) - phenethyl] - phenylazo - 2 - amino - 8-naphthol, melted at 155–157° C., with decomposition.

Example 6

5 - (2,5 - dicathyloxyphenyl) - propionamido - 1 - naphthylamine was diazotized and coupled with 8-acetoxy-2-naphthylamine according to the procedure of Example 1. The resulting product, 1-[5-(2,5-dihydroxyphenyl)-propionamido]-α-naphthylazo-2-amino-8-naphthol, melted at 250–251° C., with decomposition.

The following nonlimiting examples illustrate another method of preparation of dye developers within the scope of this invention.

Example 7

4 - (2',5' - bis - cathyloxyphenyl) - isobutyramido - 2-trifluoromethyl-aniline hydrochloride, produced as in Example B, was diazotized and coupled according to the procedures of Example 1 with 8-acetoxy-N-methyl-2-naphthylamine hydrochloride, as prepared in Example C. The hydrolyzed product, 1 - [2 - trifluoromethyl - 4 - (2,5 - dihydroxyphenyl) - isobutyramido] - phenylazo - 2 - methylamino-8-naphthol, melted at 148–150° C., with decomposition.

Example 8

4-(2,5-bis-cathyloxyphenyl)-propionamido-aniline hydrochloride produced by the procedure of Example B was diazotized and coupled according to the procedure of Example 1, with 8-acetoxy-2-N-isopropyl-naphthylamine hydrochloride, produced as in Example D. The hydrolyzed product, 1 - [4 - (2,5 - dihydroxyphenyl) - propionamido] - phenylazo-2-isopropylamino-8-naphthol, melted at 125–126° C., with decomposition.

Example 9

The 2 - trifluoromethyl - 4 - (2,5 - dicathyloxyphenyl)-propionamido-aniline hydrochloride, prepared as in Example 2, was diazotized and coupled with 8-acetoxy-2-methylamino-naphthalene hydrochloride. The hydrolyzed product was 1-[2-trifluoromethyl-4-(2,5-dihydroxyphenyl)-propionamido]-phenylazo-2-methylamino-8-naphthol.

Example 10

2 - chloro - 4 - (2,5 - bis - cathyloxyphenyl) - propionamido - aniline hydrochloride prepared as in Example 4 was reacted according to the method of Example 1 with 8 - acetoxy - 2 - methylamino - naphthalene hydrochloride. The resulting 1-(2'-chloro-4-hydroquinonylpropionamido) - phenylazo - 8 - hydroxy - 2 - N - methyl-naphthylamine melted at 168–169° C., with decomposition.

Example 11

8 - (4' - homogentisamido - 2' - chlorophenylazo) - 7-methylamino-1-naphthol was prepared according to the procedure in Example 4 using as a coupler 8-acetoxy-2-methylamino-naphthalene hydrochloride.

Example 12

1 - [4 - (2,5 - dihydroxyphenyl) - propionamido]-phenylazo-2-ethylamino-8-naphthol was prepared by coupling 2,5-diacetoxyphenyl-propionamido-aniline hydrochloride into 8-acetoxy-2-ethylamino-naphthalene, according to the procedure of Example 1. The resulting product melted at 71–72° C.

Example 13

1 - [4 - (2,5 - dihydroxyphenylpropionamido)] - phenylazo-2-methylamino-8-naphthol was prepared by diazotizing and coupling 2,5-diacetoxyphenyl-propionamido-aniline hydrochloride into 8 - acetoxy - 2 - methylamino-naphthalene hydrochloride and hydrolyzing. The product melted at 168-169.5° C.

Example 14

1 - [4' - (2'',5'' - dihydroxyphenyl) - propionamido]-phenylazo - 8 - hydroxy - 2 - (N - β - hydroxyethyl) - naphthylamine was prepared by diazotizing and coupling 2,5-diacetoxyphenyl-propionamido-aniline hydrochloride into 8-acetoxy-2-(N- β -hydroxyethyl)-naphthylamine and hydrolyzing. The product melted at 103-150° C. and showed the following analysis for the monohydrate:

	C	H	N
Calculated.....	64.27	5.59	11.11
Found.....	64.40	5.51	11.13

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

Example 15

A photosensitive element was prepared by coating a gelatin subcoated film base with a solution comprising 0.38 gm. of 1-[4-(2,5-dihydroxyphenylpropionamido)]-phenylazo-2-methylamino-8-naphthol dissolved in 10 cc. of a solution of 2% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of tetrahydrofuran and acetone. After this coating dried, a green-sensitive silver iodobromide 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..	100.0
NaOH	gm..	5.17
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington 99, Delaware, under the trade name Natrosol 250]	gm..	4.5
Sodium thiosulfate	gm..	1.15
Benzotriazole	gm..	2.3
N-benzyl- α -picolinium bromide	gm..	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 coated 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.

Example 16

The procedure described in Example 13 was repeated 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 adding 0.5 gm. of the dye developer in 0.5 cc. of N-n-butylacetanilide and 1.0 cc. of cyclohexanone to 5 gm. of 10% gelatin solution, 1.8 cc. of water and 1.67 cc. of 5% 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.

The dye developers of this invention are also useful in integral multilayer photosensitive elements for use in multicolor diffusion transfer processes. As an example of such photosensitive elements, mention may be made of the photosensitive elements disclosed and claimed in the copending U.S. application of Edwin H. Land and

Howard G. Rogers, Serial No. 565,135, filed February 13, 1956, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single common image-receiving element. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. In one of the preferred embodiments of photosensitive elements of this type, the dye developers are disposed in separate alkali-permeable layers behind the photosensitive silver halide emulsion stratum with which they are associated.

The photosensitive elements within the scope of this invention may be used in roll film units which contain a plurality of photosensitive frames. The photosensitive elements of this invention are especially useful in composite roll film intended for use in a "Polaroid Land Camera," sold by Polaroid Corporation, Cambridge 39, Massachusetts, or a similar camera structure such, for example, as the camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on February 10, 1948. In general, such composite roll films comprise a photosensitive roll, a roll of image-receiving material and a plurality of pods containing an aqueous alkaline processing solution. The rolls and pods are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pods may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of the pods used in such units are well known to the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

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

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed and claimed in the copending application of Milton Green and Howard G. Rogers, Serial No. 50,851, filed August 22, 1960, now U.S. Patent No. 3,173,786.

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

It should be noted that the dye developers of this medium are self-sufficient to provide the desired color image and do not depend upon coupling reactions to

produce the desired color. They thus provide a complete departure from conventional photographic color processes in which the color is produced by a coupling reaction between a "color former" or "coupler" and the oxidized developing agent, as well as so-called auto-coupling processes in which color is obtained by a reaction of the oxidized developing agent with unoxidized developing agent.

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

As examples of useful image-receiving materials, mention may be made of nylon, e.g., N-methoxymethyl-polyhexamethylene adipamide, polyvinyl alcohol, and gelatin, particularly polyvinyl alcohol or gelatin containing a dye mordant such as poly-4-vinylpyridine. The image-receiving element also may contain a development restrainer, e.g., 1-phenyl-5-mercaptotetrazole, as disclosed in the copending application of Howard G. Rogers and Harriet W. Lutes, Serial No. 50,849, filed August 22, 1960.

The dye developers herein set forth are also useful in the formation of colored images in accordance with the photographic products and processes described and claimed in U.S. Patent No. 2,968,554, issued to Edwin H. Land on January 17, 1961.

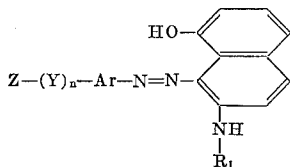
The novel compounds herein disclosed are also suitable for use as dyes for textile fibres, such as nylon.

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

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 process of forming a photographic image in color, comprising developing an exposed silver halide emulsion in the presence of an aqueous alkaline solution comprising a dye developer of the formula:



wherein Z is a dihydroxyphenyl silver halide developing radical, Y is selected from the group consisting of lower alkylene, carboxamido and alkylencarboxamido radicals, and n is an integer from 0 to 1, Ar is selected from the group consisting of phenyl and naphthyl groups, and R_1 is selected from the group consisting of hydrogen and alkyl radicals, to thereby provide a predetermined image-wise distribution of unoxidized dye developer, and transferring at least a part of said imagewise dye developer by imbibition to an image-receiving layer in superposed relationship with said silver halide emulsion to impart a dye image to said image-receiving layer.

2. A process as defined in claim 1 wherein said dye developer is disposed, prior to exposure, in the photosensitive element comprising said exposed silver halide 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.

3. The process as defined in claim 2 whereby said liquid is introduced by being spread in a substantially uniform layer as said photosensitive element and image-receiving layer are brought into superposed relationship.

4. The process as defined in claim 2 wherein said liquid contains a thickener for increasing viscosity and for facilitating the spreading thereof between said photosensitive element and said image-receiving layer.

5. A process as defined in claim 2 wherein said aqueous alkaline solution contains at least a second silver halide developing agent which is substantially colorless in its unoxidized form.

6. A process as defined in claim 1 wherein Ar is a phenyl radical, n is 1, and Y is an alkylencarboxamido radical.

7. A process as defined in claim 6 wherein the phenyl radical is substituted in the ortho position, by a substituent selected from the group consisting of halogen, methoxyl, methyl, and trifluoromethyl radicals, and R_1 is hydrogen.

8. A process as defined in claim 7 wherein said ortho substituent is a trifluoromethyl radical.

9. A process as defined in claim 6 wherein R_1 is an alkyl radical.

10. A process as defined in claim 1 wherein said dye developer is 8-(4'-homogentisamido-2'-trifluoromethyl)-phenylazo-7-amino-1-naphthol.

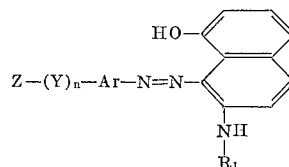
11. A process as defined in claim 1 wherein said dye developer is 1-[2'-trifluoromethyl-4'-(2'',5''-dihydroxyphenyl)-propionamido]-phenylazo-8-hydroxy-2-naphthylamine.

12. A process as defined in claim 1 wherein said dye developer is 1-[4'-(2'',5''-dihydroxyphenyl)-propionamido]-phenylazo-8-hydroxy-2-(N- β -hydroxyethyl)-naphthylamine.

13. A process as defined in claim 1 wherein said dye developer is 1-(2'-chloro-4'-hydroquinonylpropionamido)-phenylazo-8-hydroxy-2-naphthylamine.

14. A process as defined in claim 1 wherein said dye developer is 1-[4'-(2'',5''-dihydroxyphenylisobutyramido)-2'-trifluoromethyl]-phenylazo-8-hydroxy-2-naphthylamine.

15. A photographic product comprising a plurality of layers including a silver halide emulsion layer, at least one of said layers containing a dye developer of the formula:



wherein Z is a dihydroxyphenyl silver halide developing radical, Y is selected from the group consisting of lower alkylene, carboxamido, and alkylencarboxamido radicals, n is an integer from 0 to 1, Ar is selected from the group consisting of phenyl and naphthyl groups, and R_1 is selected from the group consisting of hydrogen and alkyl radicals.

16. A product as defined in claim 15, wherein Ar is a phenyl group, Y is an alkylencarboxamido radical and n is 1.

17. A product as defined in claim 16 wherein the phenyl radical is substituted in the ortho position, by a substituent selected from the group consisting of halogen, methoxyl, methyl, and trifluoromethyl radicals, and R_1 is hydrogen.

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18. A product as defined in claim 17 wherein said ortho substituent is a trifluoromethyl radical.

19. A product as defined in claim 16 wherein R_1 is an alkyl radical.

20. A product as defined in claim 15 wherein said dye developer is 8-(4'-homogentisamido-2'-trifluoromethyl)-phenylazo-7-amino-1-naphthol.

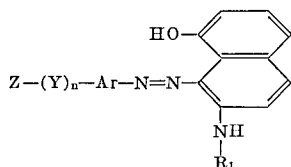
21. A process as defined in claim 15 wherein said dye developer is 1-[2'-trifluoromethyl-4'-(2'',5''-dihydroxyphenyl)-propionamido]-phenylazo-8-hydroxy-2-naphthylamine.

22. A process as defined in claim 15 wherein said dye developer is 1-4'-(2'',5''-dihydroxyphenyl)-propionamido]-phenylazo-8-hydroxy-2-(N- β -hydroxyethyl-naphthylamine.

23. A process as defined in claim 15 wherein said dye developer is 1-(2'-chloro-4'-hydroquinonylpropionamido)-phenylazo-8-hydroxy-2-naphthylamine.

24. A process as defined in claim 15 wherein said dye developer is 1-[4'-(2'',5''-dihydroxyphenylisobutyramido)-2'-trifluoromethyl]-phenylazo-8-hydroxy-2-naphthylamine.

25. A process of developing an exposed silver halide emulsion which comprises treating said emulsion for a time sufficient to develop with an aqueous alkaline solution comprising a compound of the formula:

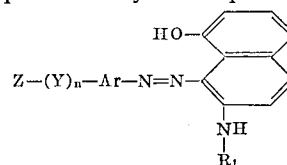


wherein Z is a dihydroxyphenyl silver halide developing radical, Y is selected from the group consisting of lower alkylene, carboxamido, and alkylenecarboxamido radicals, n is an integer from 0 to 1, Ar is selected from the group consisting of phenyl and naphthyl groups, and R_1

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is selected from the group consisting of hydrogen and alkyl radicals.

26. A photographic developer composition comprising an aqueous alkaline solution of an accelerating silver halide developer and a dye developer of the formula:



wherein Z is a dihydroxyphenyl silver halide developing radical, Y is selected from the group consisting of lower alkylene, carboxamido, and alkylenecarboxamido radicals, n is an integer from 0 to 1, Ar is selected from the group consisting of phenyl and naphthyl groups, and R_1 is selected from the group consisting of hydrogen and alkyl radicals.

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