United States Patent Office 3,297,441 Patented Jan. 10, 1967

3,297,441

PHOTOGRAPHIC PRODUCTS, COMPOSITIONS AND PROCESSES UTILIZING AZONAPHTHOL DYE DEVELOPERS

Milton Green, Newton, and Phylis T. Moore, Lexington, Mass., assignors to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Filed Mar. 4, 1963, Ser. No. 262,358
15 Claims. (Cl. 96—29)

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

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

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

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

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

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

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

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

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

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

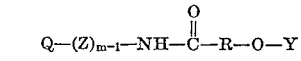
is brought into superposed position with an image-receiving element. The liquid processing composition permeates the emulsion to provide a solution of dye developer substantially uniformly distributed therein. As the exposed silver halide emulsion is developed, the oxidation product of the dye developer is immobilized or precipitated in situ with the developed silver, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. This immobilization is apparently due, at least in part, to a change in the solubility characteristics of the dye developer upon oxidation, and especially as regards its solubility in alkaline solutions. It may also be due, in part, to a tanning effect on the emulsion by the oxidized developing agent. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer. The image-receiving layer receives a depthwise diffusion, from the emulsion, of unoxidized dye developer, without appreciably distributing the imagewise distribution thereof, to provide a reversed or positive, colored image of the developed or negative image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. Imbibition periods of approximately one minute have been found to give good results, but this contact period may be adjusted where necessary to compensate for variations in temperature or other conditions. The desired positive image is revealed by separating the image-receiving layer from the silver halide emulsion at the end of the imbibition period.

The dye developers of this invention may be utilized in the photosensitive element, for example in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer is placed behind the silver halide emulsion, i.e., on the side of the emulsion adapted to be located most distant from the photographed subject when the emulsion is exposed and preferably also adapted to be most distant from the image-receiving layer when in superposed relationship therewith. Placing the dye developer behind the emulsion layer, as in the preferred embodiment, has the advantage of providing increased contrast in the positive image, and also minimizes any light-filtering action by the colored dye developer. In this preferred embodiment, the layer of dye developer may be applied by using a coating solution containing, e.g., about 0.5 to 8%, by weight, of the dye developer. Similar concentrations may be used if the dye developer is utilized as a component of the liquid processing composition. In an especially useful mode of disposing the dye developers in the photosensitive elements, the dye developer is dissolved in a water-immiscible solvent and then dispersed in a gelatin coating solution.

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

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

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

(A) 

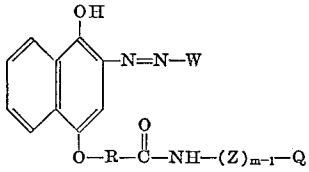
wherein Q is a dihydroxyphenyl silver halide developing radical, e.g., p-dihydroxyphenyl, o-dihydroxyphenyl, and nuclear substituted derivatives thereof, e.g., alkyl and/or halogen substituted derivatives; Z is phenylene, lower alkylene, or lower phenalkylene; *m* is a positive integer from 1 to 2; R is a lower alkylene radical; and Y is an azo dye radical; said —O— substituent being bonded directly to a nuclear carbon atom of the azo dye radical, e.g., to a nuclear carbon atom of an aromatic or heterocyclic substituent of the dye radical.

As examples of lower alkylene radicals which may be employed for said Z and/or R substituents, mention may be made of methylene, ethylene, ethylidene, propylene, isopropylene, etc.

The novel dye developers of this invention may also contain an additional silver halide developing radical linked to the dye moiety of the molecule through an appropriate organic linking group.

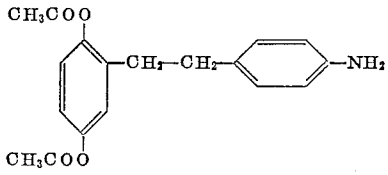
One useful class of dye developers within the scope of Formula A may be defined as azonaphthol dye developers wherein the —O— substituent is bonded directly to the naphthalene nucleus in a position meta to the azo linkage.

A preferred group are naphthol derivatives which may be represented by the formula:

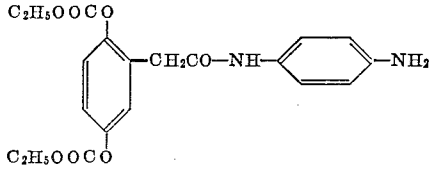
(B) 

wherein W is the radical of a diazotizable amine, preferably of the benzene or naphthalene series and R, Z, *m* and Q have the meanings heretofore noted.

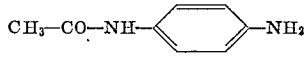
As examples of diazotizable amines which may be employed to prepare substituent W, mention may be made of the following compounds:



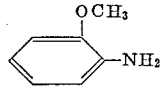
p-(β-2,5-diacetoxyphenethyl) aniline



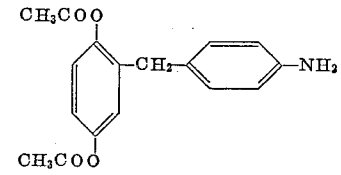
p-(β-2,5-dicathyloxy-phenylacetamido) aniline



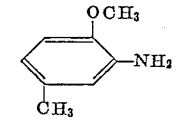
p-acetamidoaniline



o-anisidine

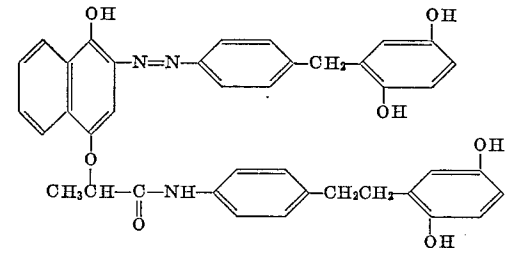


p-(2,5-diacetoxyphenylmethyl) aniline

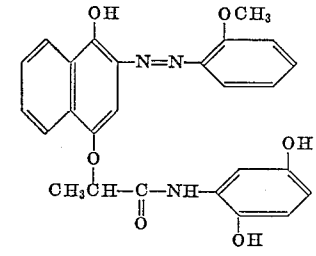


(2-methoxy-5-methyl) aniline

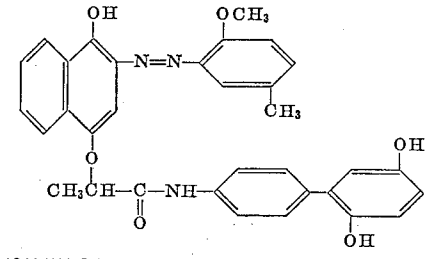
The following compounds are representative of preferred dye developers within the scope of the above-mentioned formulae:

(1) 

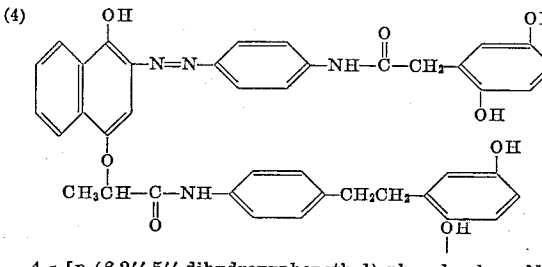
4-α-[p-(β-2'',5''-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(2'',5'' - dihydroxyphenylmethyl)-phenylazo]-1-naphthol

(2) 

4-α-(2',5'-dihydroxyphenylcarbamyl)-ethoxy-2-(2'-methoxy)-phenylazo-1-naphthol

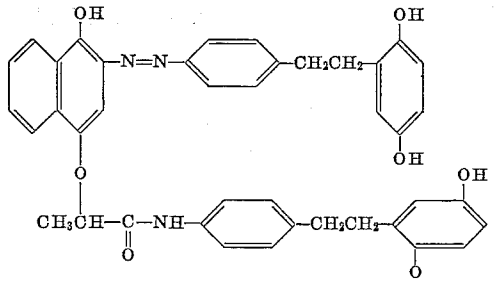
(3) 

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

(4) 

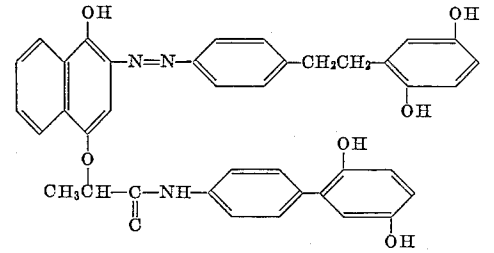
4-α-[p-(β-2'',5''-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-homogentisamido)-phenylazo-1-naphthol

(5)



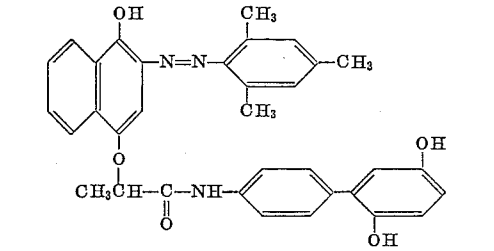
4 - α - [p - (β - 2'',5''-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy - 2 - [p-(β-2'',5''-dihydroxyphenethyl)-phenylazo]-1-naphthol

(6)



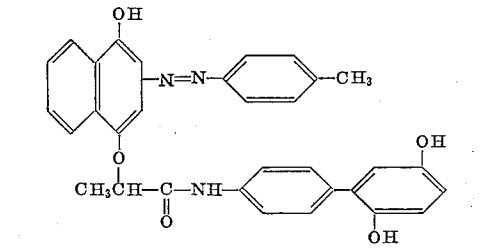
4 - α - [p-(2'',5''-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2 - [p - (β - 2'',5'' - dihydroxyphenethyl) - phenylazo]-1-naphthol

(7)



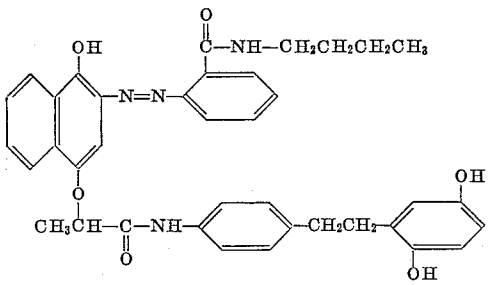
4-α-[p-(2'',5''-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2',4',6'-trimethyl)-phenylazo-1-naphthol

(8)



4-α-[p-(2'',5''-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-p-methylphenylazo-1-naphthol

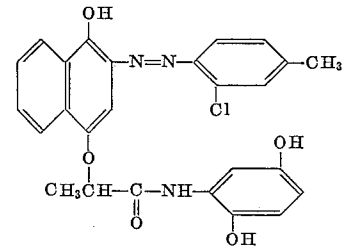
(9)



4 - α - [p - (β-2'',5''-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[2'-(N-butyl)-carbamyl]-phenylazo-1-naphthol

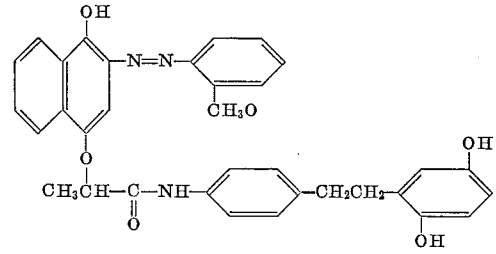
The following compounds are illustrative of other useful dye developers within the scope of the present invention:

10)



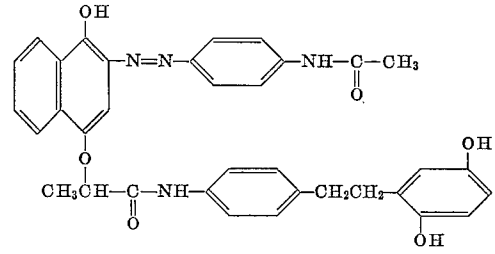
4-α-(2',5'-dihydroxyphenylcarbamyl)-ethoxy-2-(2'-chloro-4'-methyl)-phenylazo-1-naphthol

(11)



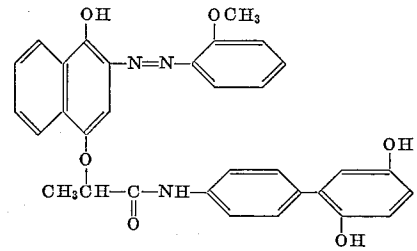
4-α-[p-(β-2'',5''-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(2'-methoxy)-phenylazo-1-naphthol

(12)



4-α-[p-(β-2'',5''-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-acetamido)-phenylazo-1-naphthol

(13)



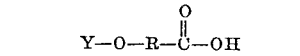
4-α-[β-p-(2'',5''-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2'-methoxy)-phenylazo-1-naphthol

It will be noted that the preferred group of dye developers of Formula B, as illustrated by the aforementioned 13 specific compounds, have the developing moiety linked to the naphthol nucleus. The linking of the developing moiety to the dye moiety according to the present invention affords advantages not heretofore obtainable, since it permits W of Formula B to be more readily substituted in a variety of positions than was heretofore possible when the developing moiety was linked to this substituent. In addition to providing a class of dye developers which may be readily synthesized, the present invention makes it possible to prepare a large class of dye developers which may contain various substituents contributing to the stability, spectral absorption characteristics, etc., of the compound. In other words, the present invention makes it possible to synthesize simply a large number of dye developers having slightly different characteristics which may be desired by the practitioner. This factor is particularly advantageous in multicolor photography where a very exacting and delicate balance of dyes is necessary to obtain a multicolor image having spectral absorption characteristics closely approximating the original subject matter. By slight modi-

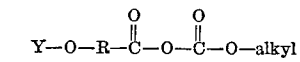
fications or substitution of various substituents, one skilled in the art may modify the physical and/or optical characteristics of the dye developers of the present invention to combine with the other dyes used in the system to obtain a multicolor image having the desired characteristics of stability, color, etc.

The preferred compounds of Formulae 1–9 have also been found, quite unexpectedly, to possess increased stability to light over azonaphthol dye developers, such as 2 - [p-(β-2',5'-dihydroxyphenethyl)-phenylazo]-4-isopropoxy-1-naphthol, which are described in copending U.S. application Serial No. 144,816, filed October 18, 1961 (now Patent No. 3,134,672). When subjected to standard heat stability tests for 40 hours at a temperature of 120° F., the compounds of Formulae 1–9 showed little or no change. When subjected to standard light stability tests with a xenon arc for periods of 40 and 100 hours, these compounds exhibited substantially increased stability, showing appreciably less fading than did the aforementioned prior azonaphthol dye developers.

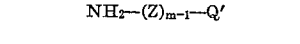
The novel dye developers of this invention may be prepared by reacting a compound of the formula:

(C) 

with a tertiary amine, e.g., trimethylamine, triethylamine, tripropylamine, tributylamine, methylpiperidine, ethylpiperidine, dimethylaniline, etc. (trialkyl amines such as triethylamine being preferred), to form the ammonium salt thereof; reacting this ammonium salt with an alkylchlorocorbonate, e.g., methyl, ethyl, isopropyl, isobutylchlorocarbonate, etc., to form a mixed anhydride of the formula:

(D) 

and thereafter reacting the mixed anhydride of Formula D with an amine of the formula:

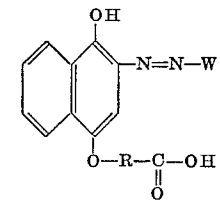
(E) 

wherein Q' is a dihydroxyphenyl silver halide developing radical or a protected derivative thereof, to form the dye developers of Formula A.

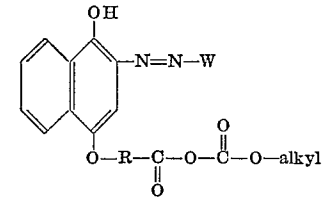
In order to prevent disproportionation of the mixed anhydride of Formula D, it is necessary to perform the final two reactions at a reduced temperature at which disproportionation is precluded, e.g., at or below 0° C., preferably at −5° C., and in an inert solvent which will not freeze at the particular temperature employed. As used herein, the term "inert solvent" means a solvent or mixture of solvents which is chemically inert to or unreactive with the reactants or the reaction product. As examples of such solvents, mention may be made of acetone, carbon tetrachloride, toluene, anisole, chloroform, etc.

While Q' of Formula E may be dihydroxyphenyl silver halide developing radical, Q' is preferably a protected derivative thereof, since any excess of tertiary amine present in the reaction mixture will permit reaction of the unprotected hydroxy groups with the mixed anhydride to form an ester rather than the desired amide. It will be appreciated, however, that where care is exercised in avoiding an excess of tertiary amine, it is not necessary to employ the protected derivatives. As examples of protected dihydroxyphenyl silver halide developing radicals, mention may be made of diacetoxyphenyl, dibenzyloxyphenyl, etc. The protective groups may be removed by hydrolysis in known manner to form the desired dye developer.

The foregoing synthesis provides a particularly useful method for preparing the preferred class of dye developers of Formula B. In the same manner as described above, an azo dye of the formula:

(F) 

is reacted with a tertiary amine to form the ammonium salt thereof; the ammonium salt is then reacted with an alkylchlorocarbonate to form a mixed anhydride of the formula:

(G) 

and the mixed anhydride is then reacted with an amine of Formula E to provide the azo dye of Formula B. As was stated previously, if a protected dihydroxyphenyl silver halide developing radical is employed in the synthesis, the azo dye must be hydrolyzed to remove the protective groups.

In Formulae C to H, it will be appreciated that the symbolic designations for the various substituents have the meanings heretofore given with reference to Formulae A and B.

Compounds of Formula F and their synthesis are described and claimed in copending application Serial No. 262,357 filed concurrently; and compounds of Formula G and their synthesis, as well as the ammonium salt intermediates, are described and claimed in copending application Serial No. 262,356, now Patent No. 3,256,269 also filed concurrently. Accordingly, these compounds and their synthesis comprise no part per se of the present invention.

The compounds of Formula E may be prepared in a manner similar to that disclosed in United States Patent No. 3,019,254, issued January 30, 1962. As examples of such compounds, mention may be made of 2,5-diacetoxyphenyl aniline; 2,5-diacetoxyaniline; 2,5-diacetoxyphenylmethyl aniline; β-2,5-diacetoxyphenethyl aniline, etc., including the corresponding aniline hydrochlorides.

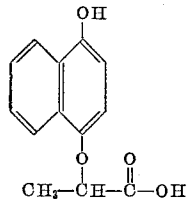
Where the starting compounds of Formula C may be converted to their acid chloride without the necessity of employing elevated temperatures to form a solution of the reactants, the novel dye developers of this invention may also be prepared by the steps of first forming the acid chloride of the acid of Formula C and thereafter reacting the acid chloride with a compound of Formula E where Q' is a protected dihydroxyphenyl silver halide developing radical. Subsequent hydrolysis of the reaction product will yield the dye developer. Compounds 7 and 10, for example, have been prepared by this alternative synthesis. Where heat is necessary to form the solution, however, it has been found that any hydroxyl radicals present in the dye molecule (e.g., the hydroxy substituent on the naphthalene nucleus of the preferred compounds of Formula B are replaced by a chlorine atom.

The following examples show by way of illustration and not by way of limitation the preparation of the novel compounds of this invention:

Example I

α-(4-hydroxy)-1-naphthoxypropionic acid, 1,4-naphthoquinone (0.144 mole) and stannous chloride (0.144 mole, anhydrous) were dissolved at room temperature with stirring in 350 ml. of ethyl lactate. The solution was

cooled to 5–10° C. and hydrogen chloride was bubbled through the solution at a brisk rate for six hours (the temperature of solution being held at 5–10° C.). The resultant clear reaction solution was poured into 750 ml. of a water-ice mixture. The oil which separated upon standing was separated by decantation of the water phase. The oily product was washed with a small volume of water then hydrolyzed. Nitrogen was bubbled through the water slurry for 1 hour with stirring. Nitrogen bubbling was continued while a solution of sodium hydroxide (.28 mole in 150 ml. of water which had been purged for 1 hour with N_2) was added over a 5 min. period with stirring (at room temperature). The resultant clear basic solution was stirred for an additional 15 min. and then acidified (to a pH of 2) by the slow addition of 6 N hydrochloric acid (keeping a nitrogen atmosphere until the hydrolysis mixture was acidic). The precipitate was dissolved in sodium bicarbonate solution, the insoluble impurities removed by filtration, and the product was precipitated from the filtrate by acidification with dilute hydrochloric acid. The product obtained had M.P. 154–161° C. and was purified further by recrystallization from toluene to yield α-(4-hydroxy)-1-naphthoxypropionic acid, M.P. 157–159° C., having the following structural formula:



Elemental analysis of the product as $C_{13}H_{12}O_4$: Found: C, 67.1; H, 5.2. Calculated: C, 67.2; H, 5.19.

Example II

4 - α - [p - (β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl] - ethoxy - 2-[p-(2″,5″-dihydroxyphenylmethyl)-phenylazo]-1-naphthol (compound 1).

p-(2,5-diacetoxyphenylmethyl) aniline hydrochloride (.015 mole) was diazotized with sodium nitrite (.015 mole) and hydrochloric acid (.030 mole) in 50 ml. water at 0–5°, and the slight excess of nitrous acid was decomposed with sulfamic acid. The diazonium solution (0–5°) was added over a 10 minute period to a solution (at 10°) of α-(4-hydroxy-1-naphthoxy) propionic acid (.015 mole) in an acetone-water mixture containing sodium bicarbonate (excess). The reaction mixture was acidified with dilute hydrochloric acid to dissolve the sodium salt of the dye acid (which had separated during the coupling) and to precipitate the dye acid, α-[3-p-(2′,5′-diacetoxyphenylmethyl) - phenylazo - 4-hydroxy-1-naphthoxy] propionic acid. A solution of the dye acid (.0083 mole) in dry acetone (minimum volume) was de-aerated with nitrogen and treated with trimethylamine (dry, .0083 mole). The acetone solution of the triethylammonium salt of the dye acid was cooled to −5° and isobutylchlorocarbonate (.0083 mole) was added. The reaction mixture was stirred at −5° (in a nitrogen atmosphere) for an additional 25 minutes. An acetone solution (de-aerated and chilled) of p-(β-2,5-diacetoxyphenethyl) aniline (.0083 mole) (which had been generated in solution from the hydrochloride by addition of triethylamine (.0083 mole)) was added with stirring over a 15 minute period to the acetone solution of the mixed anhydride at −5° (in a nitrogen atmosphere). The cooling bath was removed and the reaction mixture was stirred overnight. The reaction mixture was filtered to remove some triethylamine hydrochloride, the precipitate washed with acetone and the filtrate and washings concentrated to dryness in vacuo. The glassy residue was washed with water and dilute acid. The solid was dissolved in methyl Cellosolve (minimum volume) and the solution was purged with nitrogen and cooled to 0° C. An oxygen-free aqueous solution of sodium hydroxide (.050 mole) was added and the solution stirred for 1 hr. at 0° C. maintaining a nitrogen atmosphere. The solution was acidified with dilute hydrochloric acid and the precipitate was recrystallized from a mixture of acetone and benzene yielding 4 - α - [p - β - 2″,5″-dihydroxyphenethyl)-phenylcarbamyl] - ethoxy - 2 - [p-(2″,5″-dihydroxyphenylmethyl)-phenylazo]-1-naphthol, M.P. 194–199° C., $\lambda_{max.}$ of 522 mμ, methyl Cellosolve.

Example III

4-α-(2′,5′-dihydroxyphenylcarbamyl)-ethoxy - 2 - (2′-methoxy)-phenylazo-1-naphthol (compound 2).

o-Anisidine (.022 mole) was diazotized with sodium nitrite (.022 mole) and hydrochloric acid (.066 mole) in 50 ml. of water at 0 to 5°. The cooled diazonium solution was slowly added (over a ten minute period) to a solution of .020 mole of α-(4-hydroxy-1-naphthoxy) propionic acid in an acetone-water mixture containing an excess of sodium bicarbonate. The sodium salt of the dye acid which had precipitated from the coupling mixture was converted to the dye acid upon acidification of the coupling mixture with dilute hydrochloric acid. The precipitated acid was recrystallized from methyl Cellosolve affording α-[3-(o-methoxyphenylazo)-4-hydroxy - 1 - naphthoxy] propionic acid, M.P. 248–249°, in 90% yield. The purified and dried dye acid (.0145 mole) was dissolved in dry chloroform (minimum volume) and triethylamine (dry, .0145 mole) was added. The chloroform solution of the triethylammonium salt of the dye acid was de-aerated by bubbling nitrogen through the solution and cooled to −2°. Isobutylchlorocarbonate (.0145 mole) was added with stirring and the reaction mixture held at −2° to 0° (N_2 atmosphere) for 25 minutes whereupon the formation of the mixed anhydride was assumed to be complete. An acetone solution (de-aerated and chilled) of 2-hydroxy-5-benzoxy-aniline (.016 mole) was added gradually to the stirred silution of the mixed anhydride. The temperature of the reaction mixture was held at −2° during this addition (ca. 10 min.). The calling bath was then removed and the reaction mixture was stirred overnight (N_2 atmosphere). The reaction mixture was filtered to remove some triethylamine hydrochloride, the solid washed with acetone, and the filtrate and washings combined. The solution was concentrated to dryness (in vacuo) and the glassy residue washed with water and dilute acid. The product solidified; it was collected on a filter and dried in vacuo. The solid was dissolved in methyl Cellosolve (minimum volume) and hydrolyzed in an N_2 atmosphere as described in Example III. The dye developer after recrystallization from a methyl Cellosolve-H_2O mixture melted at 254–256° C.

Example IV

4-α-[p-(2″,5″ - dihydroxyphenyl) - phenylcarbamyl]-ethoxy-2-(2′-methoxy-5′-methyl)-phenylazo-1 - naphthol (compound 3) was prepared in a manner similar to that set forth in Example III, substituting 2-methoxy-5-methyl aniline for o-anisidine and p-hydroquinonyl aniline for 2-hydroxy-5-benzoxy aniline. The isolated dye developer melted at 251–253° C., exhibited a $\lambda_{max.}$ of 540 mμ in methyl Cellosolve and was found to be soluble in chloroform, methylene chloride and alcohols.

Example V

4-α-[p-(β - 2″,5″ - dihydroxyphenethyl) - phenylcarbamyl]-ethoxy-2-(p-homogentisamido)-phenylazo - 1 - naphthol (compound 4) was prepared in a manner similar to that set forth in Example II substituting dicathyloxy homogentisamido aniline hydrochloride for p-(2,5-diacetoxyphenylmethyl) aniline hydrochloride. The isolated dye developer, 4-α-[p-(β - 2″,5″ - dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-homogentisamido) - phenylazo-1-naphthol, melted at 201–209° C., exhibited a $\lambda_{max.}$ of 532 mμ in methyl Cellosolve and was found to be soluble in acetone and 5% aqueous sodium hydroxide.

Example VI

4-α-[p-(β-2″,5″ - dihydroxyphenethyl) - phenylcarbamyl]-ethoxy-2-[p - (β - 2″,5″ - dihydroxyphenethyl)-phenyl-azo]-1-naphthol (compound 5) was prepared in a manner similar to that set forth in Example II substituting p-(β-2,5-diacetoxyphenethyl) aniline hydrochloride for p-(2,5 - diacetoxyphenylmethyl) aniline hydrochloride. The product, 4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(β-2″,5″ - dihydroxyphenethyl)-phenylazo]-1-naphthol, melted at 211–215° C. and exhibited a $\lambda_{max.}$ of 525 mμ in methyl Cellosolve.

Example VII

4-α-[p-(2″,5″ - dihydroxyphenyl) - phenylcarbamyl]-ethoxy-2-[p-(β-2″,5″-dihydroxyphenethyl) - phenylazo]-1-naphthol (compound 6) was prepared in a manner similar to that set forth in Example II substituting p-(β-2,5-diacetoxyphenethyl) aniline hydrochloride for 2,5-diacetoxyphenethylmethyl aniline hydrochloride and p-(β-2,5-diacetoxyphenyl) aniline for p-(β-2,5-diacetoxyphenethyl) aniline hydrochloride. The isolated dye developer, 4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy - 2-[p-(β-2″,5″-dihydroxyphenethyl) - phenylazo] - 1 - naphthol, melted at 136–141° C., exhibited a $\lambda_{max.}$ of 525 mμ in methyl Cellosolve, and was found to be soluble in acetone, methanol and 5% sodium hydroxide.

Example VIII

4-α-[p-(2″,5″ - dihydroxyphenyl) - phenylcarbamyl]-ethoxy-2-(2′,4′,6′-trimethyl)-phenylazo-1-naphthol (compound 7) was prepared in a manner similar to that set forth in Example III, substituting mesidine for o-anisidine and p-hydroquinonyl aniline for 2-hydroxy-5-benzoxy aniline. The isolated dye developer, 4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2 - (2′,4′,6′ - trimethyl)-phenylazo-1-naphthol, melted at 129–134° C., exhibited a $\lambda_{max.}$ of 520 mμ in methyl Cellosolve, and was found to be soluble in acetone, ethanol and chloroform.

Example IX

4-α-[p-(2″,5″ - dihydroxyphenyl) - phenylcarbamyl]-ethoxy-2-p-methylphenylazo-1 - naphthol (compound 8) was prepared in a manner similar to that set forth in Example III, substituting a p-toluidine for o-anisidine and p-hydroquinonyl aniline for 2-hydroxy-5-benzoxy aniline. The isolated dye developer, 4-α-[p-(2″,5″ - dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-p-methylphenylazo - 1-naphthol, melted at 261–260° C. and exhibited a $\lambda_{max.}$ of 525 mμ in methyl Cellosolve.

Example X

4 - α - [p - (β - 2″,5″ - dihydroxyphenethyl) - phenylcarbamyl] - ethoxy - 2 - [2′ - (N - butyl) - carbamyl]-phenylazo-1-naphthol (compound 9) was prepared in a manner similar to that set forth in Example III. In lieu of using o-anisidine, methyl anthranilate was diazotized and coupled with α-(4-hydroxyl-naphthoxy) propionic acid. The resulting dye, α-(3-o-carbomethoxyphenylazo-4-hydroxy-1-naphthoxy) propionic acid, was then reacted with n-butylamine and the mixed anhydride of the resulting product was formed in the manner illustrated in Example III. The dye developer was prepared from the mixed anhydride by substituting β-hydroquinonylethyl aniline for 2-hydroxy-5-benzoxy aniline, according to the procedure of Example III. The isolated dye developer, 4 - α - [p - (β - 2″,5″ - dihydroxyphenethyl) - phenylcarbamyl] - ethoxy - 2 - [2′ - (N - butyl) - carbamyl]-phenylazo-1-naphthol, melted at 156–164° C. and exhibited a $\lambda_{max.}$ of 515 mμ in alcohol.

Example XI

4 - α - (2′,5′ - dihydroxyphenylcarbamyl) - ethoxy - 2-(2′ - chloro - 4′ - methyl) - phenylazo - 1 - naphthol (compound 10) was prepared in a manner similar to that set forth in Example III, substituting 2-chloro-4-methyl aniline for o-anisidine. The product, 4-α-(2′,5′-dihydroxyphenylcarbamyl) - ethoxy - 2 - (2′ - chloro - 4′ - methyl)-phenylazo-1-naphthol, melted at 237–240° C., exhibited a $\lambda_{max.}$ of 520 mμ in methyl Cellosolve, and was found to be soluble in ethanol.

Example XII

4 - α - [p - (β - 2″,5″ - dihydroxyphenethyl) - phenylcarbamyl] - ethoxy - 2 - (2′ - methoxy) - phenylazo - 1-naphthol (compound 11) was prepared in a manner similar to that set forth in Example III, substituting β-hydroquinonylethyl aniline for 2-hydroxy-5-benzoxyaniline. The isolated dye developer, 4-α-[p-(β-2″,5″-dihydroxyphenethyl) - phenylcarbamyl] - ethoxy - 2 - (2′ - methoxy)-phenylazo-1-naphthol, melted at 133–136° C., and was soluble in methyl Cellosolve and aqueous sodium hydroxide.

Example XIII

4 - α - [p - (β - 2″,5″ - dihydroxyphenethyl) - phenylcarbamyl] - ethoxy - 2 - (p - acetamido) - phenylazo - 1-naphthol (compound 12) was prepared in a manner similar to that set forth in Example III by using p-acetamido-aniline in place of o-anisidine and β-hydroquinonylethyl aniline in place of 2-hydroxy-5-benzoxy aniline. The resulting product, 4 - α - [p - (β - 2″,5″ - dihydroxyphenethyl) - phenylcarbamyl] - ethoxy - 2 - (p - acetamido)-phenylazo-1-naphthol, melted at 244° C., exhibited a $\lambda_{max.}$ of 531 mμ in methyl Cellosolve, and was soluble in acetone and dilute aqueous sodium hydroxide.

Example XIV

4 - α - [p - (β - 2″,5″ - dihydroxyphenethyl) - phenylcarbamyl] - ethoxy - 2 - (2′ - methoxy) - phenylazo - 1-naphthol (compound 13) was prepared in a manner similar to that set forth in Example III, using a p-hydroquinonyl aniline in place of 2-hydroxy-5-benzoxy aniline. The resulting product, 4 - α - [β - p - (2″,5″ - dihydroxyphenyl) - phenylcarbamyl] - ethoxy - 2 - (2′ - methoxy)-phenylazo-1-naphthol, melted at 194–197° C., exhibited a $\lambda_{max.}$ of 535 mμ in methyl Cellosolve and was soluble in methyl Cellosolve, ethanol and acetone.

The following examples show by way of illustration and not by way of limitation the photographic utilization of the novel compounds of this invention:

Example XV

A photosensitive element was prepared by coating a gelatin subcoated film base at a speed of 10 feet/minute with a solution comprising 0.43 g. of 4-α-[p-(β-2″,5″-dihydroxyphenethyl) - phenylcarbamyl] - ethoxy - 2 - [p-(2″,5″ - dihydroxyphenylmethyl) - phenylazo] - 1 - naphthol (Formula 1) dissolved in 10 cc. of 2% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran. After this coating dried, a green-sensitive silver iodobromide emulsion was coated on at a speed 5 feet/minute and allowed to dry. This photosensitive element was exposed for 2 seconds and processed by spreading, between the thus exposed photosensitive element and a superposed image-receiving element, an aqueous processing composition comprising:

Water	cc.	100
NaOH	g.	5.17
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., under the trade name of "Natrasol 250"]	g.	4.0
Benzotriazole	g.	2.3
Sodium thiosulfate	g.	1.15
N-benzyl-α-picolinium bromide	g.	2.3

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.

Example XVI

The procedure described in Example XV was repeated, except that the dye developer was dispersed in a layer of gelatin. The coating solution from which the dye developer was coated was prepared by adding 0.75 g. of the dye developer dissolved in 1 cc. of cyclohexanone and 5 cc. of di(tetrahydrofurfuryl) adipate. This mixture was agitated in a Waring blender for one minute with a solution of 5 g. of 10% gelatin solution, 1.33 cc. of water, and 1 cc. of Alkanol B. After washing with water, 5 cc. of the resulting dye dispersion was added to 10 cc. of water containing .75 cc. of saponin and two drops of succinaldehyde, and then coated on the gelatin subcoated film base at a speed of 10 feet/minute. Exposure and processing in the manner described in Example XV yielded a magenta positive image having a $d_{max.}$ 2.50 and a $d_{min.}$ of 0.50.

Substitution of the other dye developers whose preparations are described above in Examples XV and XVI gave similar positive transfer images.

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 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 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 material, 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 example 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 geatin 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.

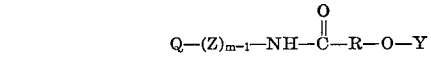
The novel compounds herein disclosed are also suitable for use as dyes for textile fibres, such as nylon.

In the preceding portions of the specification the expression "color" has been frequently used. This expressions 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 inventioin herein involved, it is intended that all matter contained in the above descriptioin 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 accelerating developing agent which is substantially colorless in at least the unoxidized form, and an azo dye developer of the formula:



wherein Q is a member selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl, and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Z is a member selected from the group consisting of phenylene, lower alkylene and phenalkylene radicals; R is an alkylene radical; *m* is a positive integer from 1 to 2, inclusive; and Y is the radical of an azonaphthol dye, said —O— substituent being bonded directly to a nuclear atom of said dye.

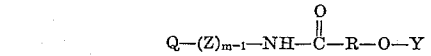
2. A photographic developer composition as defined in claim 1, wherein Z is a phenethyl radical, R is ethylidene, *m* is 2, and Q is p-dihydroxyphenyl.

3. A photographic developer composition as defined in claim 1, wherein said —O— substituent is bonded in a position meta to said azo linkage.

4. A photographic developer composition comprising an aqueous solvent, an alkaline material soluble therein, a silver halide accelerating developing agent which is substantially colorless in at least the unoxidized form, and an azo dye developer selected from the group consisting of:

4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(2″,5″-dihydroxyphenylmethyl)-phenylazo]-1-naphthol,
4-α-(2′,5′-dihydroxyphenylcarbamyl)-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy-5′-methyl)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-homogentisamido)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(β-2″,5″-dihydroxyphenethyl)-phenylazo]-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-[p-(β-2″,5″-dihydroxyphenethyl)-phenylazo]-1-naphthol,
4-α-[p-2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′,4′,6′-trimethyl)-phenylazo-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-p-methylphenylazo-1-naphthol,
4α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[2′-(N-butyl)-carbamyl]-phenylazo-1-naphthol,
4-α-(2′,5′-dihydroxyphenylcarbamyl)-ethoxy-2-(2′-chloro-4′-methyl)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-acetamido)-phenylazo-1-naphthol, and
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol.

5. 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:



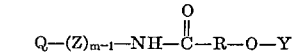
wherein Q is a member selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl, and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Z is a member selected from the group consisting of phenylene, lower alkylene and phenalkylene radicals; R is an alkylene radical; *m* is a positive integer from 1 to 2, inclusive; and Y is the radical of an azonaphthol dye, said —O— substituent being bonded directly to a nuclear atom of said azo dye.

6. A photographic product as defined in claim 5, wherein said azo dye developer is in a layer positioned between said support and said layer containing said silver halide emulsion.

7. 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 selected from the group consisting of:

4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(2″,5″-dihydroxyphenylmethyl)-phenylazo]-1-naphthol,
4-α-(2′,5′-dihydroxyphenylcarbamyl)-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy-5′-methyl)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-homogentisamido)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(β-2″,5″-dihydroxyphenethyl)-phenylazo]-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-[p-(β-2″,5″-dihydroxyphenethyl)-phenylazo]-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′,4′,6′-trimethyl)-phenylazo-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-p-methylphenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[2′-(N-butyl)-carbamyl]-phenylazo-1-naphthol,
4-α-(2′,5′-dihydroxyphenylcarbamyl)-ethoxy-2-(2′-chloro-4′-methyl)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-acetamido)-phenylazo-1-naphthol, and
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol.

8. 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 Q is a member selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl, and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Z is a member selected from the group consisting of phenylene, lower alkylene and phenalkylene radicals; R is an alkylene radical; *m* is a positive integer from 1 to 2, inclusive; and Y is the radical of an azonaphthol dye, said —O— substituent being bonded directly to a nuclear atom of said dye.

9. The process which comprises developing an exposed photosensitive silver halide emulsion with an aqueous alkaline solution of an azo dye developer selected from the group consisting of:

4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(2″,5″-dihydroxyphenylmethyl)-phenylazo]-1-naphthol,
4-α-(2′,5′-dihydroxyphenylcarbamyl)-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy-5′-methyl)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-homogentisamido)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(β-2″,5″-dihydroxyphenethyl)-phenylazo]-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-

ethoxy-2-[p-(β-2″,5″-dihydroxyphenethyl)-phenylazo]-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′,4′,6′-trimethyl)-phenylazo-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-p-methylphenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[2′-(N-butyl)-carbamyl]-phenylazo-1-naphthol,
4-α-(2′,5′-dihydroxyphenylcarbamyl)-ethoxy-2-(2′-chloro-4′-methyl)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-acetamido)-phenylazo-1-naphthol, and
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol.

10. In a process of forming a photographic image in color, the steps which comprise developing an exposed silver halide emulsion with an aqueous alkaline processing solution containing a compound of the formula:

$$Q-(Z)_{m-1}-NH-\overset{\overset{O}{\|}}{C}-R-O-Y$$

wherein Q is a member selected from the group consisting of p-dihydroxyphenyl, o-dihydroxyphenyl, and alkyl and halogen nuclear substituted p-dihydroxyphenyl and o-dihydroxyphenyl radicals; Z is a member selected from the group consisting of phenylene, lower alkylene and phenalkylene radicals; R is an alkylene radical; *m* is a positive integer from 1 to 2, inclusive; and Y is the radical of an azonaphthol dye, said —O— substituent being bonded directly to a nuclear atom of said dye, to provide in said emulsion a predetermined distribution of unoxidized dye developer, and transferring at least part of said distribution of said unoxidized dye developer, by imbibition, from said emulsion to an image-receiving material in superposed relationship with said emulsion to impart to said image-receiving material a positive dye image of the developed image.

11. The process as defined in claim **10** wherein said dye developer is disposed prior to exposure in the photosensitive element containing said emulsion, and the solution containing said dye developer is formed by permeating said photosensitive element with an alkaline aqueous liquid capable of solubilizing said dye developer.

12. The process as defined in claim **10** wherein said liquid is introduced by being spread in a substantially uniform layer between said photosensitive element and said image-receiving material as said element and material are brought into superposed relation.

13. The process as defined in claim **12** wherein said liquid contains a thickener for increasing viscosity and facilitating the spreading thereof between said photosensitive element and said image-receiving material.

14. The process as defined in claim **10** wherein said dye developer is dissolved in the aqueous alkaline solution prior to application thereof to said exposed emulsion.

15. In a process of forming a photographic image in color, the steps which comprise developing an exposed silver halide emulsion with an aqueous alkaline processing solution containing a member selected from the group consisting of:

4-α-[p-(β-2′,5′-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(2″,5″-dihydroxyphenylmethyl)-phenylazo]-1-naphthol,
4-α-(2′,5′-dihydroxyphenylcarbamyl)-ethoxy-2-(2″-methoxy)-phenylazo-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy-5′-methyl)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-homogentisamido)-phenylazo-1-naphthol,
4-α-[p-(β-2′,5′-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[p-(β-2″,5″-dihydroxyphenethyl)-phenylazo]-1-naphthol,
4-α-[p-(2′,5′-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-[p-(β-2″,5″-dihydroxyphenethyl)-phenylazo]-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′,4′,6′-trimethyl)-phenylazo-1-naphthol,
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-p-methylphenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-[2′-(N-butyl)-carbamyl]-phenylazo-1-naphthol,
4-α-(2″,5″-dihydroxyphenylcarbamyl)-ethoxy-2-(2′-chloro-4′-methyl)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol,
4-α-[p-(β-2″,5″-dihydroxyphenethyl)-phenylcarbamyl]-ethoxy-2-(p-acetamido)-phenylazo-1-naphthol, and
4-α-[p-(2″,5″-dihydroxyphenyl)-phenylcarbamyl]-ethoxy-2-(2′-methoxy)-phenylazo-1-naphthol,

to provide in said emulsion a predetermined distribution of unoxidized dye developer, and transferring at least part of said distribution of said unoxidized dye developer, by imbibition, from said emulsion to an image-receiving material in superposed relationship with said emulsion to impart to said image-receiving material a positive dye image of the developed image.

No references cited.

NORMAN G. TORCHIN, *Primary Examiner.*
J. TRAVIS BROWN, *Assistant Examiner.*