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3,365,441

## MONOAZO DYES CONTAINING A DIHYDROXY-PHENYL CONTAINING $\alpha$ -CARBAMYLETHOXY-1-NAPHTHOL MOIETY

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11 Claims. (Cl. 260—202)

### ABSTRACT OF THE DISCLOSURE

Azo hydroxynaphthoxy dyes including a dihydroxyphenyl silver halide developing radical in a substituent bonded to the oxygen atom of the naphthoxy moiety useful as silver halide developing agents capable of developing an exposed silver halide emulsion and imparting a reversed or positive image of the developed image to a super-posed image-receiving material.

This application is a division of application Ser. No. 262,358 filed Mar. 4, 1963, now U.S. Patent No. 3,297,441.

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

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

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

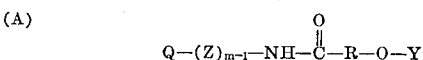
Further objects are to provide said novel silver halide developing agents, and novel products, processes and compositions suitable for use in preparing monochromatic and multichromatic photographic images by the employment of said novel silver halide developing agents.

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

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

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.

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



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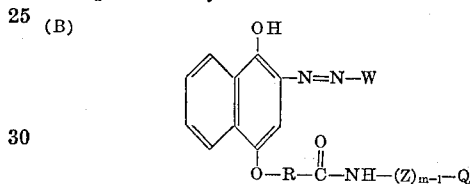
wherein Q is a dihydroxyphenyl silver halide developing radical, e.g., p-dihydroxyphenyl, o-dihydroxyphenyl, and nuclear substituted derivatives thereof, e.g., alkyl and/or halogen substituted derivatives; Z is phenylene, lower alkylene, or lower phenalkylene; m is a positive integer from 1 to 2; R is 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.

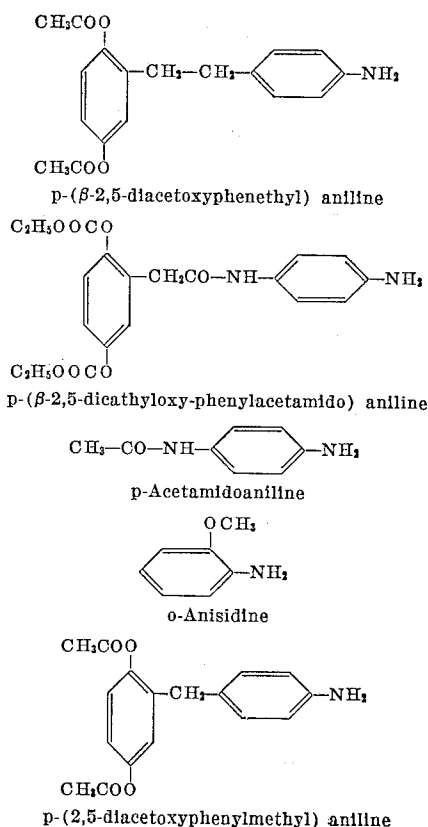
One useful class of dye developers within the scope of Formula A may be defined as azonaphthol dye developers wherein the —O— substituent is bonded directly to the naphthalene nucleus in a position meta to the azo linkage.

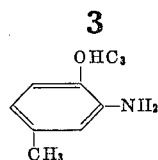
A preferred group are naphthol derivatives which may be represented by the formula:



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.

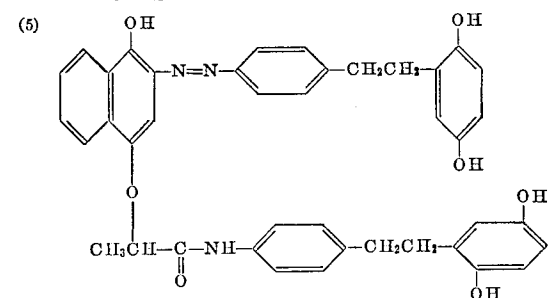
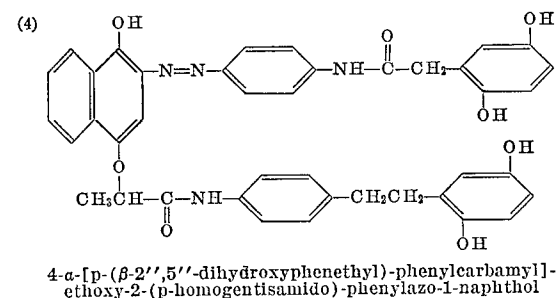
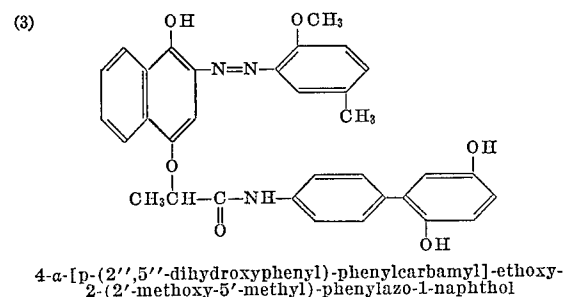
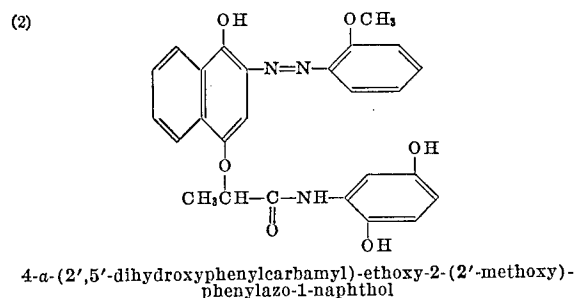
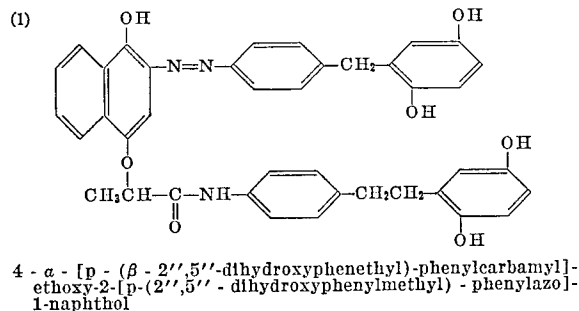
As examples of diazotizable amines which may be employed to prepare substituent W, mention may be made of the following compounds:



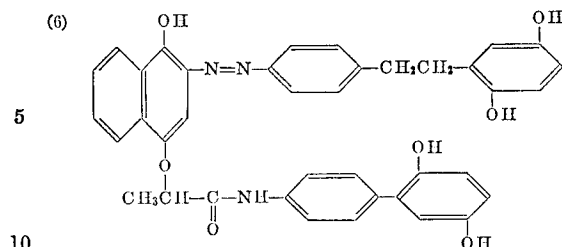


(2-methoxy-5-methyl) aniline

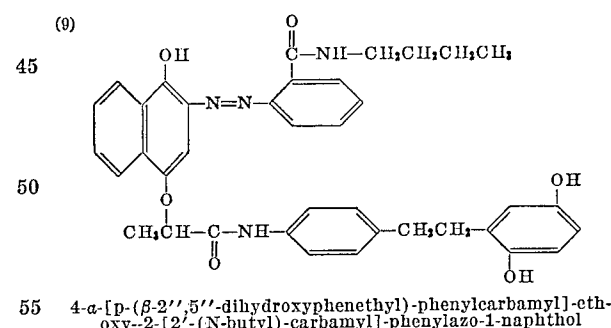
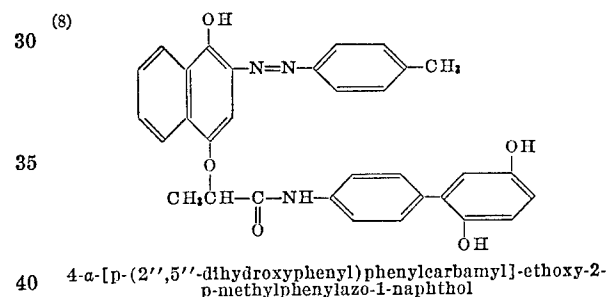
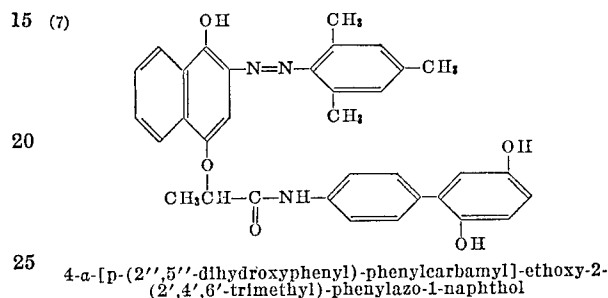
The following compounds are representative of preferred dye developers within the scope of the above-mentioned formulae:



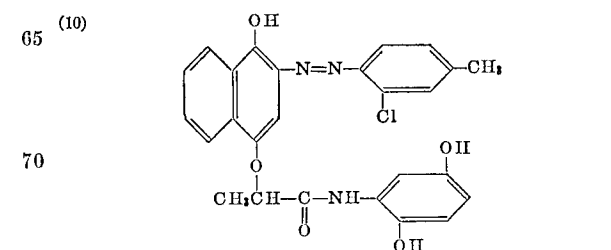
4 -  $\alpha$  - [p - ( $\beta$  - 2'',5'''-dihydroxyphenethyl)phenylcarbonyl]-ethoxy - 2 - [p-( $\beta$ -2'',5'''-dihydroxyphenethyl) - phenylazo]-1-naphthol

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4- $\alpha$ -[p-(2'',5'''-dihydroxyphenyl)-phenylcarbonyl]-ethoxy-2-[p-( $\beta$ -2'',5'''-dihydroxyphenethyl)-phenylazo]-1-naphthol

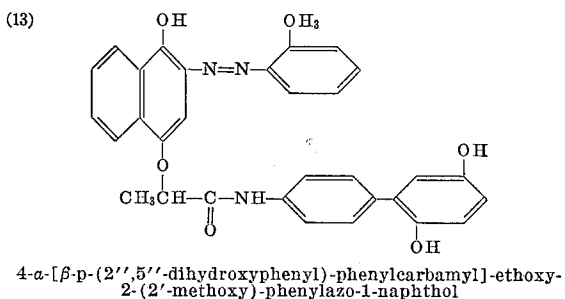
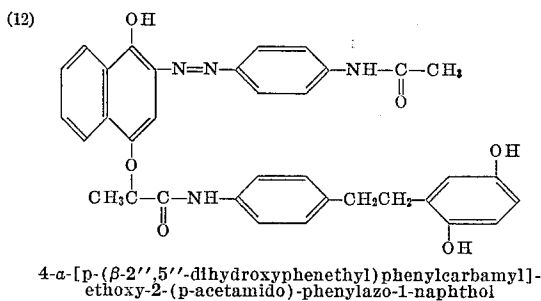
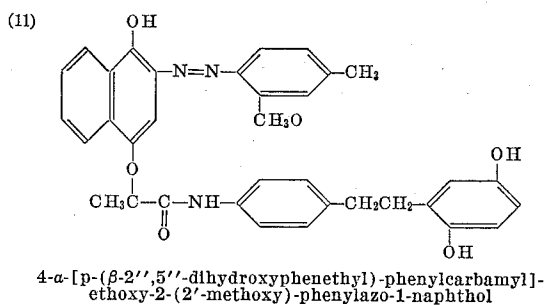


The following compounds are illustrative of other useful dye developers within the scope of the present invention:



4- $\alpha$ -(2',5'-dihydroxyphenylcarbonyl)-ethoxy-2-(2'-chloro-4'-methyl)-phenylazo-1-naphthol

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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 modifications 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 Formula 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 Ser. No. 144,816, filed Oct. 18, 1961, now U.S. Patent No. 3,134,672. When subjected to standard

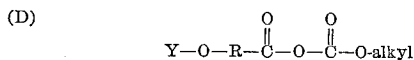
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heat stability tests for 40 hours at a temperature of 120° F., the compounds of Formulae 1-9 showed little or no change. When subjected to standard light stability tests with a xenon arc for periods of 40 and 100 hours, these compounds exhibited substantially increased stability, showing appreciably less fading than did the aforementioned prior azo-naphthol dye developers.

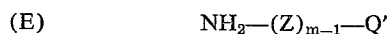
The novel dye developers of this invention may be prepared by reacting a compound of the formula:



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 alkyl-chlorocarbonate, e.g., methyl, ethyl, isopropyl, isobutyl-chlorocarbonate, etc., to form a mixed anhydride of the formula:



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

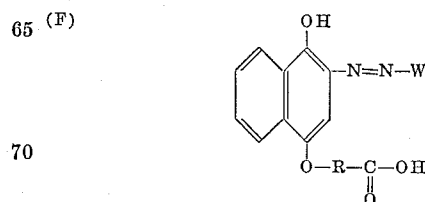


30 wherein Q' is a dihydroxyphenyl silver halide developing radical or a protected derivative thereof, to form the dye developers of Formula A.

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.

45 While Q' of Formula E may be a 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 diacetoxyphe-  
 50 nyl, dibenzoyloxyphenyl, etc. The protective groups may be removed by hydrolysis in known manner to form the desired dye developer.

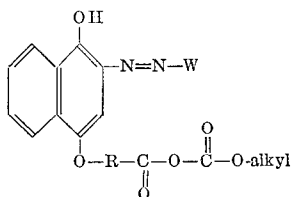
The foregoing synthesis provides a particularly useful method for preparing the preferred class of dye developers of Formula B. In the same manner as described above, an azo dye of the formula:



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 Ser. No. 262,357 filed concurrently and now U.S. Patent No. 3,328,386; and compounds of Formula G and their synthesis, as well as the ammonium salt intermediates, are described and claimed in U.S. Patent No. 3,256,269. 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 U.S. Patent No. 3,019,254, issued Jan. 30, 1962. As examples of such compounds, mention may be made of 2,5-diacetoxyphenyl aniline; 2,5-diacetoxylaniline; 2,5-diacetoxyphenylmethyl aniline;  $\beta$ -2,5-diacetoxyphenethyl aniline, etc.; including the corresponding aniline hydrochlorides.

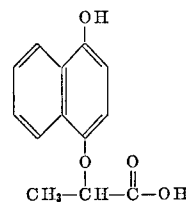
Where the starting compounds of Formula C may be converted to their acid chloride without the necessity of employing elevated temperatures to form a solution of the reactants, the novel dye developers of this invention may also be prepared by the steps of first forming the acid chloride of the acid of 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

$\alpha$ -(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<sub>2</sub>) 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  $\alpha$ -(4-hydroxy)-1-naphthoxypropionic acid, M.P. 157-159° C., having the following structural formula:



Elemental analysis of the product as C<sub>13</sub>H<sub>12</sub>O<sub>4</sub>: Found: C, 67.1; H, 5.2. Calculated: C, 67.2; H, 5.19.

#### EXAMPLE II

4 -  $\alpha$ -[p-( $\beta$ -2'',5''- dihydroxyphenethyl) - phenylcarbamy] - 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  $\alpha$  - (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,  $\alpha$ -[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 - ( $\beta$ -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- $\alpha$  - [p-( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylcarbamy] - ethoxy - 2 - [p-(2'',5''-dihydroxyphenylmethyl) - phenylazo] - 1 - naphthol, M.P. 194-199° C.,  $\lambda_{\text{max}}$  of 522 m $\mu$ , methyl Cellosolve.

## EXAMPLE III

4- $\alpha$ -(2',5' - dihydroxyphenylcarbamy) - 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  $\alpha$ -(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  $\alpha$  - [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<sub>2</sub> 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-benzoxo-aniline (.016 mole) was added gradually to the stirred solution of the mixed anhydride. The temperature of the reaction mixture was held at -2° during this addition (ca. 10 min.). The cooling bath was then removed and the reaction mixture was stirred overnight (N<sub>2</sub> 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<sub>2</sub> atmosphere as described in Example III. The dye developer after recrystallization from a methyl Cellosolve-H<sub>2</sub>O mixture melted at 254-256° C.

## EXAMPLE IV

4 -  $\alpha$  - [p - (2'',5'' - dihydroxyphenyl) - phenylcarbamy] - 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-benzoxo aniline. The isolated dye developer melted at 251-253° C., exhibited a  $\lambda_{\max}$ . of 540 m $\mu$  in methyl Cellosolve and was found to be soluble in chloroform, methylene chloride and alcohols.

## EXAMPLE V

4 -  $\alpha$  - [p - ( $\beta$ -2'',5''-dihydroxyphenethyl)-phenylcarbamy] - ethoxy - 2 - (p - homogentisamido)-phenylazo-1-naphthol (Compound 4) was prepared in a manner similar to that set forth in Example II substituting dicathyl-oxy homogentisamido aniline hydrochloride for p - (2,5-diacetoxyphenylmethyl) aniline hydrochloride. The isolated dye developer, 4- $\alpha$ -[p-( $\beta$ -2'',5'' - dihydroxyphenethyl) - phenylcarbamy] - ethoxy - 2 - (p-homogentisamido)-phenylazo-1-naphthol, melted at 201-209° C., exhibited a  $\lambda_{\max}$ . of 532 m $\mu$  in methyl Cellosolve and was found to be soluble in acetone and 5% aqueous sodium hydroxide.

## EXAMPLE VI

4 -  $\alpha$  - [p - ( $\beta$ -2'',5'' - dihydroxyphenethyl)-phenylcarbamy] - ethoxy - 2 - [p-( $\beta$ -2'',5''-dihydroxyphenethyl)-phenylazo] - 1 - naphthol (Compound 5) was prepared in a manner similar to that set forth in Example II substituting p-( $\beta$ -2,5-diacetoxyphenethyl) aniline hydro-

chloride for p-(2,5-diacetoxyphenylmethyl) aniline hydrochloride. The product, 4- $\alpha$ -[p-( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylcarbamy] - ethoxy - 2 - [p - ( $\beta$  - 2'',5''-dihydroxyphenethyl)-phenylazo] - 1 - naphthol, melted at 211-215° C. and exhibited a  $\lambda_{\max}$ . of 525 m $\mu$  in methyl Cellosolve.

## EXAMPLE VII

4- $\alpha$ -[p-(2'',5'' - dihydroxyphenyl) - phenylcarbamy] - ethoxy-2-[p-( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylazo]-1-naphthol (Compound 6) was prepared in a manner similar to that set forth in Example II substituting p-( $\beta$ -2,5-diacetoxyphenethyl) aniline hydrochloride for 2,5-diacetoxy-phenethylmethyl aniline hydrochloride and p-( $\beta$ -2,5-diacetoxyphenethyl) aniline hydrochloride. The isolated dye developer, 4- $\alpha$ -[p-(2'',5''-dihydroxyphenyl) - phenylcarbamy] - ethoxy-2-[p-( $\beta$ -2'',5'' - dihydroxyphenethyl) - phenylazo]-1-naphthol, melted at 136-141° C., exhibited a  $\lambda_{\max}$ . of 525 m $\mu$  in methyl Cellosolve, and was found to be soluble in acetone, methanol and 5% sodium hydroxide.

## EXAMPLE VIII

4- $\alpha$ -[p-(2'',5'' - dihydroxyphenyl) - phenylcarbamy] - 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-benzoxo aniline. The isolated dyed eveloper, 4- $\alpha$ -[p-(2'',5''-dihydroxyphenyl)-phenylcarbamy] - ethoxy - 2 - (2',4',6'-trimethyl)-phenylazo-1-naphthol, melted at 129-134° C., exhibited a  $\lambda_{\max}$ . of 520 m $\mu$  in methyl Cellosolve, and was found to be soluble in acetone, ethanol and chloroform.

## EXAMPLE IX

4- $\alpha$ -[p-(2'',5'' - dihydroxyphenyl) - phenylcarbamy] - 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-benzoxo aniline. The isolated dye developer, 4- $\alpha$ -[p-(2'',5''-dihydroxyphenyl)-phenylcarbamy] - ethoxy - 2 - p - methylphenylazo-1-naphthol, melted at 261-262° C. and exhibited a  $\lambda_{\max}$ . of 525 m $\mu$  in methyl Cellosolve.

## EXAMPLE X

4- $\alpha$ -[p-( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylcarbamy] - ethoxy - 2 - [2' - (N - butyl)-carbamy] - 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  $\alpha$ -(4-hydroxyl-naphthoxy) propionic acid. The resulting dye,  $\alpha$ -(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  $\beta$ -hydroquinonyl ethyl aniline for 2-hydroxy-5-benzoxo aniline, according to the procedure of Example III. The isolated dye developer, 4- $\alpha$ -[p-( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylcarbamy] - ethoxy-2-[2'-(N-butyl)-carbamy] - phenylazo-1-naphthol, melted at 156-164° C. and exhibited a  $\lambda_{\max}$ . of 515 m $\mu$  in alcohol.

## EXAMPLE XI

4- $\alpha$ -(2',5'-dihydroxyphenylcarbamy)-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- $\alpha$ -(2',5'-dihydroxyphenylcarbamy)-ethoxy-2-(2'-chloro - 4' - methyl) - phenylazo-1-naphthol, melted at 237-240° C., exhibited a  $\lambda_{\max}$ . of 520 m $\mu$  in methyl Cellosolve, and was found to be soluble in ethanol.

## EXAMPLE XII

4- $\alpha$ -[p-( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylcarbamy]l-ethoxy-2-(2'-methoxy) - phenylazo-1-naphthol (Compound 11) was prepared in a manner similar to that set forth in Example III, substituting  $\beta$ -hydroquinonyl ethyl aniline for 2-hydroxy-5-benzoxylaniline. The isolated dye developer, 4- $\alpha$ -[p-( $\beta$ -2'',5''-dihydroxyphenethyl)-phenylcarbamy]l-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- $\alpha$ -[p-( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylcarbamy]l-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-acetamidoaniline in place of o-anisidine and  $\beta$ -hydroquinonyl ethyl aniline in place of 2-hydroxy-5-benzoxylaniline. The resulting product, 4- $\alpha$ -[p-( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylcarbamy]l-ethoxy-2-(p-acetamido)-phenylazo-1 - naphthol, melted at 244° C., exhibited a  $\lambda_{\max}$ . of 531 m $\mu$  in methyl Cellosolve, and was soluble in acetone and dilute aqueous sodium hydroxide.

## EXAMPLE XIV

4- $\alpha$ -[ $\beta$ -p-(2'',5''-dihydroxyphenyl) - phenylcarbamy]l-ethoxy-2-(2'-methoxy)-phenylazo-1-naphthol (Compound 13) was prepared in a manner similar to that set forth in Example III, using p-hydroquinonyl aniline in place of 2-hydroxy-5-benzoxylaniline. The resulting product, 4- $\alpha$ -[ $\beta$ -p-(2'',5''-dihydroxyphenyl) - phenylcarbamy]l-ethoxy-2-(2'-methoxy)-phenylazo-1-naphthol, melted at 194-197° C., exhibited a  $\lambda_{\max}$ . of 535 m $\mu$  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- $\alpha$ -[p-( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylcarbamy]l - 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 of 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- $\alpha$ -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

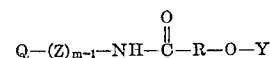
The procedure described in Example XV was repeated, except that the dye developer was dispersed in a layer of gelatin. The coating solution from which the dye developer was coated was prepared by adding 0.75 g. of the dye developer dissolved in 1 cc. of cyclohexanone and 5 cc. of di(tetrahydrofurfuryl)adipate. This mixture was

agitated in a Waring Blendor 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.

Since certain changes may be made in the above products, compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

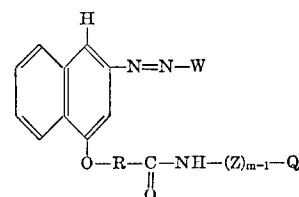
What is claimed is:

1. Azo dyes of the formula:



wherein Q is p-dihydroxyphenyl; Z is a member selected from the group consisting of phenylene, lower alkylene and lower phenalkylene radicals; R is lower alkylene; m is a positive integer from 1 to 2, inclusive; and Y is the radical of a dye of the benzeneazonnaphthol series, said —O— substituent being bonded directly to a nuclear carbon atom of the naphthol moiety of said dye.

2. Azo dyes of the formula:



wherein Q is p-dihydroxyphenyl; Z is a member selected from the group consisting of phenylene, lower alkylene and lower phenalkylene radicals; R is lower alkylene; m is a positive integer from 1 to 2, inclusive; and W is the radical of a diazotizable amine of the benzene series.

3. 4 -  $\alpha$  - [p - ( $\beta$ -2'',5''-dihydroxyphenethyl) - phenylcarbamy]l - ethoxy - 2 - [p-(2'',5''-dihydroxyphenylmethyl)-phenylazo]-1-naphthol.

4. 4 -  $\alpha$  - (2',5' - dihydroxyphenylcarbamy]l-ethoxy - 2 - (2'-methoxy)-phenylazo-1-naphthol.

5. 4 -  $\alpha$  - [p - (2'',5'' - dihydroxyphenyl) - phenylcarbamy]l - ethoxy - 2 - (2' - methoxy - 5' - methyl) - phenylazo-1-naphthol.

6. 4 -  $\alpha$  - [p-( $\beta$ -2'',5''-dihydroxyphenethyl)-phenylcarbamy]l - ethoxy - 2 - (p - homogentisamido) - phenylazo-1-naphthol.

7. 4 -  $\alpha$  - [p - ( $\beta$  - 2'',5'' - dihydroxyphenethyl) - phenylcarbamy]l - ethoxy - 2 - [p - ( $\beta$  - 2'',5'' - dihydroxyphenethyl)-phenylazo]-1-naphthol.

8. 4 -  $\alpha$  - [p - (2'',5'' - dihydroxyphenyl) - phenylcarbamy]l - ethoxy - 2 - [p - ( $\beta$  - 2'',5'' - dihydroxyphenethyl)-phenylazo]-1-naphthol.

9. 4 -  $\alpha$  - [p - (2'',5'' - dihydroxyphenyl) - phenylcarbamy]l - ethoxy - 2 - (2',4',6' - trimethyl) - phenylazo - 1-naphthol.

10. 4 -  $\alpha$  - [p - (2'',5'' - dihydroxyphenyl) - phenylcarbamy]l - ethoxy - 2 - p - methylphenylazo - 1 - naphthol.

11. 4 -  $\alpha$  - [p - ( $\beta$  - 2'',5'' - dihydroxyphenethyl) - phenylcarbamy]l - ethoxy - 2 - [2' - (N - butyl) - carbamy]l-phenylazo-1-naphthol.

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