United States Patent Office 3,076,808 Patented Feb. 5, 1963

3,076,808

ANTHRAPYRIDONE DYE DEVELOPERS

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No Drawing. Filed Nov. 7, 1961, Ser. No. 150,661
9 Claims. (Cl. 260—278)

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 disturbing the imagewise distribution thereof, to provide a reversed or positive, colored image of the developed or negative image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developed. 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 herein contemplated contain an anthrapyridone, that is, a 3-azabenzanthrone, nucleus to which is attached at least one and preferably not more than two organic groups capable of functioning as silver halide developing groups.

The novel dye developers of the present invention comprise anthrapyridone dyes characterized in that they contain at least one group of the formula:

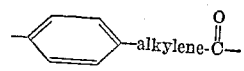
—Y—Z

wherein Y is a covalent bond or a divalent radical and Z is an aryl nucleus selected from the group consisting of benzene and naphthalene nuclei so substituted by at least two groups selected from the group consisting of hydroxyl and amino groups as to be capable of developing an exposed silver halide emulsion.

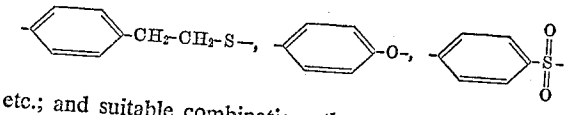
In addition to the substituents which provide the silver halide developing function, Z may be substituted by halogen, alkoxy, alkyl, etc., radicals. The term "amino" as used herein is intended to include amino groups so substituted as not to impair their respective silver halide developing function, for example, suitably substituted alkylamino and arylamino groups.

The novel compounds of this invention, as noted above, are dye developers which contain an aryl nucleus selected from the group consisting of benzene and naphthalene nuclei so substituted by at least two groups selected from the group consisting of hydroxyl and amino groups as to be capable of developing an exposed silver halide emulsion. A preferred silver halide developing group comprises a hydroquinonyl group. Other suitable developing groups include ortho-dihydroxyphenyl and ortho- and para-amino substituted hydroxyphenyl groups. In general, the developing group comprises a benzenoid developing configuration, that is, an aromatic developing group which forms quinonoid or quinone products upon oxidation.

As examples of divalent radicals, signified by the term "Y" and suitable for use in the practice of the present invention, mentioned may be made of: divalent organic radicals such as alkylene radicals, preferably lower alkylene radicals such as ethylene, isopropylene, etc.; sulfonamido; sulfamyl; carboxamido; carbamyl; arylene radicals such as phenylene, etc.; aralkylene radicals such as phenethyl, etc.; acyl radicals such as

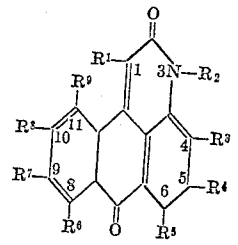


etc.; divalent radicals which contain both hetero and carbon atoms as constituent components, as for example,



etc.; and suitable combinations thereof.

The anthrapyridone dye developers may be represented by the formula:



wherein:

Each of R^1, R^3, R^4, R^5, R^6, R^7, R^8, and R^9 may be —Y—Z, hydrogen, aryl, alkyl and preferably lower alkyl, halogen, amino, cyano, acyl, nitro, carboalkoxy, carboxy, sulfo, alkoxy, hydroxyl, carboxamido, or aralkyl;

R^2 may be —Y—Z, hydrogen, alkyl and preferably lower alkyl, aryl or aralkyl;

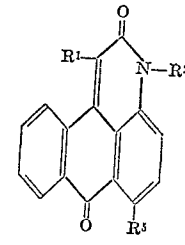
—Y—Z has the same significance as previously noted;

At least one developing group —Y—Z is present;

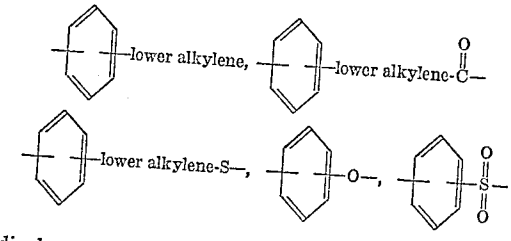
And wherein more than one developing group —Y—Z is present, each such group —Y—Z may be the same or different.

As herein used, the terms amino, alkyl, aryl, etc. are intended to include the corresponding substituted groups. Thus, amino is intended to include groups such as methylamino and anilino, alkyl is intended to include groups such as anminomethyl and β-hydroxyethyl, etc.

A preferred group of anthrapyridone dye developers may be represented by the formula:



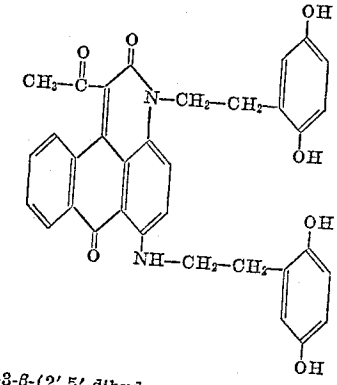
wherein R^1 is hydrogen or an acetyl radical; and each of R^2 and R^5 may be hydrogen, a lower alkyl such as methyl, ethyl, isopropyl, etc., or —Y—Z, where Y is a divalent organic linking group selected from the group consisting of lower alkylene, sulfonamido, sulfamyl, carboxamido, carbamyl, phenylene,



radicals; and Z is an aryl nucleus selected from the group consisting of benzene and naphthalene nuclei substituted by two groups selected from the group consisting of hydroxyl and amino groups, one of said groups being substituted in one of the ortho and para positions with respect to the other of said groups so as to be capable of developing an exposed silver halide emulsion, and at least one of said R^2 and R^5 is —Y—Z.

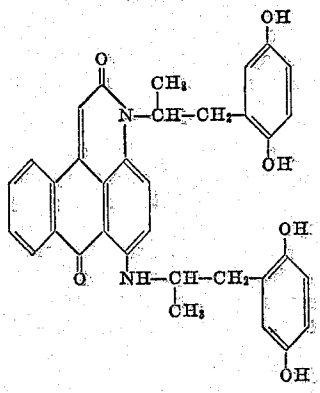
As examples of useful anthrapyridone dye developers within the scope of the last-mentioned formula, mention may be made of the following compounds:

(1)



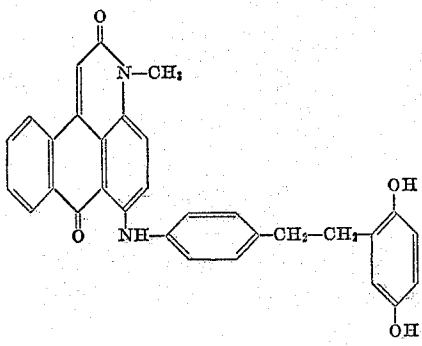
1-acetyl-3-β-(2',5'-dihydroxyphenyl)-ethyl-6-β-(2',5'-dihydroxyphenyl)-ethylamino-anthrapyridone

(2)



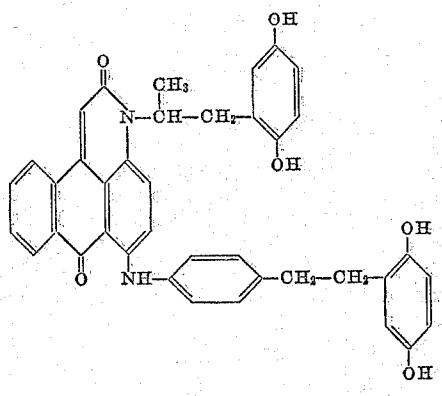
3-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethyl-6-[β-(2'5'-dihydroxyphenyl)-α-methyl]-ethylamino-anthrapyridone

(3)



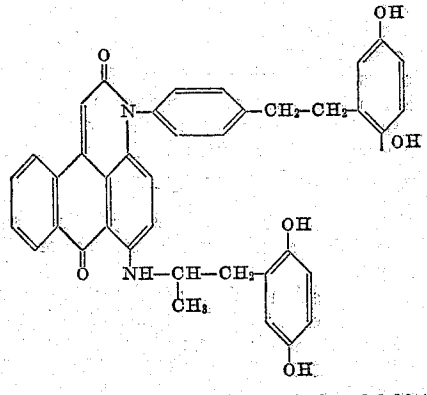
6-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-anilino-3-methyl-anthrapyridone

(4)



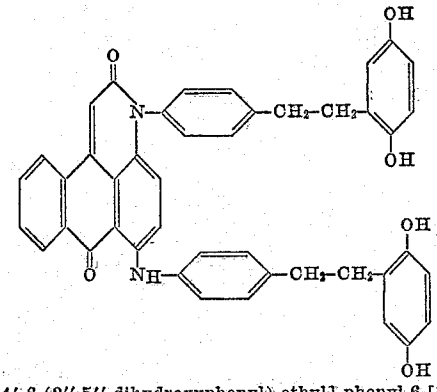
3-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethyl-6-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-anilino-anthrapyridone

(5)



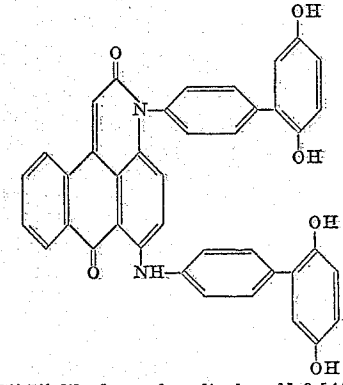
3-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-phenyl-6-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethylamino-anthrapyridone

(6)



3-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-phenyl-6-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]anilino-anthrapyridone

(7)

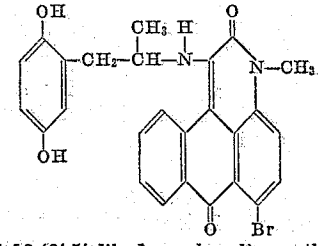


3-[4'-(2'',5''-dihydroxyphenyl)-phenyl]-6-[4'-(2'',5''-dihydroxyphenyl)-anilino]-anthrapyridone

It has been found that anthrapyridone dye developers within the preferred group, which have a 6-alkylamino or 6-arylamino substituent, are magenta dye developers having exceptionally good spectral characteristics, since they absorp only a minimal amount of light which ideally should be transmitted. Thus, these dye developers are particularly useful in multicolor products and processes such are described in the aforementioned U.S. Patent No. 2,983,606. Moreover, those analogues having a 6-arylamino substituent have been found to possess unusually good stability. It will be appreciated that the alkylamino or arylamino substituent may in turn be substituted, as illustrated in the above-named compounds, and may, for example, contain a developing function.

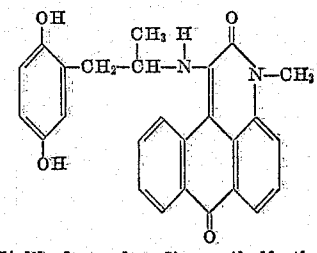
As examples of other anthrapyridone dye developers, mention may be made of the following compounds.

(8)



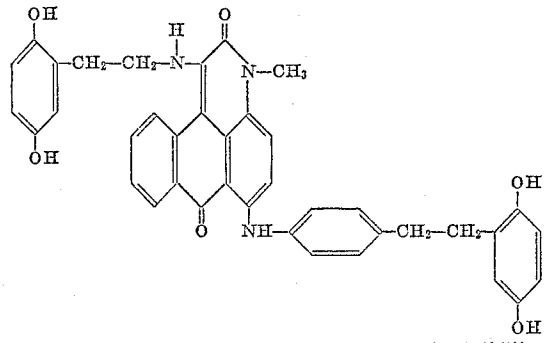
6-bromo-1-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethyl-3-methyl-anthrapyridone

(9)



1-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethyl-3-methyl-anthrapyridone

(10)



1-β-(2',5'-dihydroxyphenyl)-ethylamino-6-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-anilino-anthrapyrimidone

The anthrapyridone dye developers of this invention may be prepared by methods similar to those used to prepare anthrapyridone dyes. Thus, the anthrapyridone dye developers may be synthesized by cyclization of 1-acetamidoanthraquinones, the acetyl group of which may be unsubstituted or substituted, for example, preferably substituted with a halogen group such as chlorine, by ester condensations with anthraquinones having a primary or secondary amino group alpha to a carbonyl group, e.g., 1-aminoanthraquinone, or by cyclization of suitably substituted benzoic acids, e.g., m-carboxyanilides or phenylpropiolic acid, phenylpropionic acid or phenylpropargylic acid. The desired developer group or groups X may be introduced before or after formation of the anthrapyridone nucleus, as illustrated in Examples 1 and 2, respectively. It will be apparent that various groups may be substituted before or after formation of the anthrapyridone nucleus for the purpose of modifying the color, solubility, or other properties.

One preferred method of preparing the aforementioned anthrapyridone dye developers wherein the desired developer group or groups is introduced prior to formation of the anthrapyridone nucleus comprises condensing an anthraquinone dye having at least one group of the formula:

wherein Y and Z have the same significance as previously set forth; substituted on the anthraquinone nucleus in α-position to a carbonyl group with an ester selected from the group consisting of acetoacetic, malonic and cyanoacetic esters.

The aforementioned ester condensations are preferably effected in the presence of a suitable catalyst, as for example, a mixture of sodium acetate and cuprous chloride.

Another preferred method of preparing anthrapyridone dye developers wherein the desired developer group or groups is introduced prior to formation of the anthrapyridone nucleus comprises acetylating an anthraquinone dye developer having a secondary amino group, such as the aforementioned

substituent wherein Z is an ortho or dihydroxyphenyl radical, substituted on the anthraquinone nucleus in a position α to a carbonyl group and then internally condensing the acetylated compound to effect cyclization thereof to form the anthrapyridone. The acetylation may be accomplished, for example, by refluxing the anthraquinone dye developer with acetyl chloride. It should be noted that this treatment concurrently acetylates the developing group. The cyclization may be carried out, for example, by refluxing with an alkaline solution in an inert atmosphere, such as under a blanket of nitrogen. The acetylated developer group is hydrolyzed to the free developer during this cyclization.

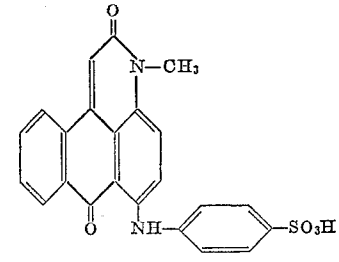
A preferred method of preparing the aforementioned anthrapyridone dye developers wherein the desired developer group or groups is introduced subsequent to formation of the anthrapyridone nucleus comprises reacting an anthrapyridone dye having a nitro or halogen group substituted in position 6 with a compound of the formula:

$$X—Y—Z^1$$

wherein Y has the same significance as previously noted, X represents a primary or secondary amino group, and Z^1 represents a protected developer group, e.g., 2',5'-diacyloxyphenyl, etc.

Another method of preparing the aforementioned anthrapyridone dye developers comprises effecting a condensation reaction between an anthrapyridone dye having substituted thereon one or more sulfonyl chloride and/or acid chloride groups and a compound within the last-mentioned formula.

As an example of the last-mentioned anthrapyridone dye intermediates, mention may be made of the sulfonyl chloride derivative of



As examples of compounds within the aforementioned formula X—Y—Z, mention may be made of the following:

Amino-ethyl-hydroquinone, the preparation of which is disclosed in the copending U.S. application of Milton Green, Serial No. 514,095, filed June 8, 1955;

Amino-phenethyl-hydroquinone, the preparation of which is disclosed in the copending U.S. application of Elkan R. Blout, Milton Green, Howard G. Rogers, Myron S. Simon and Robert B. Woodward, Serial No. 612,051, filed September 25, 1956; and in a continuation-in-part thereof, Serial No. 98,287, filed March 27, 1961, now U.S. Patent No. 3,019,107;

Amino-phenethyl-thio-hydroquinone, the preparation of which is disclosed in the copending U.S. application of Milton Green and Howard G. Rogers, Serial No. 663,876, filed June 6, 1957, now U.S. Patent No. 3,009,958;

Amino-phenoxy-hydroquinone, the preparation of which is disclosed in the copending U.S. application of Milton Green and Warren E. Solodar, Serial No. 680,406, filed August 26, 1957;

Amino-propyl-amino-hydroquinone, the preparation of which is disclosed in the copending U.S. application of Milton Green and Myron S. Simon, Serial No. 711,812, filed January 29, 1958, now U.S. Patent No. 3,002,997; and

Amino-hydroquinone, amino-phenyl-hydroquinone, and amino-phenyl-sulfonyl-hydroquinone, etc., which may be prepared by known chemical reactions.

In addition, the aforementioned anthrapyridone dye developers may be prepared by effecting a condensation reaction between an anthrapyridone dye having substituted thereon one or more primary and/or secondary amino groups and a compound of the formula:

$$W—Y—Z$$

wherein Y and Z have the same significance as previously noted and W represents an acid chloride or sulfonyl chloride group.

The enumeration and preparation of compounds within the last-mentioned formula are set forth in the following copending U.S. applications:

Serial No. 471,542, filed November 26, 1954, in the names of Elkan R. Blout, Saul G. Cohen, Milton Green, Howard G. Rogers, Myron S. Simon, and Robert B.

Woodward, and now abandoned, and in Serial No. 1,442 and 1,443, both filed January 11, 1960, and each a continuation-in-part thereof; and

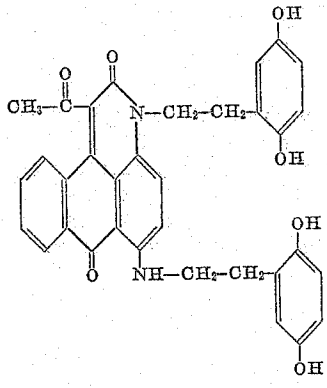
Serial No. 771,718, filed November 4, 1958, in the names of Elkan R. Blout and Richard S. Corley and now abandoned.

It may be desirable to protect the hydroxyl and/or amino groups of the developing function, during the above-mentioned reactions, to avoid undesirable side reactions, that is to employ a protected derivative of Z. The protected derivatives of Z set forth in formula X—Y—Z may be prepared by the selective acylation of Z according to the procedure disclosed in the copending U.S. application of Milton Green and Helen P. Husek, Serial No. 612,063, filed September 25, 1956, and which was abandoned in favor of Serial No. 805,673, filed April 13, 1959, now U.S. Patent No. 3,019,254. The protected derivatives of Z set forth in formula W—Y—Z may be prepared by conventional acylation of Z according to procedures well known to the art. After reaction and prior to use as a photographic dye developer, the acyloxy groups may be removed by deesterification as, for example, by hydrolysis in the presence of alkali.

The following examples show by way of illustration and not by way of limitation the preparation of novel dye developers within the scope of this invention.

Example 1

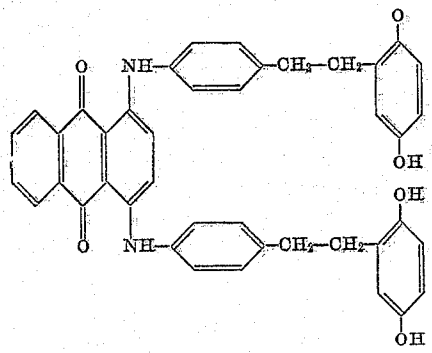
1,4-bis-[β-(2',5'-dihydroxyphenyl)-ethylamino]-anthraquinone is heated in quinoline, under nitrogen, with 3 to 4 equivalents of acetoacetic ester at 190° C., in the presence of sodium acetate and a small amount of cuprous chloride. The reaction mixture is agitated occasionally. After 5 to 6 hours, the reaction mixture is treated with excess 10% hydrochloric acid. The residue is dissolved in methyl cellosolve from which the product is precipitated by addition of water. Reprecipitation from methyl Cellosolve with benzene yields the desired anthrapyridone dye developer, 1-acetyl-3-β-(2',5'-dihydroxyphenyl)-ethyl-6-β-(2',5'-dihydroxyphenyl)-ethylamino - anthrapyridone of the structure:



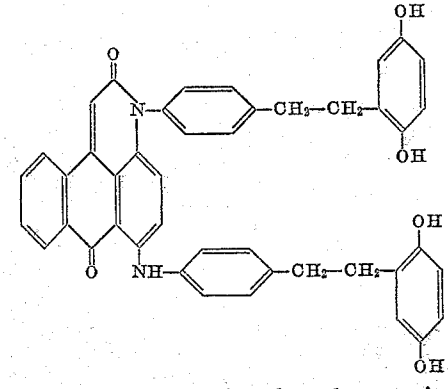
whose spectral absorption curve in ethanol exhibits absorption maxima at 514 mμ and 545 mμ.

Example 2

24.2 g. (.10 mole) of leucoquinizarin, 60.0 g. (.225 mole) of amino-phenethyl-hydroquinone hydrochloride, 12.4 g. (.2 mole) of boric acid, 21.0 g. (.25 mole) of sodium bicarbonate, and 250 ml. of methyl Cellosolve were mixed together and refluxed under a blanket of nitrogen for about 20 hours with stirring. 24.6 g. (.1 mole) of practical grade chloranil was then added and refluxing was continued until oxidation was complete. The mixture was then cooled, filtered, and the filtrate poured into excess dilute hydrochloric acid to yield a precipitate. This precipitate was filtered off, rinsed with cold water and dried to yield 56.1 g. of a cyan dye developer, 1,4-bis-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl] - anilino-anthraquinone, having a melting point of 205° C., exhibiting a spectral absorption curve in ethanol having a $\lambda_{max.}$ of 652 mμ and 607 mμ; ε=17,000 and having the following structural formula:



33.2 g. (.05 mole) of the above compound and 600 ml. of benzene were refluxed through a water trap until dry. The trap was removed and 0.5 ml. of pyridine and the 55 ml. (.77 mole) of acetyl chloride were slowly added over a 15 minute period and refluxing was continued while using a $CaCl_2$ tube to exclude moisture. After refluxing for an hour, an additional 50 ml. of acetyl chloride was added and refluxing was continued for another 15 hours. The mixture was then cooled, decanted from the sludge and evaporated dry. The residue was redissolved in about 250–350 ml. of benzene, the solution filtered, and the filtrate poured into 3 l. of hexane, the resulting pink precipitate was filtered off and dried to yield 22.5 g. of the acetyl derivative, a pink solid melting at 110–115° C., 22.5 g. (.0246 mole) of the acetyl derivative was dissolved in 250 ml. of methyl Cellosolve at room temperature and the mixture was brought to reflux under a blanket of nitrogen. A deaerated solution of 10 g. (.179 mole) of potassium hydroxide in 20 ml. of water was added dropwise to the refluxing solution under nitrogen over a period of 3 to 5 minutes and the reflux was then continued for an additional 10 to 15 minutes. The solution was then allowed to cool, poured quickly into excess dilute hydrochloric acid to form a precipitate which was filtered off, rinsed and dried. The precipitate was then crystallized from methyl Cellosolve to yield 4.6 g. of a dark purple solid, 3-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-phenyl-6-[4'-p - (2'',5'',dihydroxyphenyl)-ethyl]-anilino-anthrapyridone, which melted at 256–258° C., was soluble in pyridine, dimethyl formamide and dilute alkali, and has the following structural formula:

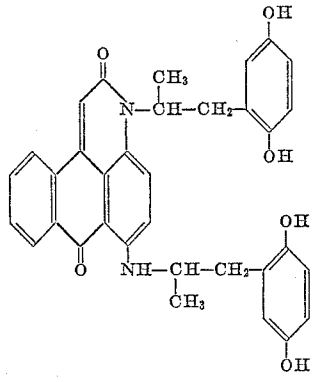


Spectral analysis of the product showed a $\lambda_{max.}$ in methyl Cellosolve=542 mμ; ε=12,300.

Example 3

A mixture of 27 g. (.95 mole) of 1,4-bis-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethylamino - anthraquinone and 62 ml. (.87 mole) of acetyl chloride were refluxed on a steam bath for 3½ hours, cooled, filtered, and then precipitated into 3 l. of hexane. The resulting red precipitate was filtered off, rinsed with hexane and air dried. 7.92 g. of the dry precipitate was refluxed under a blanket

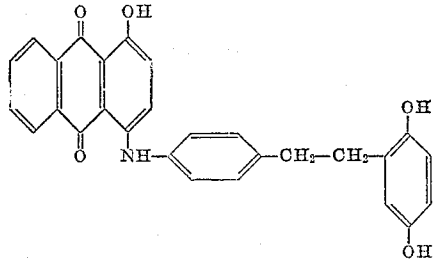
of nitrogen in 50 ml. of methyl Cellosolve. A nitrogen-deaerated solution of 5.6 g. (.1 mole) of potassium hydroxide in 20 ml. of methyl Cellosolve and 5 ml. of water was added under nitrogen over a period of 3 minutes. Reflux was then continued for an additional 7 minutes, after which the solution was cooled for 20 minutes and 10 ml. of acetic acid was added. The solution was then poured into 1 l. of dilute acetic acid to precipitate out a magenta solid, which was filtered off and dried to yield 6.1 g. of crude product. Purification by chromatography yielded 1.55 g. of 3-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethyl-6-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethylamino-anthrapyridone, having the following structural formula:



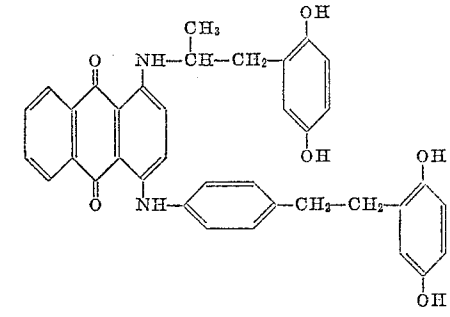
and a spectral absorption curve in methyl Cellosolve exhibiting absorption maxima at 542 and 510 mμ; ε=12,200.

Example 4

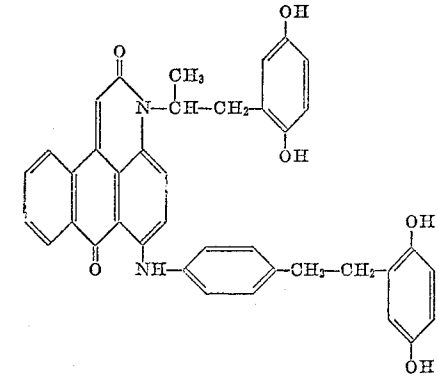
A mixture of 24.0 g. (.10 mole) of quinizarin, 60.0 g. (.226 mole) of amino-phenethyl-hydroquinone hydrochloride, 12.4 g. (.20 mole) of sodium bicarbonate and 21.0 g. of boric acid in 250 ml. of pyridine was refluxed under nitrogen for about 48 hours until no further change in the visible spectrum was observed. The mixture was then cooled under an atmosphere of nitrogen and filtered. The filtrate was poured into a large volume of an excess of cold dilute hydrochloric acid with vigorous stirring. The precipitate was filtered off and dried to yield 43 g. of 4-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-anilino-1-hydroxy-anthraquinone, having the following structural formula:



A mixture of 20.0 g. (.0443 mole) of the above compound, 14.84 g. (.060 mole) of β-(2,5-dihydroxyphenyl)-α-methyl-ethylamine hydrobromide, 5.13 g. (.061 mole) of sodium bicarbonate, and 200 ml. of methyl Cellosolve was refluxed under a blanket of nitrogen, thereby evolving carbon dioxide gas. When the evolution of gas ceased, 10 ml. of acetic acid was added and refluxing was continued for 24–48 hours until no further change in the visible spectrum was observed. The mixture was then cooled under nitrogen, filtered, and the filtrate poured into a large volume of cold dilute hydrochloric acid with vigorous stirring. The resulting precipitate was filtered off and vacuum dried to yield a crude product, 1-[β-(2',5'-dihydroxyphenyl) - α-methyl]-ethylamino-4-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-anilino-anthraquinone of the following structural formula:

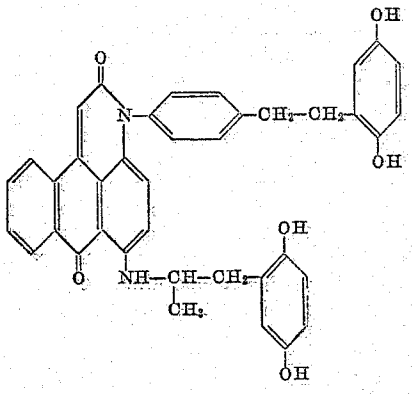


The last-mentioned product was purified by precipitation into hexane from ethyl acetate solution followed by repeated extractions in acetone and evaporations until dry, until 8 g. of purified product was recovered. 6.5 g. of the purified product (.0108 mole), 23 ml. (.324 mole) of acetyl chloride and 270 ml. of dry benzene were refluxed together on a steam bath for about 24 hours until the $\lambda_{max.}$ of the solution was about 500 mμ. This solution was then cooled and filtered and the residue was rinsed with benzene. The rinsings were also filtered and the filtrates were then combined and precipitated into about 3 l. of hexane. The precipitate was filtered off and vacuum dried to yield 6.7 g. of acetylated anthraquinone product. 4 g. of this product was refluxed in 40 ml. of methyl Cellosolve under a blanket of nitrogen. A deaerated solution of 3.92 g. (.07 mole) of potassium hydroxide in 4 ml. of water was then added under nitrogen during a one minute period. The reflux was continued for another 4 minutes, then the mixture was cooled, acidified with acetic acid and precipitated into cold dilute hydrochloric acid with vigorous stirring. The precipitate was then filtered and dried to yield 3.2 g. of crude product. Purification by chromatography gave two separate fractions: (1) 3-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethyl-6-[4'-β-(2'',5'' - dihydroxyphenyl) - ethyl]-anilino-anthrapyridone, having the following structural formula:



and (2) 3-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-phenyl-

6 - [β - (2',5' - dihydroxyphenyl) - α-methyl]-ethylamino-anthrapyridone, having the following structural formula:



Fraction 1 was soluble in alcohol and acetone, and had a single spectral absorption curve in ethyl alcohol of $\lambda_{max.}$ =526 mμ. Fraction 2 was soluble in alcohol, methy Cellosolve, tetrahydrofuran and acetone and had a spectral absorption curve in ethyl alcohol with a $\lambda_{max.}$=535 mμ and a shoulder at 512 mμ.

Examples of the photographic use of the anthrapyridone dye developers of this invention, and given as illustrations only, proportions being by weight unless otherwise indicated, are:

Example 5

A photosensitive element is prepared by coating a gelatin coated film base with a solution comprising:

	G.
Acetone	50
Tetrahydrofuran	50
Cellulose acetate hydrogen phthalate	4
1 - acetyl - 3-β-(2',5'-dihydroxyphenyl)-ethyl-6-β-(2', 5'-dihydroxyphenyl)-ethylamino-anthrapyridone	3.8

After this coating has dried, a silver iodobromide emulsion is applied. The photosensitive element is exposed and an aqueous liquid processing composition comprising:

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

is spread between the exposed photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element comprises a cellulose acetate-coated baryta paper which has been coated with a 6% aqueous polyvinyl alcohol solution. After an imbibition period of approximately one minute, the image-receiving element is separated and is found to contain a reddish-pink, positive image of the photographed subject matter.

Example 6

A photosensitive element is prepared similarly to that described in Example 2 using a solution comprising 1.8% of an anthrapyridone dye developer prepared by refluxing 1-nitro-3-methyl-6-bromo-anthrapyridone in pyridine with sodium acetate and β-aminopropylhydroquinone, in a 4% solution of cellulose acetate hydrogen phthalate in an 80–20 mixture of acetone and methanol. Processing of the exposed photo-sensitive element with an aqueous composition comprising:

	Percent
Sodium carboxymethyl cellulose	4.5
Potassium bromide	0.2
Sodium hydroxide	1.5
1-phenyl-3-pyrazolidone	0.2

gives a magenta, positive image on a superposed image-receiving element prepared as described in Example 2.

Example 7

A photosensitive element was prepared by coating a gelatin subcoated cellulose acetate film base with a solution comprising 0.25 g. of 3-[β-(2',5'-dihydroxyphenyl)-α-methyl] - ethyl - 6 - [4' - β - (2'',5'' - dihydroxyphenyl)-ethyl]-anilino-anthrapyridone, dissolved in 10 cc. of a solution of 4% cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of methanol and tetrahydrofuran. After this coating dried, a green-sensitive silver iodobromide emulsion was applied and allowed to dry. This photosensitive element was exposed and brought into superposed relationship with an image-receiving element as an aqueous composition comprising:

Water	cc.	100
NaOH	g.	5.17
Hydroxy cellulose (high viscosity) [commercially available from Hercules Power Co., under the trade name "Natrosol 250"]	g.	4.03
Sodium thiosulfate	g.	1.15
Benzotriazole	g.	2.3
N-benzyl-α-picolinium bromide	g.	2.3

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

Example 8

A photosensitive element was prepared by coating a gelatin subcoated cellulose acetate film base with a solution comprising 0.49 g. of 3-[4'-β-(2'',5''-dihydroxyphenyl) - ethyl] - phenyl - 6 - [β - (2',5' - dihydroxyphenyl)-α-methyl]-ethylamino-anthrapyridone, dissolved in 10 cc. of a solution 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 applied and allowed to dry. This photosensitive element was exposed and brought into superposed relationship with an image-receiving element as an aqueous composition comprising:

Water	cc.	100
NaOH	g.	3.0
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., under the trade name "Natrosol 250"]	g.	3.5
Sodium thiosulfate	g.	1.2
Benzotriazole	g.	1.5
N-benzyl-α-picolinium bromide	g.	2.3

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

It will be appreciated that the dye developers may, for example, be dispersed in a layer of gelatin in lieu of the procedures described in the aforementioned photographic examples. This dispersion may be made by procedures known in the art. For example, the dispersion may be made by dissolving the dye developer in a suitable organic solvent or mixture of solvents and agitating this solution in a Waring Blendor with an aqueous gelatin solution and a suitable dispersing agent. The resulting dispersion may be diluted, if desired, and coated onto a gelatin subcoated film base in the manner heretofore described.

The dye developers of this invention are also useful in integral multilayer photosensitive elements for use in multicolor diffusion transfer processes. As an example of such photosensitive elements, mention may be made of the photosensitive elements disclosed and claimed in the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13,

1956, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single common image-receiving element. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, a cyan dye developer, a magenta dye developer and a yellow dye developer. In one of the preferred embodiments of photosensitive elements of this type, the dye developers are disposed in separate alkali-permeable layers behind the photosensitive silver halide emulsion stratum with which they are associated.

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

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

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

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

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

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

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

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

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

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

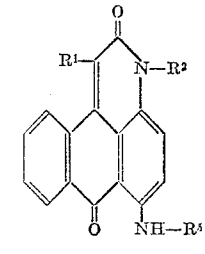
This application is in part a continuation of our copending application, Serial No. 799,425, filed March 16, 1959, and now abandoned, which in turn is in part a continuation of application Serial No. 522,848, filed July 18, 1955, and now abandoned.

Our copending U.S. application, Serial No. 150,657, filed November 11, 1961, claims the photographic utilization of the novel compounds of the present invention.

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

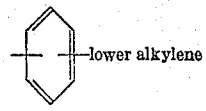
What is claimed is:

1. A dye developer of the formula:



wherein R^1 is selected from the group consisting of hydrogen and acetyl; R^2 is selected from the group consisting of benzene and naphthalene snuclei substituted by two groups the group consisting of hydrogen and —Y—Z; Y is a di-

valent organic linking group selected from the group consisting of lower alkylene, phenylene, and



Z is an aryl nucleus selected from the group consisting of benzene and naphthaleen nuclei substituted by two groups selected from the group consisting of hydroxyl and amino groups, one of said groups being substituted in one of the ortho and para positions with respect to the other of said groups so as to be capable of developing an exposed silver halide emulsion and at least one of said R^2 and R^5 is —Y—Z.

2. 1-acetyl-3β-(2',5' - dihydroxyphenyl) - ethyl-6-β-(2',5'-dihydroxyphenyl)-ethylamino-anthrapyridone.

3. 3-[β-(2',5' - dihydroxyphenyl)-α-methyl]-ethyl-6-]β-(2',5'-dihydroxyphenyl)-α-methyl] - ethylamino - anthrapyridone.

4. 3-[β-(2',5'-dihydroxyphenyl) - α - methyl]-ethyl-6-[4'-β-(2'',5''-dihydroxyphenyl) - ethyl] - anilino-anthrapyridone.

5. 3-[4' - β - (2'',5''-dihydroxyphenyl)-ethyl]-phenyl-6-[β-(2',5'-dihydroxyphenyl)-α-methyl] - ethylamino-anthrapyridone.

6. 3-[4'-β-(2'',5'' - dihydroxyphenyl) - ethyl]-phenyl-6-[4'-β-(2''-5''-dihydroxyphenyl)-ethyl] - anilino-anthrapyridone.

7. The process of preparing 3-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethyl - 6 - [β - (2',5' - dihydroxyphenyl)-α-methyl]-ethylamino-anthrapyridone which comprises acetylating 1,4-bis-[β-(2',5'-dihydroxyphenyl)α-methyl]-ethylamino-anthraquinone by refluxing with acetyl chloride, and internally condensing said last-named compound to effect cyclization thereof, thereby forming said pyrimidone.

8. The process of forming a compound selected from the group consisting of 3-(β-(2',5'-dihydroxyphenyl)-α-methyl] - ethyl-6-[4'-β-(2'',5'' - dihydroxyphenyl)-ethyl]-anilino-anthrapyridone and 3-[4' - β - (2'',5''-dihydroxyphenyl)-ethyl]-phenyl - 6 - [β-(2',5'-dihydroxyphenyl)-α-methyl]-ethylamino-anthrapyridone which comprises refluxing quinizarin with amino-phenethyl-hydroquinone hydrochloride in an inert atmosphere; refluxing the resulting product with β-(2,5-dihydroxyphenyl) - α - methyl-ethylamine hydrobromide in an inert atmosphere to form a 1,4-bis-substituted anthraquinone dye developer, acetylating said dye developer by refluxing with acetyl chloride; and condensing the acetylated reaction product to effect cyclization thereof, thereby forming an isomeric mixture comprising 3-[β-(2',5'-dihydroxyphenyl) - α - methyl]-ethyl-6 [β-(2',5'-dihydroxyphenyl) - α - methyl]-ethylamino - anthrapyridone and 3-[β-(2',5'-dihydroxyphenyl)-α-methyl]-ethyl - 6 - [4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-anilino-anthrapyridone.

9. The process which comprises acetylating 1,4-bis-[4'-β-(2'',5'' - dihydroxyphenyl) - ethyl]-anilino-anthraquinone to form 1,4-bis-(2',5'-diacetoxy)-phenethyl-acetanilido-anthraquinone and condensing said last-named compound, thereby effecting cyclization thereof, to form 3-[4'-β-(2'',5''-dihydroxyphenyl)-ethyl] - phenyl - 6[4'-β-(2'',5''-dihydroxyphenyl)-ethyl]-anilino-anthrapyridone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,644,821 Peter et al. ---------- July 7, 1953

FOREIGN PATENTS

525,091 Great Britain ---------- Aug. 21, 1940

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,076,808 February 5, 1963

Elkan R. Blout et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 41, for "absorp" read -- absorb --; column 8, line 41, after "September 25, 1956" insert -- , now U. S. Patent No. 3,019,107 --; lines 42 and 43, strike out ", now U. S. Patent No. 3,019,107 --; column 10, line 66, for "542" read -- 532 --; column 14, line 17, for "Hydroxy" read -- Hydroxyethyl --; column 16, line 74, for "benzene and naphthalene snuclei substituted by two groups" read -- hydrogen, lower alkyl and -Y-Z; R^5 is selected from --; column 17, line 10, for "naphthaleen" read -- naphthalene --; column 18, line 4, for "3-(β-" read -- 3-[β- --.

Signed and sealed this 26th day of November 1963.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWIN L. REYNOLDS

Acting Commissioner of Patents