United States Patent Office 3,047,386 Patented July 31, 1962

3,047,386

ANTHRAQUINONE DYE DEVELOPERS

Elkan R. Blout, Belmont, and Myron S. Simon, Newton Center, Mass., assignors to Polaroid Corporation, Cambridge, Mass., a corporation of Delaware

No Drawing. Filed Aug. 26, 1957, Ser. No. 680,437
22 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 colored developing agents are used to develop a latent image.

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

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

A further object is to provide novel compounds which are useful as intermediates and color-providing materials.

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 novel photographic developing agents employed in this invention possess the properties of both dye and a developing agent; thus they may be referred to as dye developers. The nature of these dye developers will be described hereinafter.

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

The copending application of Howard G. Rogers, Serial No. 415,073, filed March 9, 1954, now abandoned and replaced by a continuation-in-part thereof, Serial No. 748,421, filed July 14, 1958, which issued May 9, 1961 as U.S. Patent No. 2,983,606, discloses diffusion transfer-reversal processes wherein a photographic negative material such as a photographic element comprising an exposed silver halide emulsion layer containing a latent image, is processed, using a dye developer, to impart to an image-receiving element a reversed or positive dye image of said latent image by permeating into said emulsion layer a suitable liquid processing composition and bringing said emulsion layer into superposed relationship with an appropriate image-receiving layer. It is an object of this invention to provide additional dye developers suitable for use in such processes.

In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on a sheetlike support element, which may be utilized as an image-

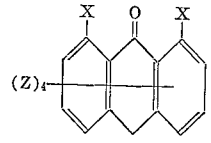
receiving element. In a preferred embodiment, the photosensitive element contains a layer of dye developer, and the liquid processing composition is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed position with an image-receiving element. It is also within the scope of this invention to apply the liquid processing composition prior to exposure, in accordance with the disclosure in the copending application of Edwin H. Land, Serial No. 498,672, filed April 1, 1955. The liquid processing composition permeates the emulsion to provide a solution of dye developer substantially uniformly distributed therein. As the latent image 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, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation, and especially as regards its solubility in alkaline solution. 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 or element, said transfer substantially excluding silver or oxidized dye developer. Under certain circumstances, the layer of the liquid processing composition may be utilized as the image-receiving layer. The latter element 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 image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the diffused dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. Imbibition periods of approximately one minute have been found to give good results, but this contact period may be adjusted where necessary to compensate for variations in temperature or other conditions. The desired positive image is revealed by stripping the image-receiving element from the photosensitive element 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 element 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 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, concentrations as low as 0.2% in the liquid processing composition being suitable in certain instances.

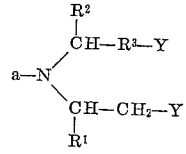
The liquid processing composition above referred to comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate, and may contain the dye developer.

In some instances, it may contain a minor amount of a conventional 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 the film-forming material of the type which, when said composition is spread and dried, 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.

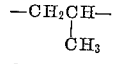
The novel dye developers of this invention may be represented by the formula:



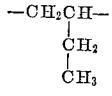
wherein each X is a hydrogen, alkyl, alkoxy, halogen, or nitro group or



radical, provided that at least one X and not more than two X's are said radicals; each Y is an unsubstituted, alkyl-substituted, or halogen-substituted ortho or para dihydroxyphenyl group; R^1 is a hydrogen, methyl or ethyl group; R^2 is a hydrogen or alkyl group and preferably an alkyl group containing no more than 5 carbon atoms such as methyl, ethyl, propyl, etc. groups; R^3 is an alkylene group and preferably an alkylene group containing no more than 5 carbon atoms such as methylene $—CH_2—$, ethylene $—CH_2CH_2—$, propylene $—CH_2CH_2CH_2—$, isopropylene

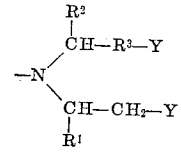


1,4-butylene $—CH_2CH_2CH_2CH_2—$, 1,2-butylene

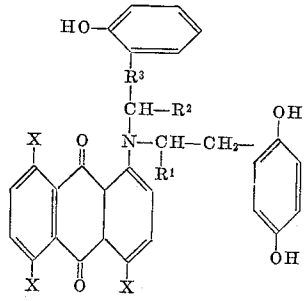


etc. groups; and each Z may be hydrogen, a sulfo, carboxyl, cyano, halogen, alkyl, aryl, aryloxy, alkoxy, sulfonamido or carboxamido group.

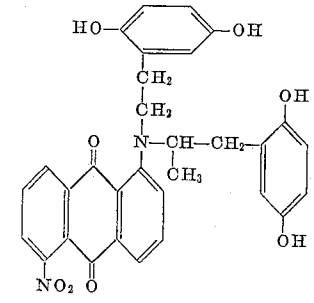
In a preferred embodiment, X in the one position is a



radical and each Y is a p-dihydroxyphenyl group. Such compounds may be presented by the formula:



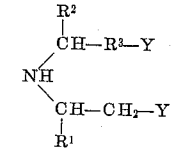
The preferred dye developer of this invention is



1-[α-methyl-β,β'-bis(2',5'-dihydroxyphenyl)-diethylamino]-5-nitroanthraquinone

The novel compounds of this invention may be prepared by condensing a suitable halogen or nitro-substituted anthraquinone with an amine of the structure

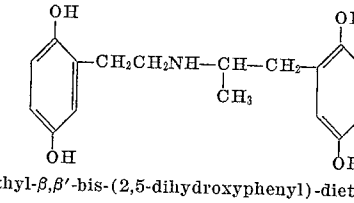
(A)



or a salt thereof, wherein Y, R^1, R^2 and R^3 have the same meaning as above. As examples of suitable halogen and nitro-substituted anthraquinones useful in preparing the dye developers of this invention, mention may be made of 1-nitroanthraquinone, 1,5-dinitroanthraquinone, 1,8-dinitroanthraquinone, 1-chloroanthraquinone and 1,4-dichloroanthraquinone.

Amines within Formula A may be prepared by the processes disclosed in the copending application of Elkan R. Blout, Milton Green and Myron S. Simon, Serial No. 680,405, filed August 26, 1957, now U.S. Patent No. 2,949,359 issued August 16, 1960.

As an example of such an amine, mention may be made of:



α-Methyl-β,β'-bis-(2,5-dihydroxyphenyl)-diethylamine

It should be noted that it is within the scope of this invention to use a mixture of the novel dye developers of this invention in the processes herein disclosed. Thus, in certain instances it is unnecessary to separate a mixture of mono and disubstituted material which may be produced as a result of the synthesis, or to remove residual alkali-insoluble starting materials.

The following nonlimiting example illustrates the preparation of a novel dye developer of this invention.

Example 1

0.75 gm. of 1,5-dinitroanthraquinone, 4.8 gms. of α-methyl-β,β'-bis-(2,5-dihydroxyphenyl)-diethylamine hydrobromide and 1.06 gms. of sodium acetate are dissolved in 8 cc. of pyridine and 1 cc. of water. The solution is deaerated with nitrogen and refluxed for five hours. The solution becomes magenta almost immediately and then turns red after about a half hour. At the end of the reflux period, the product is precipitated with dilute hydrochloric acid, filtered, and washed with water. The precipitate is purified by dissolving it in methyl Cellosolve and precipitating with water. After repeating the purification step two additional times, 1-[-α-methyl-β,β'-bis-(2',5'-dihydroxyphenyl)diethylamino] - 5 - nitro-anthra-

quinone, exhibiting an absorption maximum, in dimethylformamide, at 500 mu, ϵ=13,500, is obtained, possibly mixed with unreacted 1,5-dinitro-anthraquinone.

The following nonlimiting example illustrates the use of a dye developer in the processes of this invention.

Example 2

A photosensitive element is prepared by coating a gelatin-coated film base with a solution comprising 3% of 1-[α-methyl - β,β' - bis-(2',5'-dihydroxyphenyl)-diethylamino]-5-nitro-anthraquinone (as prepared in Example 1) and 4% cellulose acetate hydrogen phthalate dissolved in an 80:20, by volume, solution of acetone and tetrahydrofuran. After this coating has dried, a silver iodobromide emulsion is applied thereon. This photosensitive element is exposed and processed by spreading an aqueous liquid processing composition comprising:

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

between said photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element comprises a cellulose acetate-coated baryta paper which has been coated with a 4% solution of Nylon Type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware, for N-methoxymethyl polyhexamethylene adipamide) in isopropanol. After an imbibition period of approximately one minute, the image-receiving element is separated and contains a salmon pink positive image of the photographed subject.

It should be noted that certain dye developers are sensitive to pH changes. Since the dye developer is rendered effective by solution in an aqueous alkaline processing composition, it accordingly is necessary to assure that the environment in which the transferred and unreacted dye developer is deposited has or is capable of attaining the requisite pH affording the desired color to the diffused dye developer. This may be accomplished by use of a volatile basic compound such as diethylamine in the liquid processing composition. If sodium hydroxide is utilized in the processing liquid, it becomes carbonated after processing and by contact with the air and this is effective to provide the desired pH change. Further control of the pH of the transferred and unreacted dye developer may be had by utilizing an image-receiving element which is difficultly penetrable by alkali, for example an appropriate nylon such as N-methoxymethyl polyhexamethylene adipamide, or by the use of a receiving element in which an acid or an acid-forming compound, e.g., oleic acid, has been incorporated.

It will be noted that the liquid processing composition may, and in the above example does, contain a small amount of an auxiliary or accelerating developer, such as Metol, amidol, benzylaminophenol, or a 3-pyrazolidone, such as 1-phenyl-3-pyrazolidone (Phenidone). The preferred auxiliary developer is 1-phenyl-3-pyrazolidone. This auxiliary developer serves to accelerate and possibly initiate the action of the dye developer. A portion of the dye developer may be oxidized by an energy transfer reaction with oxidized auxiliary developer.

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 to 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 invention 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 involving the oxidized developing agent.

It should be noted that it is within the scope of this invention to use mixtures of dye developers to obtain a desired color.

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 the U.S. Patent No. 2,647,049 to Edwin H. Land.

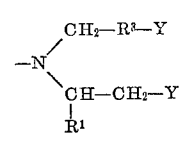
The inventive concepts herein set forth are also adaptable for the formation of colored images in accordance with the photographic products and processes described and claimed in the copending application of Edwin H. Land, Serial No. 448,441, filed August 9, 1954, now U.S. Patent 2,968,554 issued January 17, 1961, and also the copending application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956.

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, as well as the use of a single black dye developer.

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

What is claimed is:

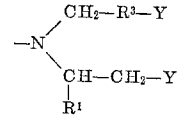
1. A photographic developer composition comprising an aqueous alkaline solution containing at least one auxiliary silver halide developing agent and a dye developer having an anthraquinone nucleus, at least one and not more than two of the nuclear carbon atoms in the one, four, five and eight positions of said anthraquinone nucleus having linked directly thereto a group of the formula:



wherein R^1 is selected from the group consisting of methyl and ethyl groups, R^3 is an alkylene group containing less than six carbon atoms and each Y is selected from the group consisting of ortho- and para-dihydroxyphenyl radicals.

2. A photographic developer composition comprising an aqueous alkaline solution containing at least one auxiliary silver halide developer agent and a dye developer having an anthraquinone nucleus, the nuclear carbon in

the one position of said anthraquinone nucleus having directly linked thereto a group of the formula:



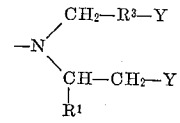
wherein R^1 is selected from the group consisting of methyl and ethyl groups, R^3 is an alkylene group containing less than six carbon atoms and each Y is selected from the group consisting of ortho- and para-dihydroxyphenyl radicals.

3. A photographic developer composition as defined in claim 2 wherein each Y is a para-dihydroxyphenol group.

4. A photographic developer composition as defined in claim 3 wherein R^1 is a methyl group.

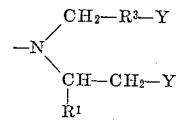
5. A photographic developer composition comprising an aqueous alkaline solution containing at least one auxiliary silver halide developing agent and 1-[α-methyl-β,β'-bis-(2',5'-dihydroxyphenyl)-diethylamino]-5-nitro-anthraquinone.

6. A photographic product comprising a plurality of layers including a silver halide emulsion layer and a layer, contiguous with said silver halide emulsion layer, containing a dye developer having an anthraquinnone nucleus, at least one and not more than two of the nuclear carbon atoms in the one, four, five and eight positions of said anthraquinone nucleus having linked directly thereto a group of the formula:



wherein R^1 is selected from the group consisting of methyl and ethyl groups, R^3 is an alkylene group containing less than six carbon atoms and each Y is selected from the group consisting of ortho- and para-dihydroxyphenyl radicals.

7. A photographic product comprising a plurality of layers including a silver halide emulsion layer and a layer, contiguous with said silver halide emulsion, containing a dye developer having an anthraquinone nucleus, the nuclear carbon in the one position of said anthraquinone nucleus having directly linked thereto a group of the formula:



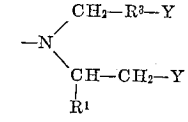
wherein R^1 is selected from the group consisting of methyl and ethyl groups, R^3 is an alkylene group containing less than six carbon atoms and each Y is selected from the group consisting of ortho- and para-dihydroxyphenyl radicals.

8. A photographic product as defined in claim 7 wherein each Y is a para-dihydroxyphenyl group.

9. A photographic product as defined in claim 7 wherein R^1 is a methyl group.

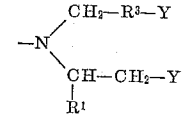
10. A photographic product comprising a plurality of layers including a silver halide emulsion layer and a layer, contiguous with said silver halide emulsion layer, containing 1-[α-methyl-β,β'-bis-(2',5'-dihydroxphenyl) - diethylamino]-5-nitro-anthraquinone.

11. In a process of forming a photographic image in color, the steps which comprise developing an exposed silver halide emulsion with an aqueous alkaline solution containing a dye developer having an anthraquinone nucleus, at least one and not more than two of the nuclear carbon atoms in the one, four, five and eight positions of said anthraquinone nucleus having linked directly thereto a group of the formula:



wherein R^1 is selected from the group consisting of methyl and ethyl groups, R^3 is an alkylene group containing less than six carbon atoms and each Y is selected from the group consisting of ortho- and para-dihydroxyphenyl radicals, providing as a function of the development an image-wise distribution of unoxidized dye developer in undeveloped areas of said emulsion, and transferring at least part of said distribution of said unoxidized dye developer, by imbibition, from said emulsion to an image-receiving layer in superposed relationship with said emulsion to impart to said image-receiving layer a positive dye image.

12. In a process of forming a photographic image in color, the steps which comprise developing an exposed silver halide emulsion with an aqueous alkaline solution containing a dye developer having an anthraquinone nucleus, the nuclear carbon in the one position of said anthraquinone nucleus having directly linked thereto a group of the formula:



wherein R^1 is selected from the group consisting of methyl and ethyl groups, R^3 is an alkylene group containing less than six carbon atoms and each Y is selected from the group consisting of ortho- and para-dihydroxyphenyl radicals, providing as a function of the development an image-wise distribution of unoxidized dye developer in undeveloped areas of said emulsion, and transferring at least part of said distribution of said unoxidized dye developer, by imbibition, from said emulsion to an image-receiving layer in superposed relationship with said emulsion to impart to said image-receiving layer a positive dye image.

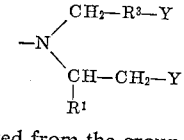
13. A process as defined in claim 12 wherein each Y is a para-dihydroxyphenyl group.

14. A process as defined in claim 12 wherein R^1 is a methyl group.

15. A process as defined in claim 12 wherein said dye developer is 1-[α-methyl-β,β'-bis(2',5'-dihydroxyphenyl)-diethylamino]-5-nitro-anthraquinone.

16. A process as defined in claim 12 wherein said aqueous alkaline solution contains a small amount of an auxiliary silver halide developing agent.

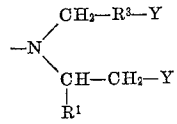
17. A process of developing an exposed photosensitive silver halide emulsion which comprises developing an exposed silver halide emulsion with an aqueous alkaline processing solution containing a dye developer having an anthraquinone nucleus, at least one and not more than two of the nuclear carbon atoms in the one, four, five and eight positions of said anthraquinone nucleus having linked directly thereto a group of the formula:



wherein R^1 is selected from the group consisting of methyl and ethyl groups, R^3 is an alkylene group containing less than six carbon atoms and each Y is selected from the group consisting of ortho- and para-dihydroxyphenyl radicals.

18. A process of developing an exposed photosensitive silver halide emulsion which comprises developing said exposed silver halide emulsion with an aqueous alkaline processing solution containing a dye developer having an

anthraquinone nucleus, the nuclear carbon atom in the one position of said anthraquinone nucleus having directly linked thereto a group of the formula:



wherein R^1 is selected from the group consisting of methyl and ethyl groups, R^3 is an alkylene group containing less than six carbon atoms and each Y is selected from the group consisting of ortho- and para-dihydroxyphenyl radicals.

19. A process as defined in claim 18 wherein each Y is a para-dihydroxyphenyl group.

20. A process as defined in claim 18 wherein R^1 is a methyl group.

21. A process of developing an exposed photosensitive silver halide emulsion which comprises developing said exposed silver halide emulsion with an aqueous alkaline processing solution containing 1-[α-methyl-β,β'-bis-(2',5'-dihydroxyphenyl)-diethylamino]-5-nitro - anthraquinone.

22. A process as defined in claim 18 wherein said aqueous alkaline solution contains a small amount of an auxiliary silver halide developing agent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,132,169	Kumetat	Oct. 4, 1938
2,206,126	Schinzel	July 2, 1940
2,292,306	Vittum et al.	Aug. 4, 1942
2,353,010	Buxbaum	July 4, 1944
2,434,765	Grossmann	Jan. 20, 1948
2,698,244	Land	Dec. 28, 1954
2,710,804	Schenk	June 14, 1955
2,774,668	Rogers	Dec. 18, 1956
2,892,710	Cohler et al.	June 30, 1959
2,983,605	Corley	May 9, 1961
2,983,606	Rogers	May 9, 1961

UNITED STATES PATENT OFFICE

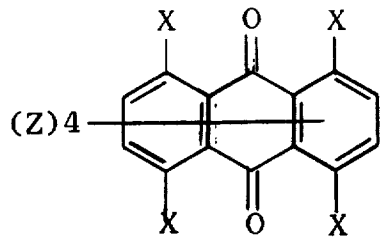
CERTIFICATE OF CORRECTION

Patent No. 3,047,386 July 31, 1962

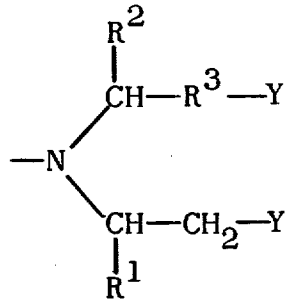
Elkan R. Blout et al.

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.

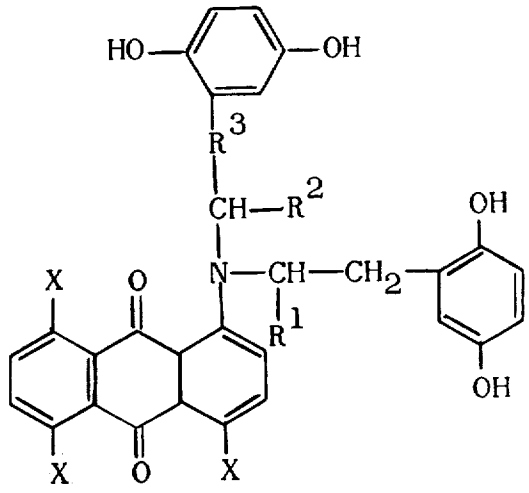
Column 3, lines 18 to 23, the formula should appear as shown below instead of as in the patent:



line 25, for "nitro group or" read -- nitro group or a --; lines 26 to 32, the formula should appear as shown below instead of as in the patent:



same column 3, lines 61 to 75, the formula should appear as shown below instead of as in the patent:



column 6, line 74, for "developer", first occurrence, read -- developing --; column 7, line 15, for "para-dihydroxyphenol" read -- para-dihydroxyphenyl --.

Signed and sealed this 17th day of September 1963.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents