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3,288,778

AZO AND ANTHRAQUINONE DYE DEVELOPERS

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No Drawing. Filed Oct. 5, 1964, Ser. No. 401,714
13 Claims. (Cl. 260—163)

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

This application is in part a continuation of our copending U.S. application Serial No. 1,442, filed January 11, 1960 (now abandoned) which in turn is in part a continuation of application Serial No. 471,542, filed November 26, 1954 (now abandoned).

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 developing 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 photographic 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.

U.S. Patent No. 2,983,606, issued to Howard G. Rogers on May 9, 1961, discloses diffusion-transfer reversal 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 layer a suitable liquid processing composition and bringing said emulsion into superposed relationship with an appropriate image-receiving layer. The inventive concepts herein set forth provide novel dye developers for use in such processes.

In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on an image-receiving element. In a preferred embodiment, the photosensitive element contains a layer of dye developer, and the liquid processing composition is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed position with an image-receiving element. It is also within the scope of this invention to apply the liquid processing composition prior to exposure, in accordance with the disclosure in U.S. Patent No. 3,087,816. 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 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 layer from the silver halide emulsion at the end of the imbibition period.

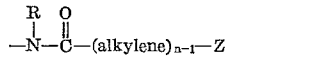
The dye developers of this invention may be utilized in the photosensitive element, for example, in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer 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 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. In an especially useful mode of dispersing 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 which is used in the process

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 compounds of the present invention comprise dyes, preferably azo, anthraquinone, indophenol, indoaniline, and azomethine dyes, characterized in that they contain at least one and preferably not more than two groups of the formula:

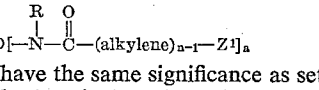
(1)



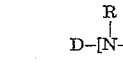
wherein n is a positive integer from 1 to 2; R represents hydrogen or an alkyl group, preferably a lower alkyl group comprising from 1 to 5 carbon atoms, inclusive, for example, methyl, ethyl, etc.; and Z is a benzenoid developing group, preferably comprising an aryl nucleus selected from the group consisting 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, the aromatic nucleus of Z may contain other substituents, e.g., halo, lower alkyl, lower alkoxy, etc.

The preferred compounds may be represented by the formula:

(2)



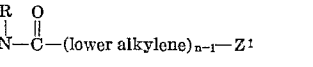
wherein n and R have the same significance as set forth in regard to Formula 1; a is 1 or 2; and D represents the radical of a dye molecule



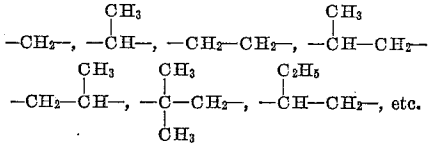
wherein a has the same significance as previously noted and most preferably wherein D comprises an anthraquinone or azo system; and Z^1 is a benzene nucleus substituted by hydroxyl or amino groups ortho or para to one another, e.g., o- or p-dihydroxyphenyl, o- or p-hydroxyanilino, etc., and halo, lower alkyl and lower alkoxy derivatives thereof.

One preferred group of compounds comprises azo and anthraquinone dyes having one or two groups of the formula:

(3)



wherein the lower alkylene moiety comprises 1–6 carbon atoms, e.g.,



Depending upon whether an azo or an anthraquinone dye developer is contemplated, the group of Formula 3 is preferably bonded to a carbon atom of an azo dye molecule or contained in a substituent bonded directly to a nuclear carbon atom of an anthraquinone dye nucleus. In the latter case, the group may comprise the entire substituent so bonded to the anthraquinone nucleus, or it may be but a part of the said substituent, as exemplified in the illustrative compounds recited hereinafter.

The novel compounds of this invention, as noted above, are dye developers which contain not less than one and not more than two benzenoid developing groups. A preferred silver halide developing group comprises a hydroquinonyl group. Other suitable developing groups include orthodihydroxyphenyl 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. Preferred aromatic developing groups which form quinonoid or quinone oxidation products comprise aryl nuclei selected from the group consisting of benzene and naphthalene nuclei substituted by at least two groups selected from the group consisting of hydroxyl and amino groups so as to be capable of developing an exposed silver halide emulsion.

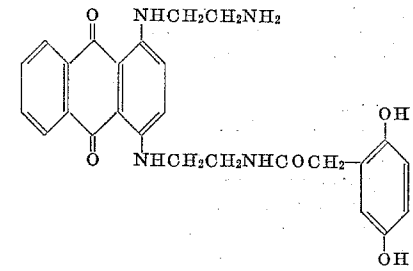
Experience has indicated that in the most useful dye developers the term "alkylene" represents lower alkylene groups such as a methylene group, and preferably a lower alkylene group comprising from 1 to 5 carbon atoms. It should be noted that the alkylene group may possess either a branched or straight chain configuration and that the number of carbon atoms possessed by the alkylene group is only restricted by the proviso that the resulting dye developer is capable of being dissolved in the liquid processing composition and its oxidation product rendered immobile in the developed emulsion layer.

Although the dye preferably contains not in excess of two groups of Formula 1, it will be recognized that the number of such groups is only limited by the operational functionability of the resultant dye developer. In that the designated groups generally impart increased solubility to the dye molecule, it will be recognized that employment of more than two of such groups may be desirable where increased solubility of the resultant dye developer molecule is intended. For example, a dye molecule which is initially insoluble in the fluid processing composition may be made soluble therein by the employment of a sufficient number of the designated groups. It must be noted, however, that the number of groups employed must be so balanced as to provide a dye developer soluble in the fluid processing composition, the oxidation product of which is rendered immobile in the exposed areas of the photosensitive element.

The term "amino," as used above, is intended to include substituted amino groups, for example, alkylamino and arylamino groups. It will be recognized that the substituents on the amino groups preferably comprise radicals which provide little or no decrease in the silver halide developing function of the amino groups.

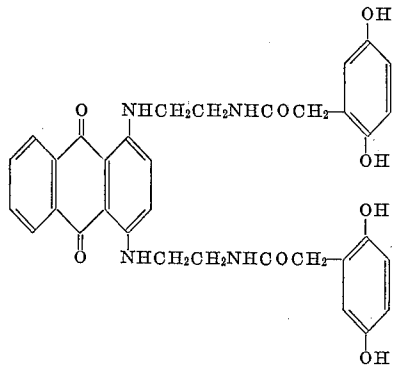
As examples of dye developers within the scope of the present invention, mention may be made of:

(I)



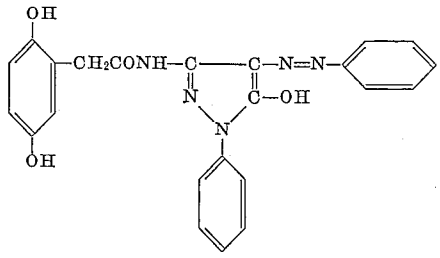
1-β-aminoethylamino-4-β-(homogentisamido)-ethylamino-anthraquinone

(II)



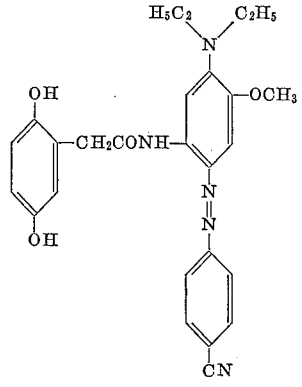
1,4-bis-β-(homogentisamido)-ethylamino-anthraquinone

(III)



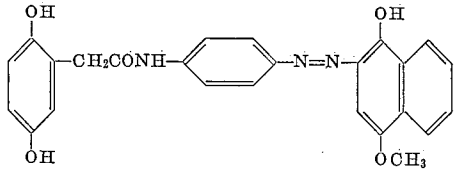
3-homogentisamido-1-phenyl-4-phenylazo-5-pyrazolone

(IV)



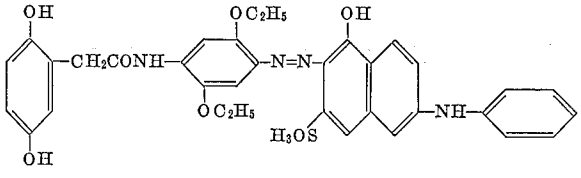
4-(p-cyanophenylazo)-5-homogentisamido-2-methoxy-N,N-diethylaniline

(V)



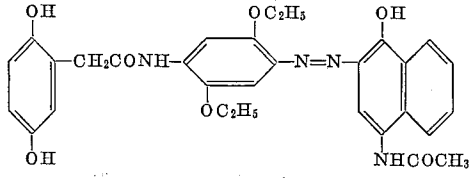
2-(p-homogentisamido-phenylazo)-4-methoxy-1-naphthol

(VI)



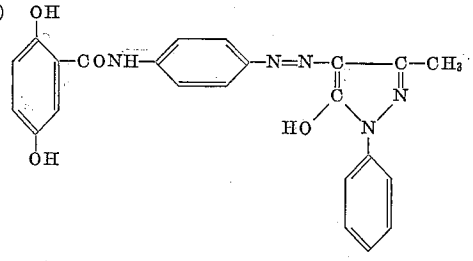
6-anilino-2-(2′,5′-diethoxy-4′-homogentisamido-phenylazo)-1-naphthol-3-sulfonic acid

(VII)



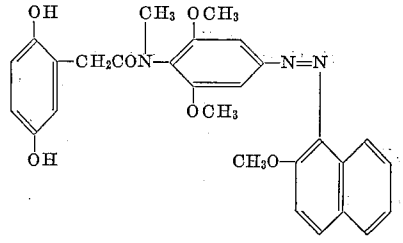
4-acetamido-2-(2′,5′-diethoxy-4′-homogentisamido-phenylazo)-1-naphthol

(VIII)



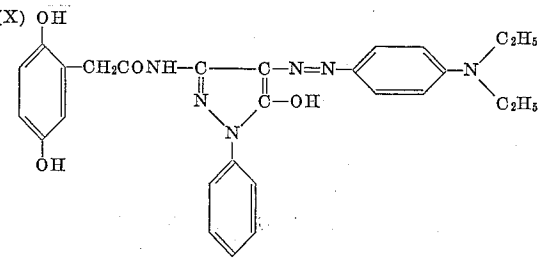
4-(p-gentisamido-phenylazo)-3-methyl-1-phenyl-5-pyrazolone

(IX)



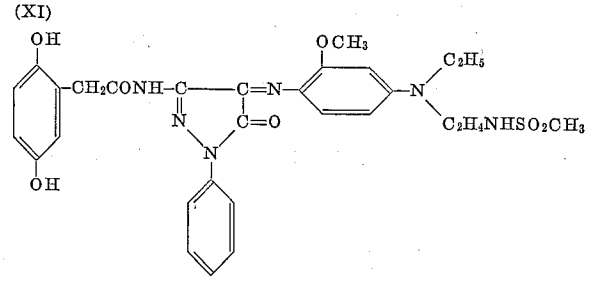
1-(2′,5′-dimethoxy-4′-[N-methyl-homogentisamido]-phenylazo)-2-methoxy-naphthalene

(X)



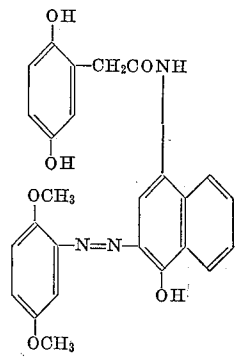
4-(4′-[N,N-diethylamino]-phenylazo)-3-homogentisamido-1-phenyl-5-pyrazolone

(XI)



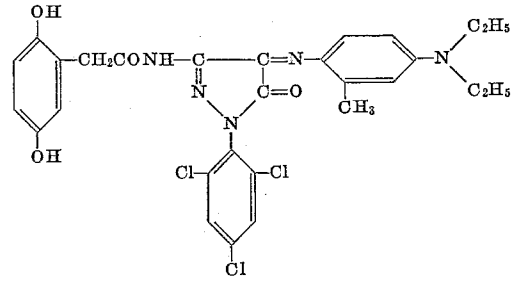
4-(4′-[N-ethyl-N-(β-[methylsufonamido]-ethyl) - amino] - 2′-methoxy - phenylimino) - 3 - homogentisamido-1-phenyl-5-pyrazolone

(XII)



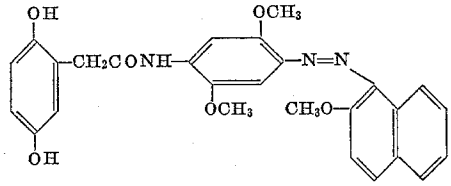
2-(2′,5′-dimethoxyphenylazo)-4-homogentisamido-1-naphthol

(XIII)



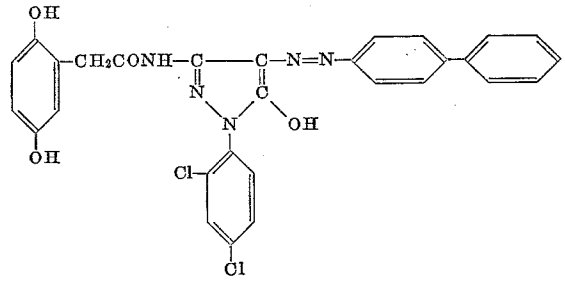
4-(4'-[N,N-diethylamino]-2'-methyl-phenylimino)-3-homogentisamido-1-(2',4',6'-trichlorophenyl)-5-pyrazolone

(XIV)



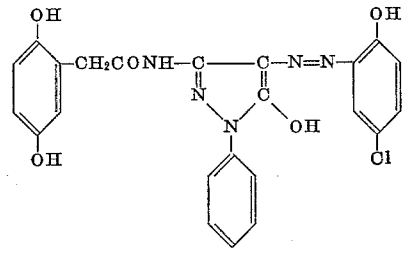
1-(2',5'-dimethoxy-4'-homogentisamido-phenylazo)-2-methoxy-naphthalene

(XV)



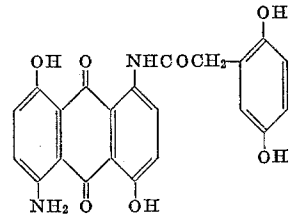
4-biphenylazo-3-homogentisamido-1-(2',4',6'-trichlorophenyl)-5-pyrazolone

(XVI)



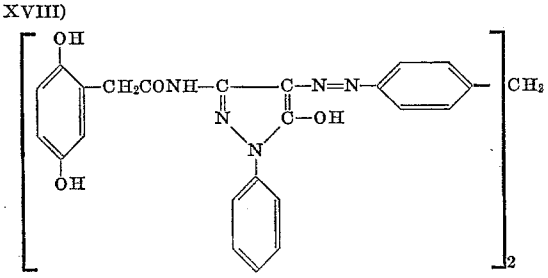
4-(5'-chloro-2'-hydroxy-phenylazo)-3-homogentisamido-1-phenyl-5-pyrazolone

(XVII)



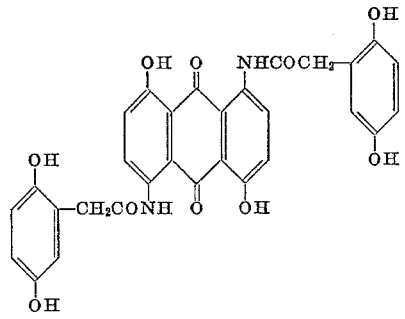
5-amino-4,8-dihydroxy-1-homogentisamido-anthraquinone

XVIII)



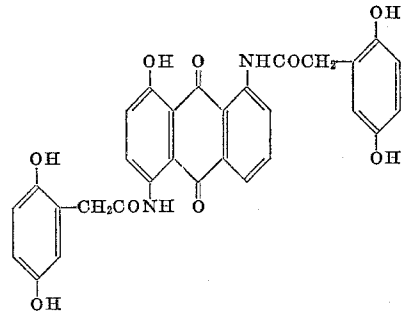
Bis-(4-[3'-homogentisamid-1'-phenyl-5'-pyrazolone-4'-azo]-phenyl)-methane

(XIX)



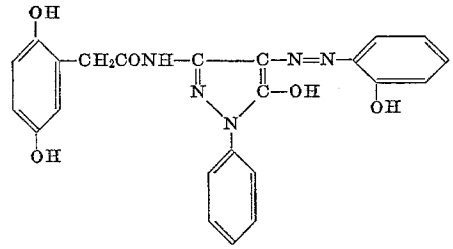
1,5-bis-homogentisamido-4,8-dihydroxy-anthraquinone

(XX)



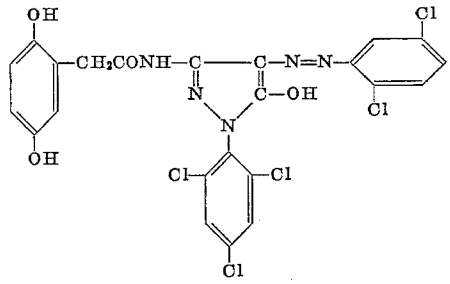
1,5-bis-homogentisamido-anthraquinone

(XXI)



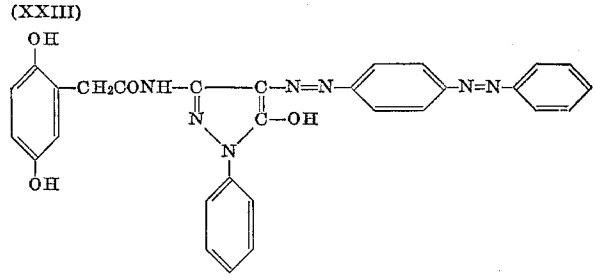
3-homogentisamido-4-(2'-hydroxyphenylazo)-1-phenyl-5-pyrazolone

(XXII)



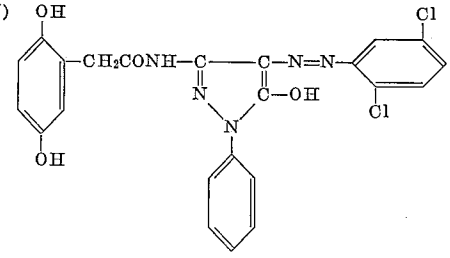
4-(2',5'-dichlorophenylazo)-1-(2',4',6'-trichlorophenyl)-3-homogentisamido-5-pyrazolone

(XXIII)



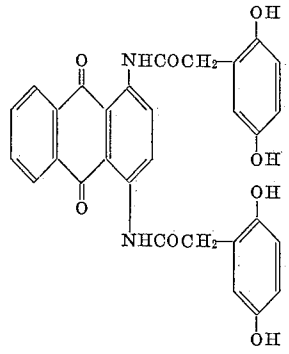
3-homogentisamido-4-(p-phenylazo-phenylazo)-1-phenyl-5-pyrazolone

(XXIV)



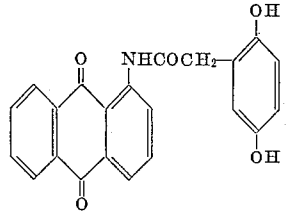
4-(2',5'-dichlorophenylazo)-3-homogentisamido-1-phenyl-5-pyrazolone

(XXV)



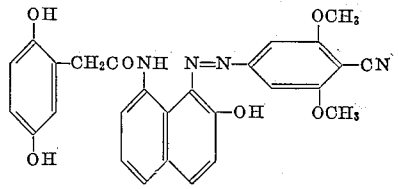
1,4-bis-homogentisamido-anthraquinone

(XXVI)



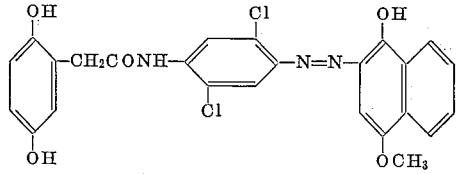
1-homogentisamido-anthraquinone

(XXVII)



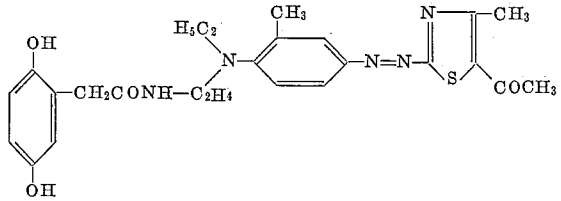
1-(4'-cyano-2',5'-dimethoxy-phenylazo)-8-homogentisamido-2-naphthol

(XXVIII)



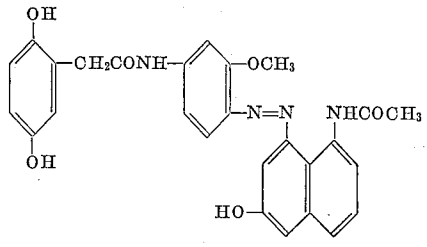
2-(2',5'-dichloro-4'-homogentisamido-phenylazo)-4-methoxy-1-naphthol

(XXIX)



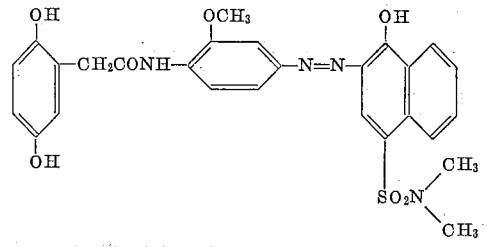
2-(4'-[N-(β-homogentisamido-ethyl)-N-ethyl]-2'-methyl-phenylazo)-4-methyl-5-acetyl-thiazole

(XXX)



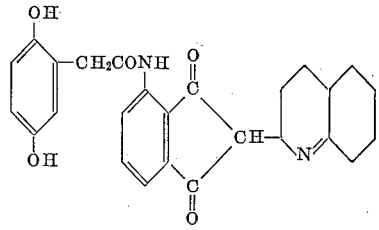
8-acetamido-1-(4'-homogentisamido-2'-methoxy-phenylazo)-2-naphthol

(XXXI)



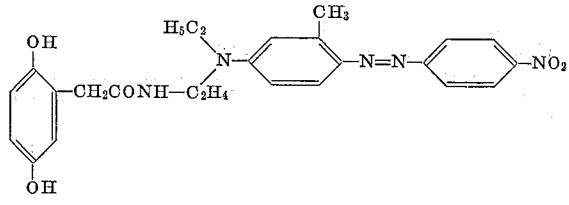
2-(4'-homogentisamido-2'-methoxy-phenylazo)-4-(N,N-dimethylsulfamyl)-1-naphthol

(XXXII)



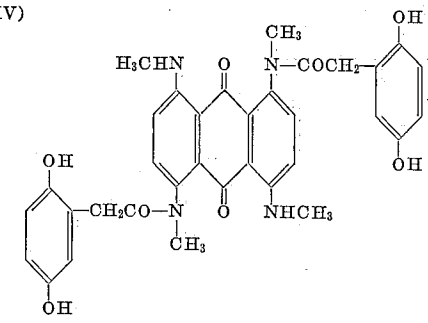
3'-homogentisamido-quinophthalone

(XXXIII)



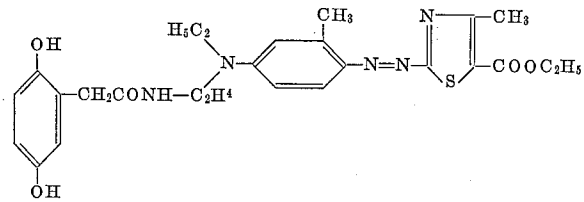
N-ethyl-N-(β-homogentisamido-ethyl)-3-methyl-4-(p-nitro-phenylazo)-aniline

(XXXIV)



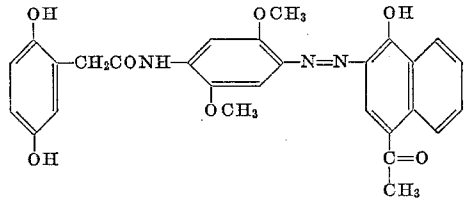
5,8-dimethylamino-1,5-bis-(N-methyl-homogentisamido)-anthraquinone

(XXXV)



2-(4'-[N-(β-homogentisamido-ethyl)-N-ethyl]-2'-methyl-phenylazo)-4-methyl-5-carbethoxy-thiazole

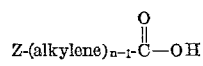
(XXXVI)



2-(4'-homogentisamido-2',5'-dimethoxy)-4-aceto-1-naphthol

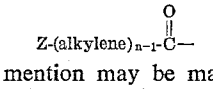
One method of preparing the novel dye developers of this invention, designated throughout the specification as procedure (A), comprises reacting a dye, preferably an azo, anthraquinone, indophenol, indoaniline, or azomethine dye, having not less than one and preferably not more than two reactive primary or secondary amino groups with a suitable derivative of a compound such as set forth in the formula:

(4)



as, for example, the corresponding lactone or acid halide, preferably the acid chloride. In this formula Z and n have the same significance as previously set forth. However, where a dye has more than two available reactive hydroxyl or primary or secondary amino groups, reaction may occur at two or more of such groups.

As examples of suitable compounds, within Formula 4, from which



may be derived, mention may be made of the following: gentisic acid, homogentisic acid, 2,5-dihydroxyhydrocinnamic acid, homogentisic acid lactone, 2,3-diaminobenzoic acid, 2,5-diaminobenzoic acid, 3-amino-2-hydroxybenzoic acid, 5-amino-2-hydroxybenzoic acid, 2,3-dihydroxybenzoic acid, β-2,5-dihydroxyphenylpropionic acid, β-2,5-dihydroxyphenylpropionic acid lactone, etc.

When reacting some of the above compounds with amino-substituted dyes, it is preferred to protect the hydroxyl or amino groups in Z which provide the developing function in order to avoid undesirable side reactions; this may be accomplished by acylation, for example, by reaction with an alkyl or aryl chloroformate to form carboalkoxyl deivatives.

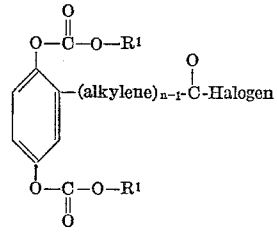
As examples of alkyl and aryl chloroformates available to provide suitable protection, mention may be made of: methyl chloroformate, ethyl chloroformate, n-propyl chloroformate, n-butyl chloroformate, benzyl chloroformate, phenyl chloroformate, etc.

After reaction, and prior to photographic use, the protective groups are removed, as for example, by hydrolysis in the presence of alkali.

Examples of protected compounds include homogentisic acid chloride dibenzoate and 2,5-dicarbomethoxygentisyl chloride. It will be apparent that one advantage of using homogentisic acid lactone is that it is unnecessary to further protect the hydroxyl groups and hence no hydrolysis step is necessary.

The preferred protected derivatives comprise compounds of the general formula:

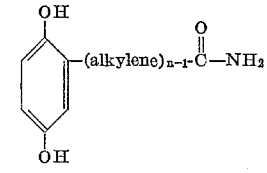
(5)



wherein each R^1 is an alkyl group, preferably a lower alkyl group such as methyl, ethyl, etc.; n has the same significance as previously noted; and the halogen radical comprises preferably a chlorine radical.

A second method of preparing the compounds of Formula 5 comprises reacting a compound of the formula:

(6)



wherein n has the same significance as in Formula 1; for example, gentisamide, homogentisamide, etc., with an alkyl chloroformate, such as for example, one of the aforementioned chloroformates, to form the carboalkoxyl derivatives of said compound.

Treatment of the aforementioned carboalkoxylated amido derivatives with nitrous acid results in the formation of the corresponding free acid.

The acid halide derivatives of the carboalkoxylated free acid, prepared by either of the aforementioned procedures, comprises replacing the hydoxyl group of the free acid's carboxyl group with a suitable halogen radical, such as a chlorine radical, for example, by reacting the free acid with phosphorous trichloride, phosphorous pentachloride, thionyl chloride, etc.

As examples of dyes possessing not less than one and not more than two reactive primary and secondary amino groups, mention may be made of:

1,4-bis-(β-aminoethylamino)-anthraquinone;
1-amino-4-(p-aminoanilino)-2-anthraquinone;
4-amino-azobenzene;
1,4-bis-(p-aminoanilino)-anthraquinone;
1,4-diamino-anthraquinone;
1,4-bis-(p-aminobenzylamino)-anthraquinone;
1-amino-anthraquinone;
1-amino-2-methyl-anthraquinone;
1-N-methylamino-anthraquinone;
1-amino-4-bromo-anthraquinone;
1-methylamino-4-p-aminoanilino-anthraquinone;
1,4-bis-methylamino-anthraquinone;
1-amino-4-acetamido-anthraquinone;
1-amino-4-N-methylamino-anthraquinone;
1,4-diamino-5-nitro-anthraquinone;
1,4-diamino-2-methoxy-anthraquinone;
1,5-diamino-anthraquinone;
1,4-bis-(β-aminoethylamino)-anthraquinone;
3'-amino-quinaphthalone;
3-amino-1-phenyl-4-phenylazo-5-pyrazolone;
3-amino-4-(2',5'-dichlorophenylazo)-1-phenyl-5-pyrazolone;
3-amino-4-(4'-[phenylazo]-phenylazo)-1-phenyl-5-pyrazolone;
3-amino-4-(2',5'-dichlorophenyl)-1-(2',4',6'-trichlorophenylazo)-5-pyrazolone;
3-amino-4-(o-hydroxyphenylazo)-1-phenyl-5-pyrazolone;
1-(2',5'-dimethoxy-4'-[N-methylamino]-phenylazo)-2-methoxy-naphthalene;
3-amino-4-(4'-N-ethyl-N-β-methylsulfonamidoethyl-amino-2'-methoxyphenylimino)-1-phenyl-5-pyrazolone;
1-(2',4',6'-trichlorophenyl)-4-(4'-[N,N-diethylamino]-2'-methyl-phenylimino)-5-pyrazolone;
1-(4'-amino-2',5'-dimethoxy-phenylazo)-2-methoxy-naphthalene;
3-amino-4-biphenylazo-1-(2',4',6'-trichlorophenyl)-5-pyrazolone;
tetramethylamino-anthraquinone; and
4,8-diamino-anthrarufin.

As previously noted, it will be recognized that where a dye has more than two available reactive primary and/or secondary amino groups, reaction may take place at two or more of such amino groups.

Synthetic procedure (A) will be illustrated in greater detail in conjunction with the following specific example which sets out a representative application of this procedure, which, however, is not limited to the details therein set forth and is intended to be illustrative only.

Example (a)

2.00 g. of 4,8-diamino-anthrarufin is dissolved in 100 cc. of o-dichlorobenzene in a flask equipped with an air reflux condenser, a nitrogen gas inlet tube and protected from moisture by a tube of Drierite. The solution is deaerated with nitrogen, brought to a boil and 3.00 g. (1:1 mole ratio) of 2,5-dicarbethoxyhomogentisyl chloride is added under nitrogen. After 20 minutes at the boiling point, the solution is cooled, the product collected, washed with acetone and hexane, and dried. The resultant product comprises 2.50 g. of 5-amino-1-(2',5'-dicarbethoxy-homogentisamido)-4,8-dihydroxy - anthraquinone, blue-black crystals with a bronze reflex. A second crop provided 0.45 g. of the same product.

The first crop above, 2.50 g., is finely ground, added under nitrogen to 110 cc. of hot deaerated water containing 5.0 g. of potassium hydroxide, 2–3 cc. of methanol, and kept at approximately 90° C. for 60 seconds. The mixture is filtered, under nitrogen, into excess dilute acetic acid. The precipitated product is then filtered and washed with water. The product, a deep blue powder, 5 - amino - 4,8 - dihydroxy - 1 - homogentisamido - anthraquinone, Formula XVII, is moderately soluble in acetone and ethanol; very soluble in pyridine and 2% aqueous alkali. The product exhibits a spectral absorption curve which shows a $\lambda_{max.}$ at 612 mμ; ϵ=20,000.

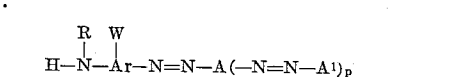
Analysis for $C_{22}H_{16}N_2O_7$ containing 22.3 wt. percent sodium acetate.—Calculated: 7, 55.4; H, 3.9; N, 5.2; Ash, 10.6. Found: C, 55.1; H, 4.4; N, 5.2; Ash, 10.6.

A second synthetic procedure, designated throughout the specification as procedure (B), is concerned with the preparation of specified dye developers within generic Formulae 1 and 2; specifically mono- and diazo dye developers wherein the phrase



set forth in Formula 2 represents the residue of a dye molecule:

(7)

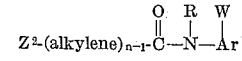


wherein R has the same significance as previously noted; W is a primary amino, a secondary amino, a tertiary amino, or a hydroxyl group in ortho or para position with regard to the azo group; Ar is an aryl group which may be substituted as for example by alkyl, halogen, alkoxy, acid (e.g., carboxyl, sulfo, etc.), sulfonyl, acyl, nitro, or amino groups or a heterocyclic group; p is 0 or 1; and A and A^1 are each the nucleus of a diazotizable aromatic primary amine, e.g., a benzene, naphthalene, diphenyl or heterocyclic nucleus, which nucleus may be the same or different.

As illustrations of suitable aromatic primary amines from which A and A^1 may be derived, mention may be made of any cyclic amine of the benzene, naphthalene, diphenyl or heterocyclic series, which is capable of diazotization. Where a disazo compound is desired, i.e., where p is 1 in the above formula, any cyclic amine of the azobenzene, azonaphthalene, or azoheterocyclic series, as well as azo compounds containing dissimilar nuclei, may be employed in the practice of this invention. The nucleus may be unsubstituted or it may be substituted in any or all positions by any monovalent group, such as for example, hydroxy, alkyl, aryl, aryloxy, halogen, nitro, sulfonyl, acid, acyl, cyano and others. As representative of the many diazotizable amines which can be used as the diazo component in the process of this invention, mention may be made of: 3-nitro-4-chloro-aniline, 2-nitro-4-amino-toluene, 2-chloro-4-aminophenetole, 2-nitro-benzidine, dianisidine, thioaniline, 4,4'-diamino-benzophenone, benzidine-sulfone, beta-amino-anthraquinone, 2-amino-methyl-thiazole, 2-amino-benzothiazole, 2-amino-6-ethoxy-benzothiazole, 5-amino-quinoline, 6-amino-quinoline, ortho-, meta and para-toluidines, -xylidines, -anisidines and -phenetidines, ortho-, meta- and para-chloro (and -bromo-) anilines, 4-chloro-2-amino-toluene, chloro-anisidines and -phenetidines, nitro-toluidines and anisidines such as 2-nitro-4-aminotoluene and 2-nitro-4-amino-anisol, amino-phenyl-sulfones such as 4-amino-phenyl-methyl-sulfone, 3-amino-phenyl-ethyl-sulfone and 4-amino-diphenyl-sulfone, m- and p-amino-acetanilide, 2-, 3- and 4-amino-diphenyl, 2-, 3- and 4-amino-diphenyl ether, o-, m- and p-amino-phenyl-sulfon-dimethyl-amide, o-, m- and p-amino-benzamide, p-amino-acetanilide, 2,5-dimethoxy-aniline, p-anisidine, o-anisidine, alpha-naphthylamine, m-nitro-acetanilide, aniline, m-anisidine, m-amino-acetanilide, 5-amino-1,2,4-triazol, 2-phenyl-4,5-diamino-tetrazol, 1-phenyl-5-amino-triazol, 5-amino-tetrazol, 4,4'-diaminoazobenzene, and 4-amino-1,1'-azobenzene.

We have discovered that these dye developers may be prepared by coupling an appropriate diazonium salt into a compound of the general formula:

(8)

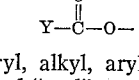


wherein n, R, W, and Ar have the same significance as previously noted; and Z^2 represents the protected derivative of a benzenoid developing group, preferably the acylated derivative thereof, more preferably an o-bis-acyloxyphenyl or a p-bis-acyloxyphenyl group. The protecting or insulating groups are removed prior to photographic utilization of the dye developers, for example, removal of the acyloxy protective groups of Z^2 to effect thereby reconstitution of hydroxyl groups, the removal being accomplished, for example, by hydrolysis in the presence of alkali.

The compounds of Formula 8 are disclosed and claimed in the copending U.S. application of Milton Green, Helen P. Husek and Sidney Kasman, Serial No. 200,639, filed June 7, 1962, and now U.S. Patent No. 3,214,469, a continuation-in-part of Serial No. 709,001, filed January 15, 1958 (now abandoned).

Synthetic procedures of the last-mentioned type are disclosed and claimed in the copending U.S. application of Sidney Kasman and Helen P. Husek, Serial No. 339,615, filed January 23, 1964, a continuation-in-part of Serial No. 75,127, filed December 12, 1960, and now abandoned, which in turn is a continuation-in-part of Serial No. 709,005, filed January 15, 1958, and now abandoned.

The term "acyloxy" is meant to signify the grouping



wherein Y is an aryl, alkyl, aryloxy, or alkoxy group. The terms "alkyl" and "aryl" are intended to signify also substituted aryl and alkyl groups, for example, aralkyl and alkaryl groups.

As examples of compounds within the scope of Formula 8, mention may be made of:

5-(2',5'-bis-carbethoxyphenylacetamido)-2-methoxy-N,N-diethylaniline;

p-(2,5-bis-carbethoxyphenylacetamido)-aniline;

4-(2',5'-bis-carbethoxyphenylacetamido)-2,5-diethoxy-aniline;

3-(2',5'-bis-carbethoxyphenylacetamido)-N,N-diethyl-aniline;

3-(2',5'-bis-carbethoxyphenethylcarboximido)-N,N-diethylaniline;

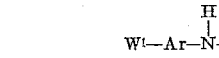
3-(2',5'-bis-carbethoxyphenylacetamido)-N,N-diethyl-naphthylamine;

3-(acetamido-6-(2',5'-bis-carbethoxyphenylacetamido)-N,N-diethylaniline;

3-acetamido-5-(2',5'-bis-carbethoxyphenylacetamido)-N,N-diethylaniline;
2-acetamido-5-(2',5'-bis-carbethoxyphenylacetamido)-N,N-diethylaniline;
2-(2',5'-bis-carbethoxyphenylacetamido)-5-methylsulfonyl-N,N-diethylaniline; and
3-(2',5'-bis-carbethoxyphenylacetamido)-5-methylsulfonyl-N,N-diethylaniline.

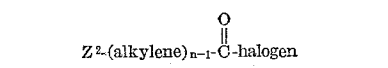
One method of preparing the compounds of Formula 8 comprises reacting a compound of the formula:

(9)



wherein R and Ar have the same significance as noted in Formula 8 and W^1 is a hydroxyl, a nitro, a tertiary amino or, where R is hydrogen, a secondary amino group; with a compound of the formula:

(10)



wherein n and Z^2 have the same significance as noted in Formula 8.

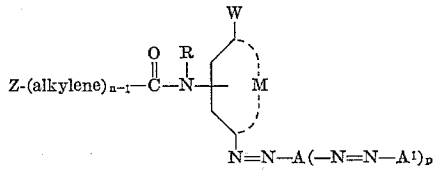
The product of the aforementioned reaction wherein W^1 is a nitro group may be directly reduced to yield a compound where W^1 is a primary amino group.

The preferred halogen component of Formula 10 is chlorine.

The preferred hydroxyl-protected derivatives of the ortho- and para-dihydroxyphenyl groups represented by the term Z^2 in Formula 10 may be prepared by esterification of the ortho- or para-dihydroxyphenyl group. After reaction, and prior to use in a photographic developing process, the protective groups may be removed by deesterification, such as for example, by hydrolysis in the presence of alkali.

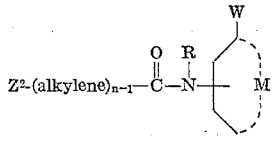
In a preferred embodiment of this synthesis, compounds of the general formula:

(11)



wherein Z, n, R, A, A^1, p and W have the same significance as previously noted and M represents the carbon atoms necessary to complete an aryl nucleus; may be synthesized by coupling a diazonium salt with a compound of the general formula:

(12)



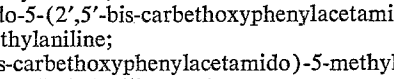
wherein Z^2, n, R, W and M have the same significance as previously noted, said coupling occurring on the aryl nucleus at an unsubstituted position para in respect to W; and removing the acyloxy groups of Z^1, for example, by hydrolysis in the presence of an alkali subsequent to completion of the coupling reaction.

Where both the ortho and para positions are unsubstituted on the nucleus, coupling occurs almost exclusively in the para position. However, although there is a marked preference for para substitution, coupling occurs in the unsubstituted ortho position if said para position is substituted.

Where it is desired to separate respective ortho and para coupled products, this may be accomplished by suitable methods known to the art, such as for example, their differential solubilities in alkaline media, steam distillation, etc. For many purposes, separation of a mixture or ortho and para coupled products may be unnecessary.

The diazonium salts utilized in the practice of this invention may be represented by the formula:

(13)



wherein A^1 and p have the same significance as previously noted. The preferred halogen is a chlorine.

It must be noted that coupling of a diazotizable cyclic amine into the compounds of Formula 8 wherein W is an amino group is preferably performed in an acid medium; however, where W is a hydroxyl group and coupling is preferably performed in an alkaline medium, care must be observed that the pH of the reaction mixture does not attain a concentration such that the acyloxy protective derivatives of the dihydroxyphenyl group may be hydrolyzed prior to the coupling reaction.

Synthetic procedure (B) will be illustrated in greater detail in conjunction with the following specific example which sets out a representative application of this procedure, which, however, is not limited to the details therein set forth and is intended to be illustrative only.

Example (b)

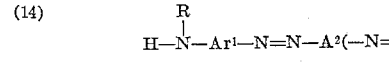
0.59 g. of p-cyanoaniline (0.005 mole) is dissolved in 7.5 cc. of water and 1.5 cc. of concentrated hydrochloric acid (0.018 mole). The p-cyanoaniline is diazotized at 5° C. by the addition with constant stirring of 0.35 g. of sodium nitrite (0.005 mole) in 2 cc. of water. The resultant diazo solution is then added at 5 to 10° C. with constant stirring to a solution of 2.49 g. of 5-(2',5'-bis-carbethoxyphenylacetamido) - 2 - methoxy - N,N-diethylaniline hydrochloride (0.0047 mole) in 10 cc. of pyridine. The resultant solution is stirred for 10 minutes at 5° C. and 50 cc. of water is added dropwise. A crystalline precipitate forms which is filtered, washed with water and dried under vacuum. The crystalline product, 5-(2',5'-bis-carbethoxyphenylacetamido) - 4 - (p-cyanophenylazo)-2-methoxy-N,N-diethylaniline, a brick red solid, M.P. 100 to 102° C., forms a scarlet colored solution in acetone, the spectral absorption curve of which exhibits a $\lambda_{max.}$ at 515 mμ; ϵ=25,800.

205 g. of 5-(2',5'-bis-carbethoxyphenylacetamido)-4-(p-cyanophenylazo)-2-methoxy-N,N-diethylaniline is suspended in 30 cc. of 95% ethanol. 2 g. of potassium hydroxide (0.0357 mole) is dissolved in 7.5 cc. of water, deaerated, added to the alcohol suspension, warmed, and agitated for 10 minutes. 2.05 cc. of acetic acid (0.037 mole) is added, the mixture cooled and resultant precipitate filtered, washed with water and dried. The product, 4-(p-cyanophenylazo) - 5 - homogentisamido-2-methoxy-N,N-diethylaniline, Formula (IV), a brownish-red solid, M.P. 183 to 185° C., exhibits a spectral absorption curve which shows a $\lambda_{max.}$ at 515 mμ in acetone; ϵ=28,400.

A third synthetic procedure, designated throughout the specification as procedure (C), is concerned with the preparation of specified dye developers within generic Formulae 1 and 2; specifically mono- and disazo dye developers wherein the phrase

set forth in Formula 2 represents the residue of a dye molecule:

(14)



wherein R has the same significance as previously noted; Ar^1 is an aryl group which may be substituted by alkyl, halogen, alkoxy, acid, sulfonyl, acyl, nitro, amino, or amino groups; A^2 and A^3 are each the residue of an azo coupling component, which coupling component may be the same or different.

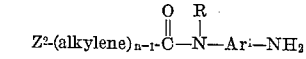
As illustrations of suitable azo coupling components or couplers from which A^2 and A^3 may be derived, mention may be made of phenols and aromatic amines having a

free position ortho or para to the hydroxyl or amino group, e.g., phenols, anilines, naphthols, anthrols, naphthylamines, etc.; heterocyclic aromatic compounds containing hydroxyl or amino groups, such as pyrazolones or pyrroles; aliphatic or alicyclic activated methylene couplers, i.e., compounds having an aliphatic or alicyclic methylene group activated by two adjacent keto, aldehyde, ester or nitrile groups, which may be the same or different, or a keto, aldehyde, ester or nitrile group in combination with an amide group, e.g., 1,3-diketones or β-ketonic acid arylamides; etc.; and substituted derivatives thereof. Examples of groups which may be present in such substituted derivatives include alkyl, sulfo, alkoxy, aryl, aryloxy, amino, keto, alkylamino, arylamino, hydroxyl, cyano, alkylamido, arylamido, carbalkoxy, carboxamido, sulfonamido, etc.

As used herein with reference to A^2 and A^3, the expression "residue of a phenolic coupler" is intended to refer to hydroxyphenyl, hydroxynaphthyl, hydroxyanthryl, etc. radicals, and substituted derivatives thereof; the expression "residue of an aromatic amino coupler" is intended to refer to aminophenyl, aminonaphthyl, etc. radicals, and substituted derivatives thereof; and the expressions "residue of a heterocyclic aromatic coupler," "residue of an aliphatic activated methylene coupler" and "residue of an alicyclic activated methylene coupler" are to be similarly construed.

It has been discovered that certain dye developers, within Formula 1, may be prepared by diazotizing a compound of the formula:

(15)



wherein Z^2, Ar^1, n, and R have the same significance as previously noted; coupling the diazonium compound into the desired coupling component A^2; and removing the protective groups of Z^2 to effect thereby reconstitution of the Z, said removal being accomplished, for example, by hydrolysis of acyl groups in the presence of alkali.

The compounds of Formula 15 are disclosed and claimed in the previously cited copending U.S. application Serial No. 200,639, now U.S. Patent No. 3,214,469.

Synthetic procedures of the last-mentioned type are disclosed and claimed in the copending U.S. application of Milton Green and Helen P. Husek, Serial No. 75,128, filed December 12, 1960, and now U.S. Patent No. 3,158,595, a continuation-in-part of Serial No. 709,002, filed January 15, 1959, and now abandoned.

The coupling component employed to provide the residue A^2 may be a coupler containing a diazotizable amino group. It is to be understood, however, that one may employ a coupler having a group convertible to a diazotizable amino group, e.g., a nitro group, and that the diazotizable amino group may be on a nucleus other than the nucleus substituted by the azo grouping. Thus, where a disazo compound is desired, that is, where p is 1 in Formula 14, the monoazo intermediates may be employed, in subsequent diazotization and coupling steps, prior to removal of the protective groups of Z^2. For example, the initial coupling may be into 2,5-dimethoxyaniline and the resulting monoazo product diazotized and coupled into the desired second coupler.

The coupling is generally performed at a pH which is preferably not greater than about 9.

By the use of two moles of the diazonium salt to each mole of the coupling component, one may couple twice into certain of the coupling components which provide the residue A^2, as, for example, phenols and aromatic amines which have two directing groups and two free coupling positions, such as 1,6-dihydroxy naphthalene and 1,5-diaminonaphthalene.

Where the coupling component is a phenolic coupler, and particularly a naphthol, it has been found that coupling ortho to the hydroxyl group gives a dye developer of superior color properties. It has also been found that such ortho-coupled dye developers exhibit essentially no pH sensitivity over a fairly wide range on either side of neutral.

As examples of additional coupling components which may be employed to provide A^2 and A^3, mention may be made of:

4-benzyl-1-naphthol
4-methyl-1-napthol
4-methoxy-α-naphthylamine
4-acetamido-α-naphthylamine
Phenol
Aniline
1,5-naphthalenediamine
p-Cresol
1-hydroxyanthracene
1-hydroxy-2-naphthanilide
Diketohydrindene
Malonitrile
Acetoacetanilide

Synthetic procedure (C) will be illustrated in greater detail in conjunction with the following specific example which sets out a representative application of this procedure, which, however, is not limited to the details therein set forth and is intended to be illustrative only.

Example (c)

0.011 mole of p-(2,5-bis-carbethoxyphenylacetamido)-aniline hydrochloride is dissolved in 0.033 mole of concentrated hydrochloric acid and 100 cc. of water. The mixture is cooled in an ice bath and diazotized at 0 to 5° C. with sodium nitrite. The resultant diazo solution is clarified and added, with constant stirring over a twenty-minute interval, to a mixture of 0.01 mole of 4-methoxy-1-naphthol, 100 cc. of acetone, 150 cc. of saturated sodium bircarbonate solution, and 50 cc. of water. The resulting slurry is stirred, filtered and the filter cake subjected to a water wash. The resultant product, 2-(p-[2′, 5′ - bis-carbethoxyphenylacetemido]-phenylazo)-4-methoxy-1-naphthol, is a magenta dye.

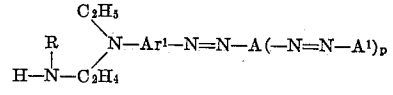
This product is treated in vacuo with a solution containing 5 g. of potassium hydroxide in 15 cc. of water and 70 cc. of alcohol. The mixture is intermittently warmed in a steam bath for three minutes and the desired product precipitated from the mixture with dilute hydrochloric acid. Purification of the product is accomplished by dissolving the product in methyl Cellosolve and reprecipitating with a 1% solution of hydrochloric acid. The resultant product, 2-(p-homogentisamido-phenylazo)-4-methoxy-1-naphthol, Formula V, a magenta dye, exhibits a spectral absorption curve which displays a $\lambda_{max.}$ at 534 mμ in ethanol; ϵ=24,000.

A fourth synthetic procedure, designated throughout the specification as procedure (D), is concerned with the preparation of specified dye developers within generic Formulae 1 and 2; specifically mono- and disazo dye developers wherein the phrase



set forth in Formula 2 represents the residue of a dye molecule:

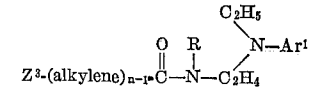
(16)



wherein R, Ar^1, A, A^1, and p have the same significance as previously noted.

We have discovered that these dye developers may be prepared by coupling an appropriate diazonium salt into a compound of the general formula:

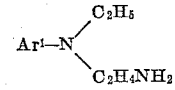
(17)



wherein n, R and Ar^1 have the same significance as previously noted; and Z^3 represents the protected derivative of a hydroquinonyl group, preferably the acylated derivative thereof; and effecting removal of the protecting groups from Z^3 to provide a hydroquinonyl group as Z.

The compounds of Formula 17 may be prepared by reacting homogentisic lactone with a compound of the formula:

(18)



such as N-(2-aminoethyl)-N-ethyl-m-toluidine and forming the protecetive derivative of the product's hydroquinone group as by acylation.

Synthetic procedure (D) will be illustrated in greater detail in conjunction with the following specific example which sets out a representative application of this procedure, which, however, is not limited to the details therein set forth and is intended to be illustrative only.

Example (d)

2.76 g. (0.02 mole) of p-nitroaniline is dissolved at 35° C. in dilute hydrochloric acid. The solution is cooled to approximately 5° C. and diazotized with 1.4 g. (0.02 mole) of sodium nitrate. 8.25 g. (0.02 mole) of N-(β-[2,5 - diacetoxyphenylacetamido] - ethyl) - N - ethyl - m-toluidine is dissolved in 20 cc. of acetic acid and added to the diazonium solution. The resultant mixture is stirred for approximately 30 minutes, poured into a mixture of ice and water, and neutralized. The solid precipitate is separated and crystallized from a water-alcohol mixture. The resultant product is recrystallized from toluene. The product, 3.2 g. of N-ethyl-N-(β-[2,5-diacetoxyphenylacetamido] - ethyl) - 3 - methyl - 4 - (p-nitro-phenylazo)-aniline, melting at 162 to 165° C., exhibits a spectral absorption curve which shows a $\lambda_{max.}$ at 502 mμ in methyl Cellosolve; ϵ=34,400.

Analysis for $C_{29}H_{31}N_5O_7$.—Calculated: N, 12.5%. Found: N, 12.4%.

0.56 g. (0.001 mole) of the product is dissolved in 15 cc. of 95% aqueous ethanol in a nitrogen atmosphere. 0.23 g. (0.004 mole) of potassium hydroxide is dissolved in 4 cc. of ethanol, deaerated with nitrogen and added to the product solution. The mixture is maintained at 50 to 60° C. for two hours, cooled, acidified with hydrochloric acid. The resultant precipitate is removed by filtration and the resultant product crystallized from an alcohol-water mixture. The product, 0.12 g. of the yellow dye developer, N-ethyl-N-(β-homogentisamido-ethyl)-3-methyl-4-(p-nitro-phenylazo)-aniline, Formula XXXIII, melting at 190 to 191° C. exhibits a spectral absorption curve which shows a $\lambda_{max.}$ at 492 mμ in ethanol; ϵ=33,000.

Analysis for $C_{25}H_{27}N_5O_5$.—Calculated: C, 62.88%; H, 5.70%; N, 14.67%. Found: C, 62.83%; H, 6.17%; N, 15.01%.

The invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative preparation and photographic utilization of the novel compounds of this invention, which however are not limited to the details therein set forth and are intended to be illustrative only.

The indicated dye intermediates, developer intermediates, synthetic procedure, resultant product, and characterization thereof are hereinafter set forth in tabular form in the interest of clarity.

TABLE I

Dye Developer No.	Dye Intermediate	Developer Intermediate	Synthetic Procedure	Dye Color
I	1,4-bis-(β-aminoethylamino)-anthraquinone.	homogentisic lactone	A	Cyan.
II	do	do	A	Do.
III	3-amino-1-phenyl-4-phenylazo-5-pyrazolone.	2,5-dibenzoyl-homogentisyl chloride	A	Yellow.
IV	p-Cyanoaniline hydrochloride	5-(2′,5′-dicarbethoxy-phenylacetamido)-2-methoxy-N,N-diethyl-aniline.	B	Magenta.
V	4-methoxy-1-naphthol	p-(2,5-dicarbethoxy-phenylacetamido)-aniline hydrochloride.	C	Do.
VI	6-anilino-1-naphthol-3-sulphonic acid	4-(2′,5′-dicarbethoxy-phenylacetamido)-2,5-diethoxy-aniline hydrochloride.	C	Do.
VII	4-acetamido-1-naphthol	do	C	Purple.
VIII	3-methyl-1-phenyl-5-pyrazolone	4-(2′,5′-diacetoxygentisamido)-aniline hydrochloride.	C	Yellow.
IX	1-(2′,5-dimethoxy-4′-[N-methylamino]-phenylazo)-2-methoxy-naphthalene.	2,5-dicarbethoxy-homogentisyl chloride	A	Magenta.
X	4-(4′-[N,N-diethylamino]-phenylazo)-3-amino-1-phenyl-5-pyrazolone.	do	A	Yellow.
XI	3-amino-4-(4′-N-ethyl-N-β-methylsulfonamidoethylamino-2′-methoxyphenylimino)-1-phenyl-5-pyrazolone.	do	A	Magenta.
XII	2,5-dimethoxyaniline hydrochloride	4-(2′,5′-dicarbethoxyhomogentisamido)-1-naphthol.	B	Do.
XIII	1-(2′,4′,6′-trichlorophenyl)-4-(4′-[N,N-diethylamino]-2′-methylphenylimino)-5-pyrazolone.	2,5-dicarbethoxyhomogentisyl chloride	A	Do.
XIV	1-(4′-amino-2′,5′-dimethoxyphenylazo)-2-methoxy-naphthalene.	do	A	Do.
XV	3-amino-4-biphenylazo-1-(2′,4′,6′-trichlorophenyl)-5-pyrazolone.	2,5-dibenzoylhomogentisyl chloride	A	Yellow.
XVI	3-amino-4-(5′-chloro-2′-hydroxyphenylazo)-1-phenyl-5-pyrazolone.	2,5-dicarbethoxy-homogentisyl chloride	A	Do.
XVII	4,8-diaminoanthrarufin	do	A	Blue.
XVIII	p,p′-Methylenedianiline	3-(2′,5′-dicarbethoxyhomogentisamido)-1-phenyl-5-pyrazolone.	B	Yellow.
XIX	4,8-diaminoanthrarufin	2,5-dicarbethoxyhomogentisyl chloride	A	Magenta.
XX	1,5-diaminoanthraquinone	2,5-dibenzoylhomogentisyl chloride	A	Salmon.
XXI	3-amino-4-(2′-hydroxyphenylazo)-1-phenyl-5-pyrazolone.	2,5-dicarbethoxy-homogentisyl chloride	A	Yellow.
XXII	3-amino-4-(2′,5′-dichloro-phenylazo)-1-(2′,4′,6′-trichlorophenyl)-5-pyrazolone.	do	A	Do.
XXIII	3-amino-4-(p-[phenylazo]-phenylazo)-1-phenyl-5-pyrazolone.	2,5-dibenzoyl-homogentisyl chloride	A	Do.
XXIV	3-amino-4-(2′,5′-dichlorophenylazo)-1-phenyl-5-pyrazolone.	do	A	Do.
XXV	1,4-diamino-anthraquinone	do	A	Purple.
XXVI	1-amino-anthraquinone	do	A	Yellow-orange.
XXVII	4-cyano-2,5-dimethoxy-aniline hydrochloride.	8-(2′,5′-dicarbethoxy-homogentisamido)-2-naphthol.	B	Magenta.
XXVIII	4-methoxy-1-naphthol	4-(2′,5′-dicarbethoxy-homogentisamido)-2,5-dichloroaniline hydrochloride.	C	Do.
XXIX	2-amino-4-methyl-5-acetyl-thiazole	N-(β-[2,5-diacetoxy-phenylacetamido]-ethyl)-N-ethyl-m-toluidine.	D	Do.

TABLE I—Continued

Dye Developer No.	Dye Intermediate	Developer Intermediate	Synthetic Procedure	Dye Color
XXX	8-acetamido-2-naphthol	4-(2',5'-dicarbethoxy-homogentisamido)-2-methoxy-aniline hydrochloride.	C	Do.
XXXI	4-(N,N-dimethyl-sulfamyl)-1-naphthol	do	C	Do.
XXXII	3'-amino-quinaphthalone	2,5-dicarbethoxyhomogentisyl chloride	A	Yellow.
XXXIII	p-Nitroaniline hydrochloride	N-(β-[2,5-diacetoxyphenylacetamido]-ethyl)-N-ethyl-m-toluidine.	D	Do.
XXXIV	Tetramethylamino-anthraquinone	2,5-dicarbethoxy-homogentisyl chloride	A	Magenta.
XXXV	2-amino-4-methyl-5-carbethoxy-thiazole	N-β-[2,5-diacetoxy-phenylacetamido]-ethyl)-N-ethyl-m-toluidine.	D	Do.
XXXVI	4-aceto-1-naphthol	4-(2',5'-dicarbethoxy-homogentisamido)-2,5-dimethoxy-aniline hydrochloride.	C	Do.

As previously mentioned, the novel compounds of this invention are useful dye developers. In the following examples, all parts are given by weight except where otherwise noted, and all operations involving light-sensitive materials are carried out in the absence of actinic radiation. These examples are intended to be illustrative only of the photographic use of the dye developers and should not be construed as limiting the invention in any way.

Each of the photographic examples set forth in Table II was effected as follows: a photosensitive element is prepared by coating a gelatin-coated film base with the dye layer coating solution set forth in the table, when a dye layer is employed. After this coating has dried, a silver iodobromide emulsion is applied. This photosensitive element is exposed and processed by spreading an aqueous liquid processing composition, comprising the components set forth in the table, between said photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element, except where otherwise noted, comprises a cellulose acetate-coated baryta paper which has been coated with the image-receiving layer coating set forth in the table. After the designated imbibition period, the image-receiving element is separated and contains a positive dye image of the photographed subject.

TABLE II

Dye Developer No.	Concentration	Disposition	Emulsion	Processing Composition	Inbibition Time	Image Color	Image-Receiving Layer Coating Composition
I	3.0 grams	In a dye layer formed from a coating composition comprising 4.0 grams of cellulose acetate hydrogen phthalate; 80 cc. of acetone; and 20 cc. of methanol.	Silver iodobromide.	Sodium hydroxide 2.5 grams; metol 0.1 gram; potassium bromide 0.1 gram; urea 1.0 gram; sodium carboxymethyl cellulose 5.0 grams; and 100 cc. of water.	1 minute	Cyan	(1)
I	1.0%	In processing composition.	do	Sodium hydroxide 1.5%; sodium sulfite 1.0%; and potassium bromide 0.1%.	Conventional development 1 minute.	Negative: grayish-blue image.	None.
III	2.0 grams	In a dye layer formed from a coating composition comprising 4.0 grams of cellulose acetate hydrogen phthalate in 100 cc. of methyl Cellosolve.	do	Water 100 cc.; sodium carboxymethyl cellulose 4.5 grams; sodium hydroxide 1.5 grams; and metol 0.1 gram.	1 minute	Yellow	4.0 grams of N-methoxymethyl polyhexamethylene adipamide; 80 cc. of isopropanol; and 20 cc. of water.
IV	4.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran.	do	Sodium carboxymethyl cellulose 5.0%; 1-phenyl-3-pyrazolidone 0.6%; sodium hydroxide 3.0%; 6-nitrobenzimidazole 0.08%; and 2,5-bis-ethyleneimino-hydroquinone 0.4%.	do	Magenta	4.0% N-methoxymethyl polyhexamethylene adipamide in 80% aqueous ethanol.
V	3.0%	do	do	Sodium hydroxide 1.25%; potassium bromide 0.2%; 1-phenyl-3-pyrazolidone 0.2%; and sodium carboxymethyl cellulose 4.25%.	do	do	Do.
VII	3.0%	do	do	Sodium hydroxide 2.0%; potassium bromide 0.2%; 1-phenyl-3-pyrazolidone 0.2%; and sodium carboxymethyl cellulose 4.5%.	do	Purple.	Do.
VIII	3.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 80:20 mixture, by volume, of acetone and methanol.	do	Sodium hydroxide 1.5%; potassium bromide 0.2%; 1-phenyl-3-pyrazolidone 0.2%; and sodium carboxymethyl cellulose 4.5%.	do	Orange-yellow.	Do.

See footnote at end of table.

TABLE II—Continued

Dye Developer No.	Concentration	Disposition	Emulsion	Processing Composition	Inhibition Time	Image Color	Image-Receiving Layer Coating Composition
IX	3.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran.	do	Sodium carboxymethyl cellulose 4.5%; 1-phenyl-3-pyrazolidone 0.2%; sodium hydroxide 1.5%; and potassium bromide 0.2%.	do	Magenta	Do.
X	2.5%	do	do	do	do	do	Do.
XI	3.0%	do	do	Sodium carboxymethyl cellulose 4.5%; 1-phenyl-3-pyrazolidone 0.2%; sodium hydroxide 2.0%; and potassium bromide 0.2%.	do	Red-brown.	Do.
XII	4.0%	do	do	Sodium hydroxide 2.0%; potassium bromide 0.2%; 1-phenyl-3-pyrazolidone 0.2%; and sodium carboxymethyl cellulose 4.5%.	do	Magenta	Do.
XIII	1.5%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 80:20 mixture, by volume, of acetone and tetrahydrofuran.	do	Sodium carboxymethyl cellulose 4.5%; 1-phenyl-3-pyrazolidone 0.2%; sodium hydroxide 1.5%; and potassium bromide 0.2%.	do	do	6% aqueous polyvinyl alcohol.
XIV	3.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 80:20 mixture, by volume, of acetone and methanol.	do	Sodium carboxymethyl cellulose 4.5%; 1-phenyl-3-pyrazolidone 0.2%; sodium hydroxide 2.5%; and potassium bromide 0.2%.	do	do	Do.
XV	3.0%	do	do	Sodium hydroxide 2.0%; potassium bromide 0.2%; 1-phenyl-3-pyrazolidone 0.2%; sodium carbonate 2.0%; and sodium carboxymethyl cellulose 4.5%.	do	Yellow	4.0% N-methoxymethyl polyhexamethylene adipamide in 80% aqueous alcohol.
XVI	3.0%	do	do	Sodium hydroxide 1.5%; potassium bromide 0.2%; 1-phenyl-3-pyrazolidone 0.2%; and sodium carboxymethyl cellulose 4.5%.	do	Orange	6% aqueous polyvinyl alcohol.
XVII	3.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 80:20 mixture, by volume of acetone and tetrahydrofuran.	do	Sodium carboxymethyl cellulose 4.5%; 1-phenyl-3-pyrazolidone 0.2%; sodium hydroxide 2.0%; and potassium bromide 0.2%.	do	Blue	4.0% N-methoxymethyl polyhexamethylene adipamide in 80% aqueous ethanol.
XVII	3.0%	do	do	do	do	do	6.0% aqueous polyvinyl alcohol.
XVIII	4.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran.	do	Sodium carboxymethyl cellulose 4.5%; 1-phenyl-3-pyrazolidone 0.2%; sodium hydroxide 3.0% and potassium bromide 0.5%.	do	Yellow	4.0% N-methoxymethyl polyhexamethylene adipamide in 80% aqueous ethanol.
XVIII	1.2 grams	In emulsion	1.2 grams of dye developer is ground in 3 cc. of water and 4 drops of Antarox D-100.[2] The mixture is added to 30 cc. of a silver iodobromide emulsion and coated on a support.	do	do	do	Do.
XIX	2.75%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran.	Silver iodobromide.	Sodium carboxymethyl cellulose 4.5%; 1-phenyl-3-pyrazolidone 0.2%; sodium hydroxide 1.5%; and potassium bromide 0.2%.	do	Magenta	6% aqueous polyvinyl alcohol.

TABLE II—Continued

Dye Developer No.	Concentration	Disposition	Emulsion	Processing Composition	Inhibition Time	Image Color	Image-Receiving Layer Coating Composition
XX	3.00%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 80:20 mixture, by volume, of acetone and methanol.	do	do	do	Salmon	4% N-methoxymethyl polyhexamethylene adipamide in 80% aqueous ethanol.
XXI	2.0%	do	do	Sodium hydroxide 1.5%; potassium bromide 0.2%; 1-phenyl-3-pyrazolidone 0.2%; and sodium carboxymethyl cellulose 4.5%.	do	Yellow	4.0% N-methoxymethyl polyhexamethylene adipamide in 80% aqueous alcohol.
XXII	3.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 80:20 mixture, by volume, of acetone and tetrahydrofuran.	do	Sodium hydroxide 2.0%; metol 0.2%; potassium bromide 0.2%; and sodium carboxymethyl cellulose 4.5%.	do	do	Do.
XXIII	3.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in tetrahydrofuran.	do	Sodium hydroxide 2.0%; metol 0.2%; potassium bromide 0.2%; sodium carbonate 2.0%; and sodium carboxymethyl cellulose 4.5%.	do	Orange	6% aqueous polyvinyl alcohol.
XXIV	2.5%	do	do	do	do	Yellow	4.0% N-methoxymethyl polyhexamethylene adipamide in 85% aqueous ethanol and 15% furfural alcohol.
XXV	2.5%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 80:20 mixture, by volume, of acetone and methanol.	do	Sodium carboxymethyl cellulose 4.5%; metol 0.1%; and sodium hydroxide 1.5%.	do	Purple	Do.
XXVII	3.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran.	do	Sodium carboxymethyl cellulose 5.0%; 1-phenyl-3-pyrazolidone 0.8%; sodium hydroxide 3.0%; potassium bromide 0.4%; and 2,5-bis-ethylene-iminohydroquinone 0.6%.	do	Magenta	4.0% N-methoxymethyl polyhexamethylene adipamide in 80% aqueous ethanol.
XXVIII	3.0%	do	do	1-phenyl-3-pyrazolidone 0.6%; sodium hydroxide 2.0%; 6-nitrobenzimidazole 0.08%; 2,5-bis-ethyleneimino-hydroquinone 0.4%; and sodium carboxymethyl cellulose 4.5%.	do	do	Do.
XXIX	3.0%	do	do	Sodium hydroxide 1.5%; 1-phenyl-3-pyrazolidone 0.4%; 2,5-bis-ethyleneimino-hydroquinone 0.2%; 6-nitrobenzimidazole 0.08%; and sodium carboxymethyl cellulose 4.5%.	do	do	Do.
XXX	3.0%	In a dye layer formed from a coating composition comprising a 2% solution of cellulose acetate hydrogen phthalate in tetrahydrofuran.	do	Sodium hydroxide 3.0%; sodium carboxymethyl cellulose 5.0%; 1-phenyl-3-pyrazolidone 1.2%; 2,5-bis-ethyleneimino-hydroquinone 0.9%; and 6-nitrobenzimidazole 0.12%.	2 minutes	do	Do.
XXXI	3.5%	In a dye layer formed from a coating composition comprising a 2% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran.	do	Sodium hydroxide 1.0%; sodium carboxymethyl cellulose 4.25%; 4,4-dimethyl-1-phenyl-3-pyrazolidone 0.6%; xylohydroquinone 0.4%; and 6-nitrobenzimidazole 0.06%.	1 minute	do	Do.
XXXII	3.0%	In a dye layer formed from a coating composition comprising a 2% solution of cellulose acetate hydrogen phthalate in methyl Cellosolve.	do	Sodium hydroxide 3.0%; 1-phenyl-3-pyrazolidone 1.2%; 2,5-bis-ethylene-imino-hydroquinone 0.9%; 6-nitrobenzimidazole 0.12%; and sodium carboxymethyl cellulose 5.0%.	do	Yellow	Do.

TABLE II—Continued

Dye Developer No.	Concentration	Disposition	Emulsion	Processing Composition	Inhibition Time	Image Color	Image-Receiving Layer Coating Composition
XXXIII	1.5%	In a dye layer formed from a coating composition comprising a 2% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran.	do	Sodium hydroxide 2.5%; 1-phenyl-3-pyrazolidone 1.0%; t-butyl-hydroquinone 0.45%; 6-nitrobenzimidazole 0.2%; and sodium carboxymethyl cellulose 4.5%.	3 minutes	Magenta	Do.
XXXIV	4.5%	do	do	Sodium hydroxide 1.0%; 1-phenyl-3-pyrazolidone 0.8%; 2,5-bis-ethyleneimino-hydroquinone 0.6%; 6-nitrobenzimidazole 0.08%; and sodium carboxy methyl cellulose 4.25%.	1 minute	do	Do.
XXXV	3.0%	In a dye layer formed from a coating composition comprising a 4% solution of cellulose acetate hydrogen phthalate in tetrahydrofuran.	do	Sodium hydroxide 1.5%; 1-phenyl-3-pyrazolidone 0.6%; 2,5-bis-ethyleneimino-hydroquinone 0.4%; 6-nitrobenzimidazole 0.08%; and sodium carboxy methyl cellulose 4.5%.	do	do	Do.
XXXVI	5.2%	In a dye layer formed from a coating composition comprising a 2% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran.	do	Sodium hydroxide 1.0%; sodium carboxymethyl cellulose 4.25%; 4,4-dimethyl-1-phenyl-3-pyrazolidone 0.6%; xylohydroquinone 0.4%; and 6-nitrobenzimidazole 0.06%.	do	do	Do.

[1] The image-receiving element was prepared by coating a polyvinyl butyral-coated baryta paper with a solution comprising:

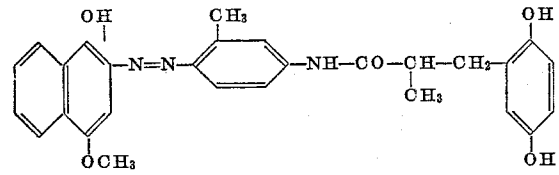
Acetone	cc.. 100
Partially hydrolyzed polyvinyl acetate (sold under the name of "Vinylite MA-28-18")	g.. 30
Stearto—chromic chloride (hardening agent sold in isopropanol under the name of "Quilon")	g.. 1.5
Benzoic anhydride	g.. 1.5
Diethyl malate	g.. 7.5

followed by coating with a solution of 50 g. of silica suspension and 25 cc. of water, after which a coating was applied comprising 6 g. of polyvinyl alcohol and 0.375 g. of phosphoric acid in 100 cc. of water.

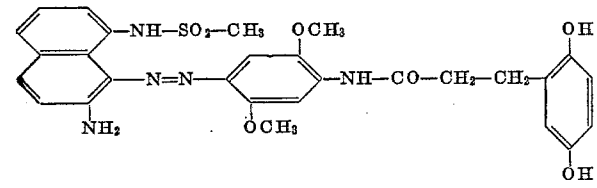
[2] Trade name for an aliphatic polyglycol ether non-ionic emulsifier and disperser.

In addition to the aforementioned illustrative dye developers (I to XXVI) disclosed in the parent application, Serial No. 1,442, the following additional dye developers useful in photographic processes such as disclosed in Table II also have been prepared:

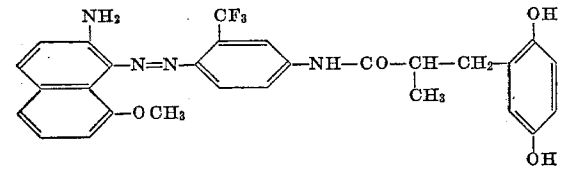
XXXVII



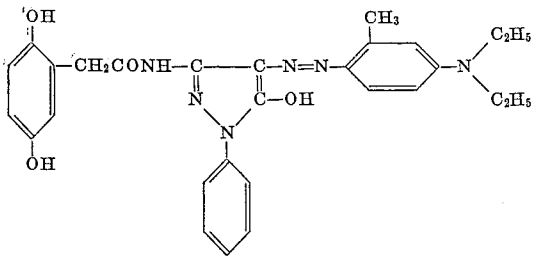
XXXVIII



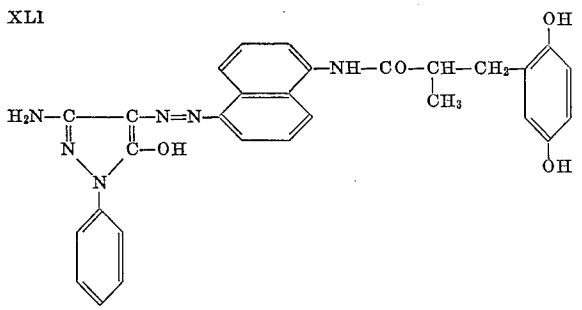
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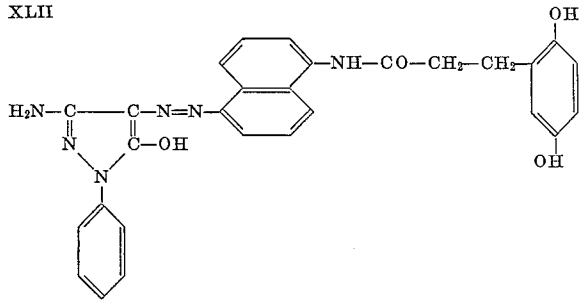
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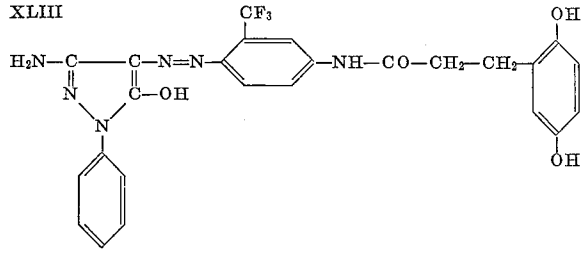
XLI



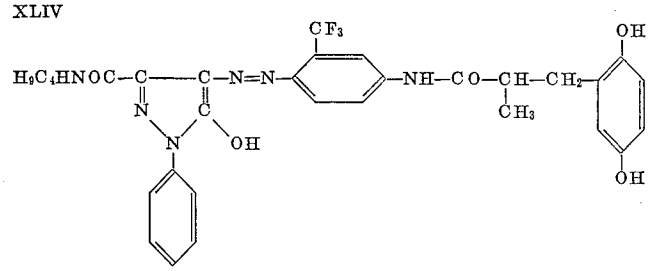
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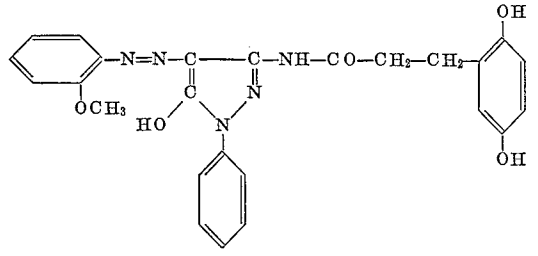
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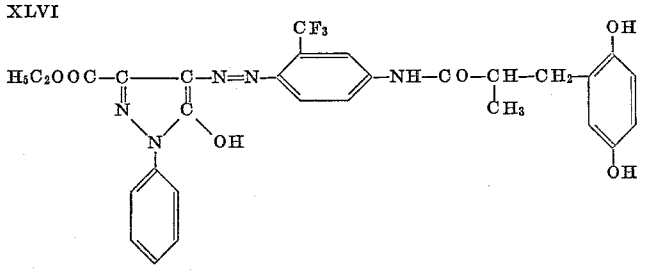
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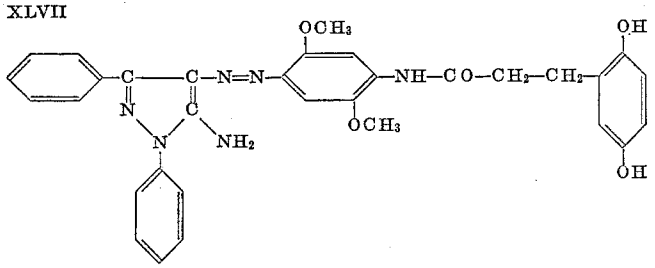
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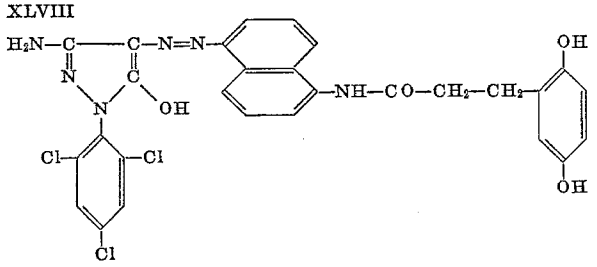
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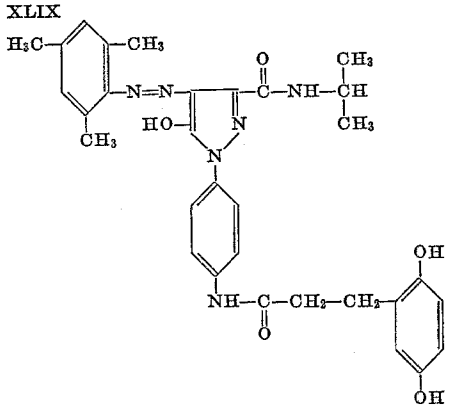
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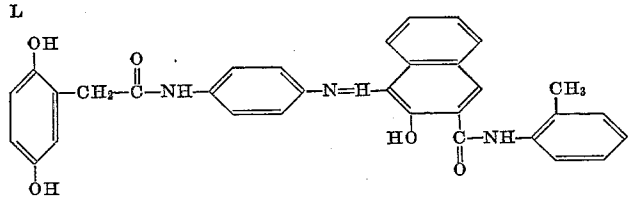
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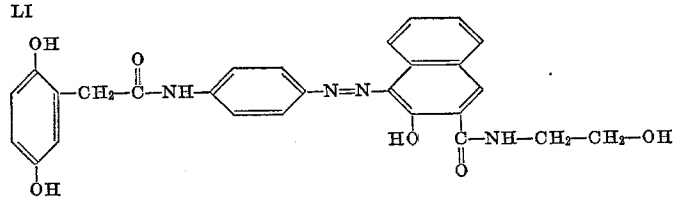
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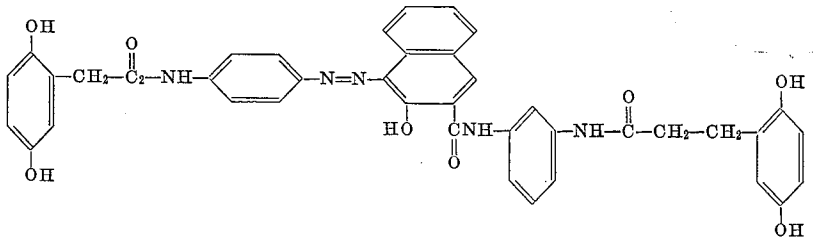
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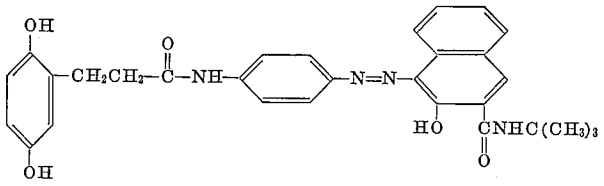
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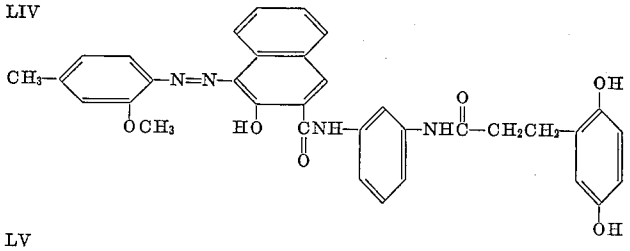
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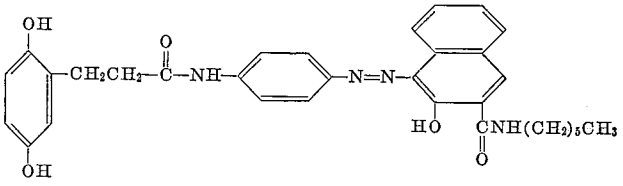
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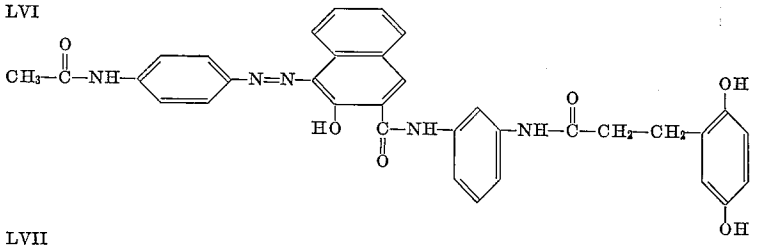
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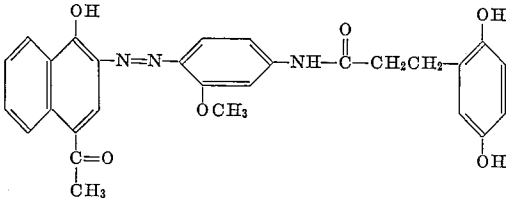
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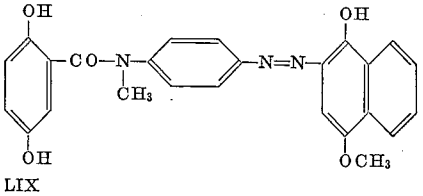
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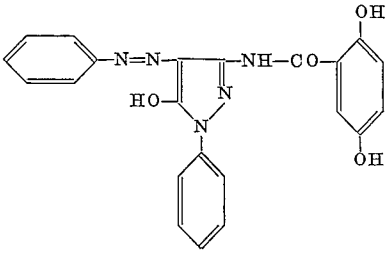
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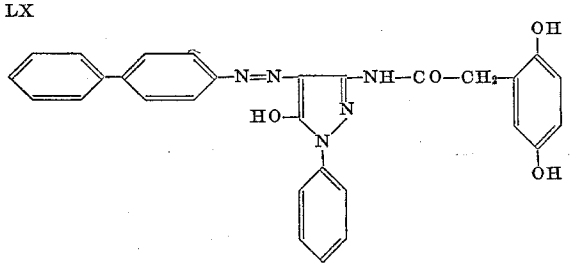
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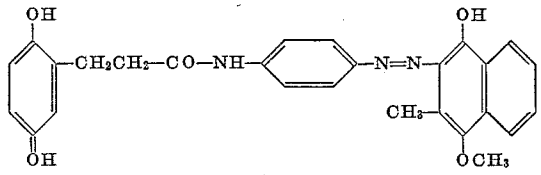
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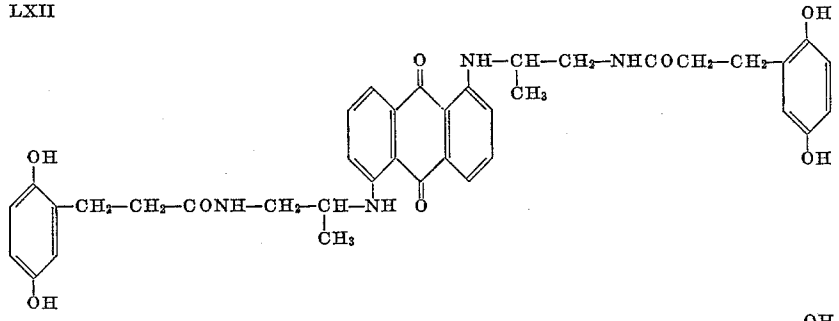
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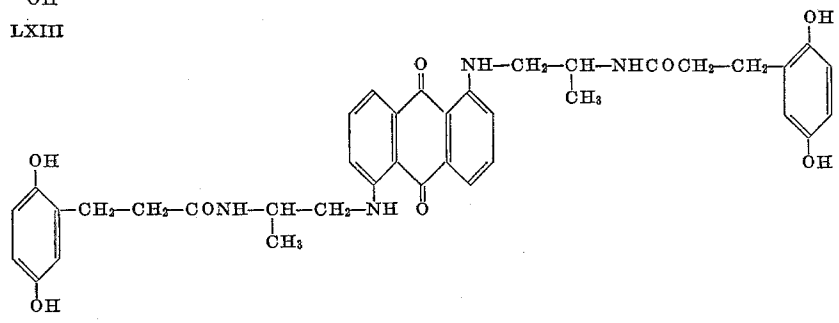
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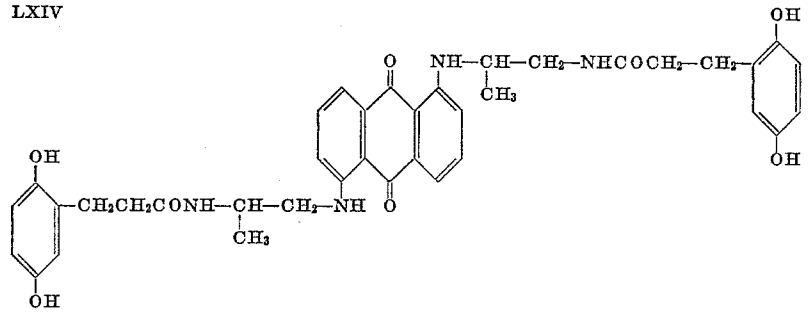
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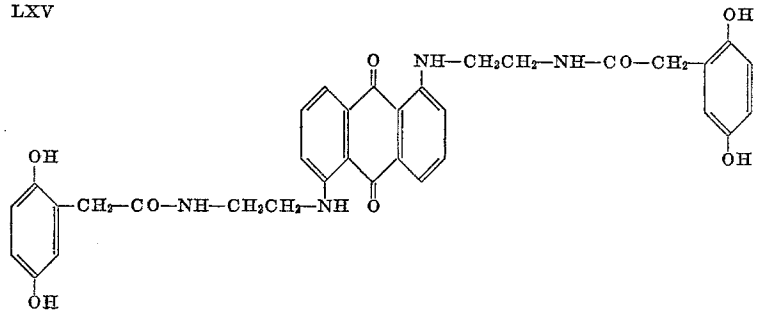
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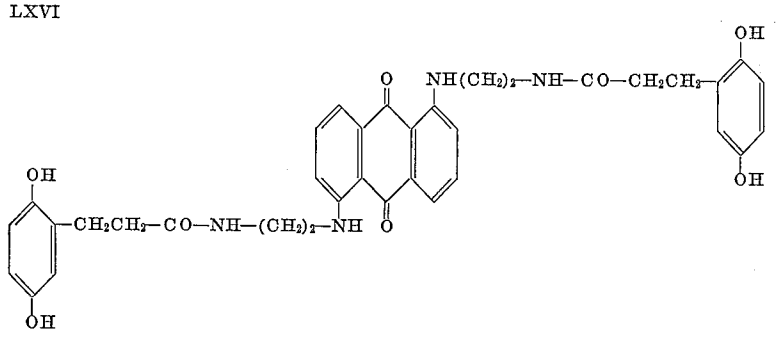
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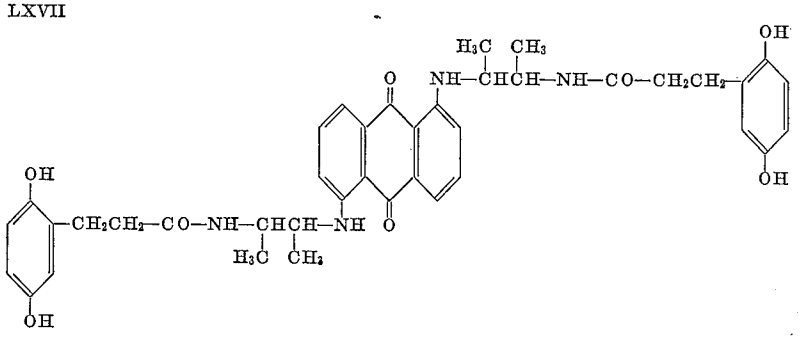
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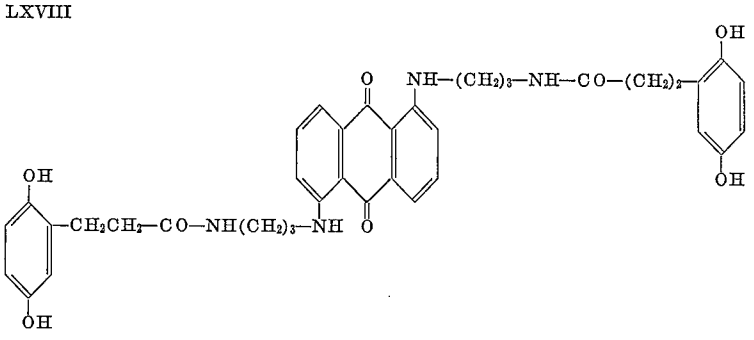
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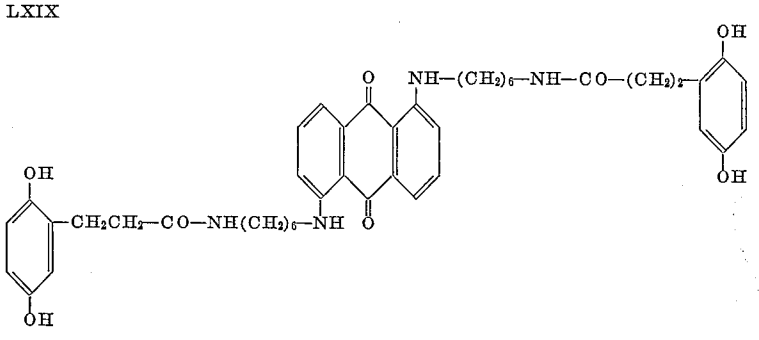
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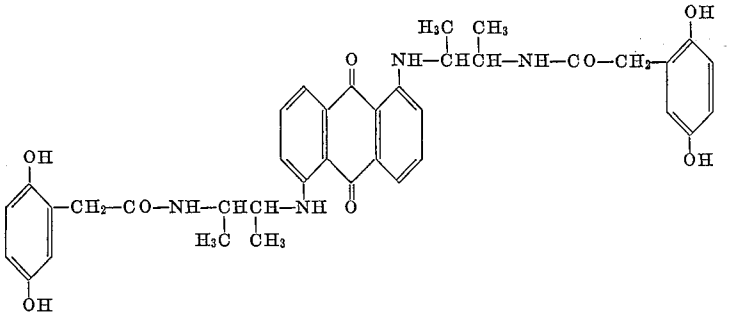
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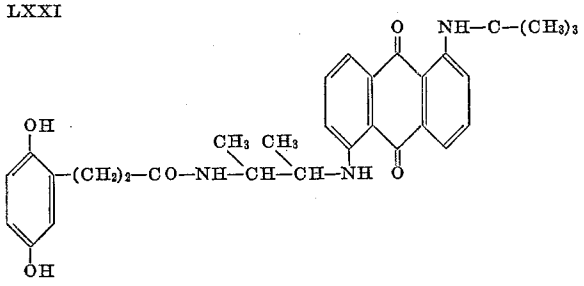
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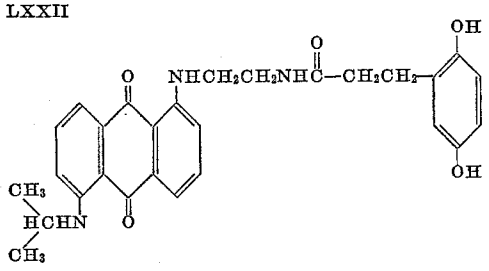
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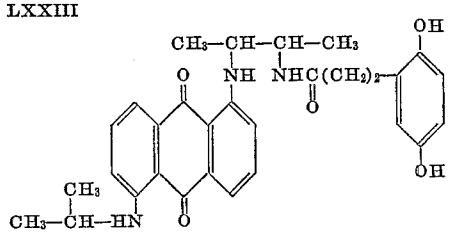
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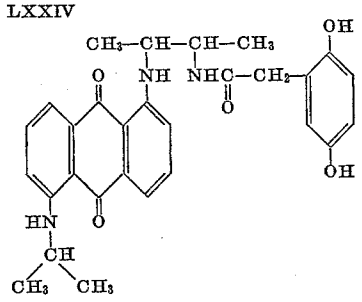
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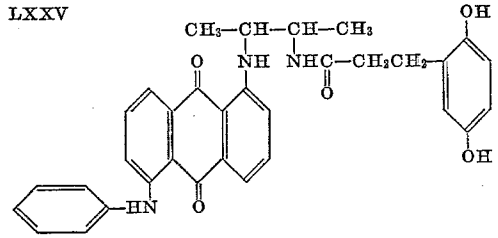
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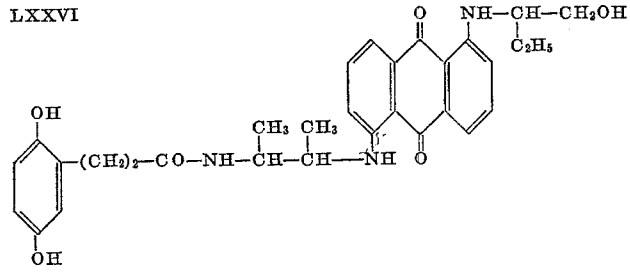
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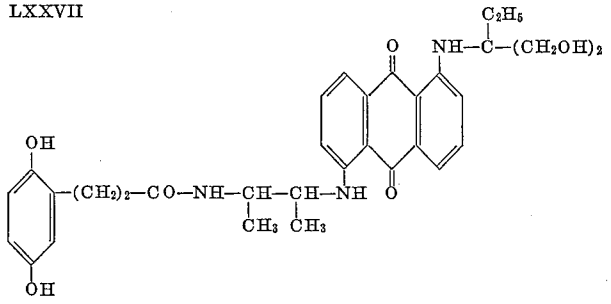
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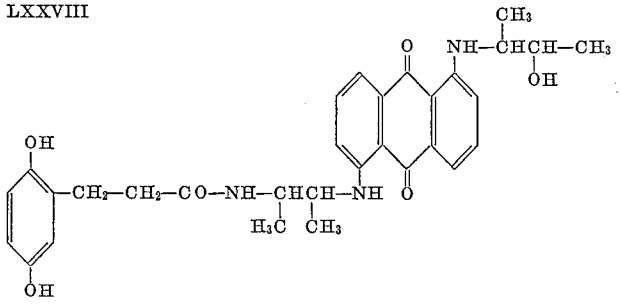
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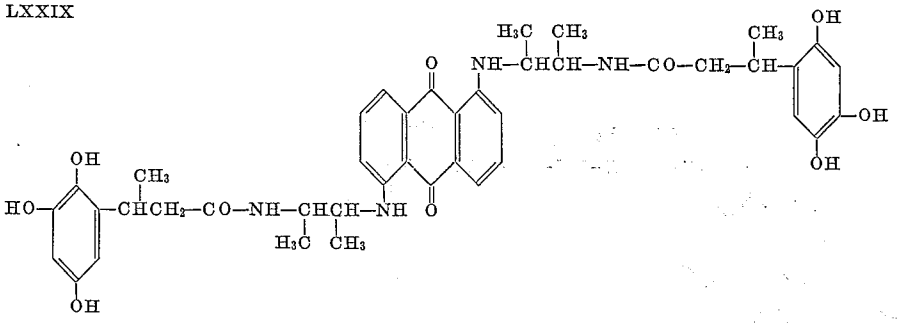
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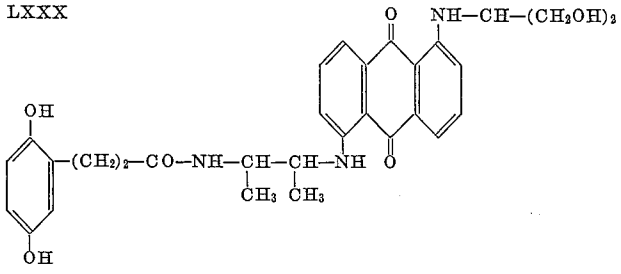
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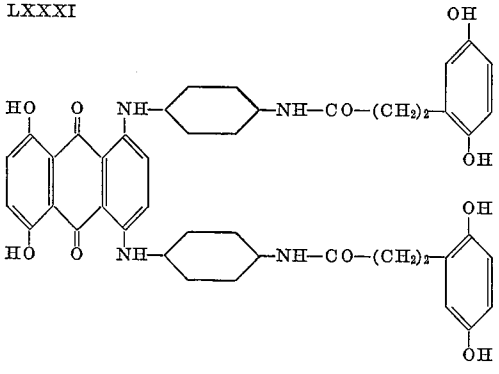
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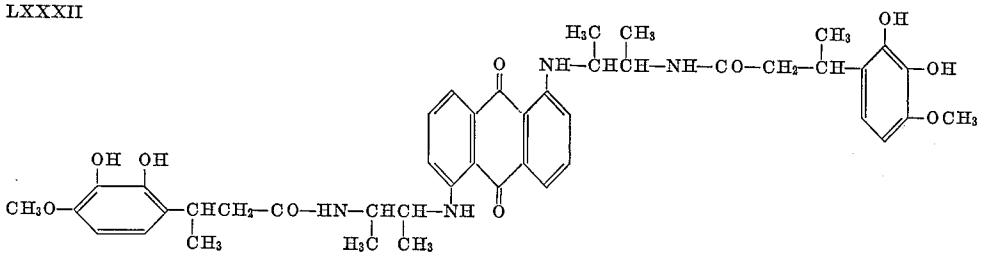
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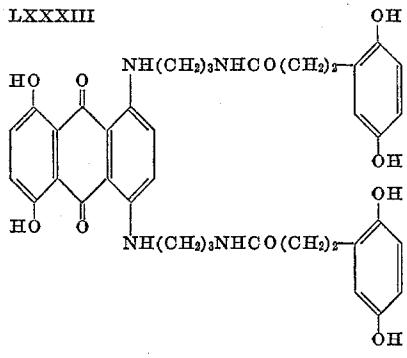
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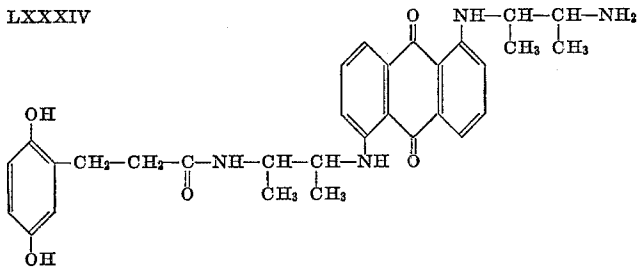
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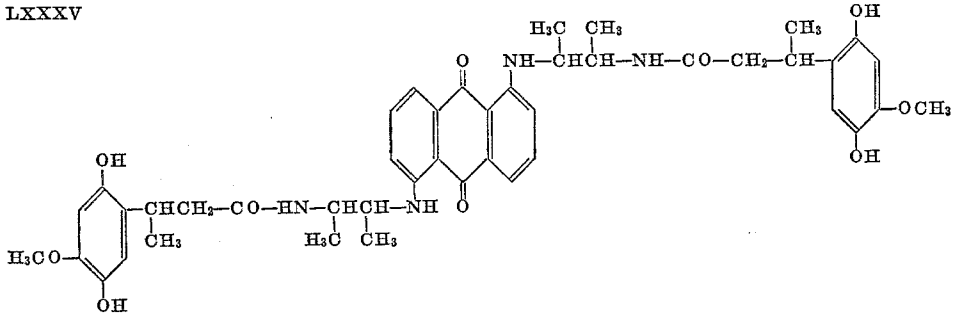
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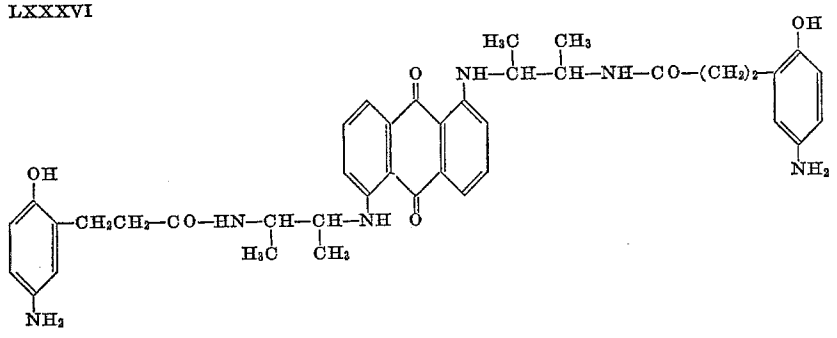
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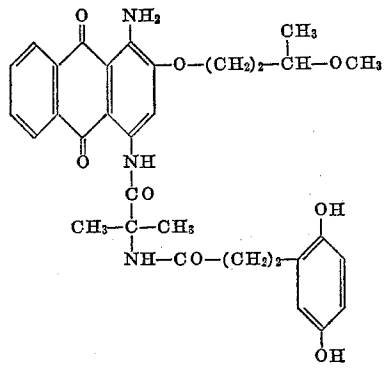
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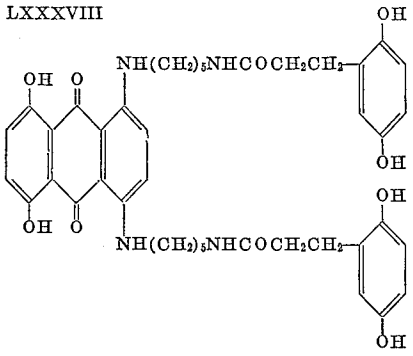
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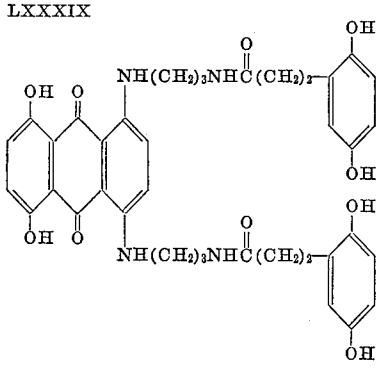
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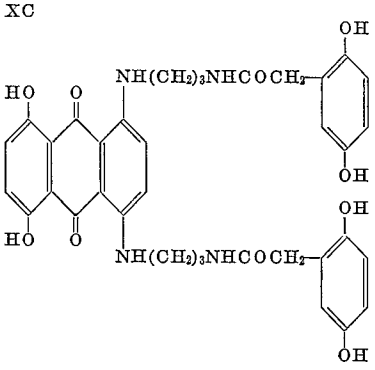
LXXXVIII



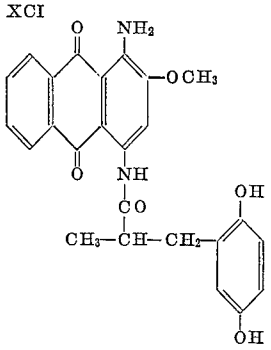
LXXXIX



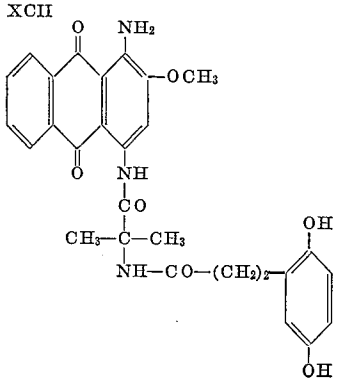
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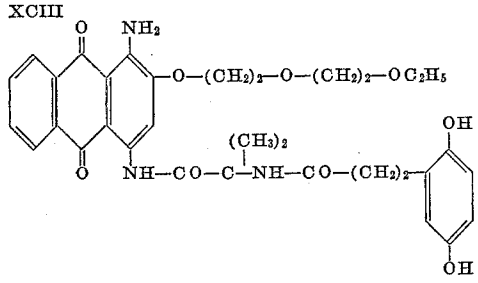
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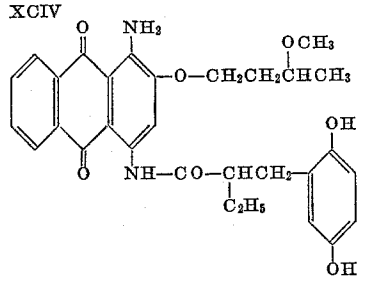
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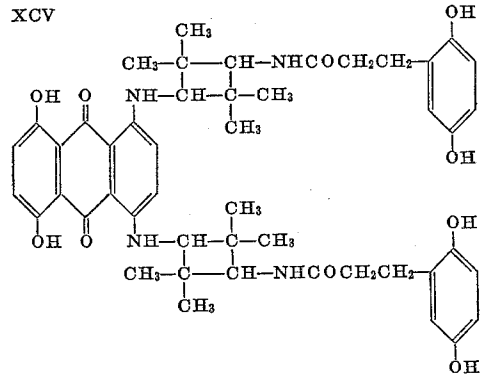
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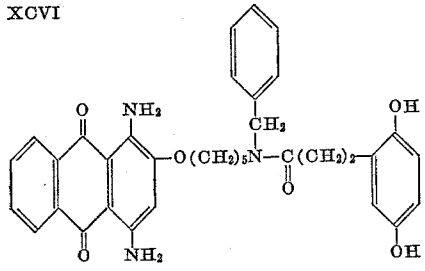
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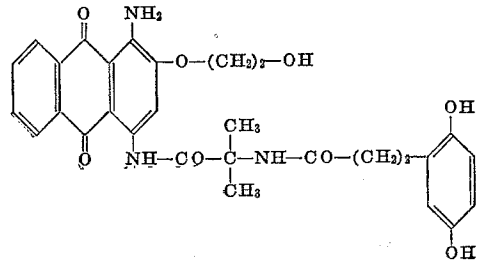
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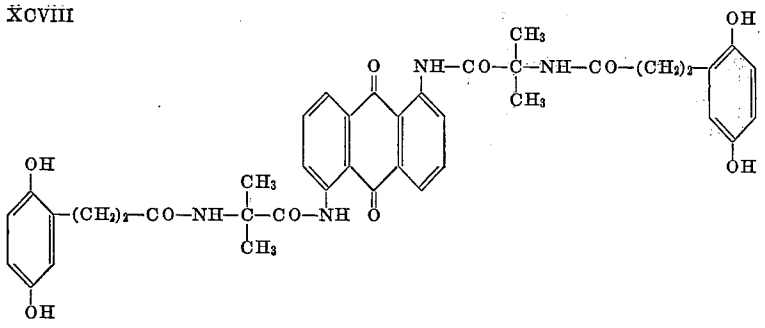
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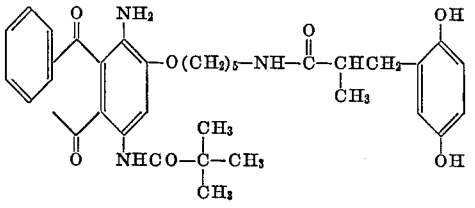
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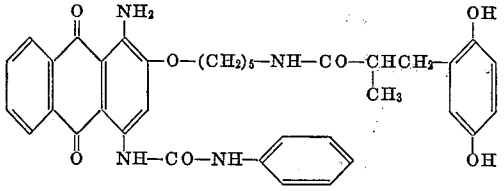
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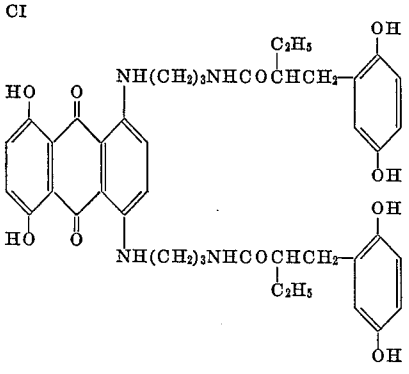
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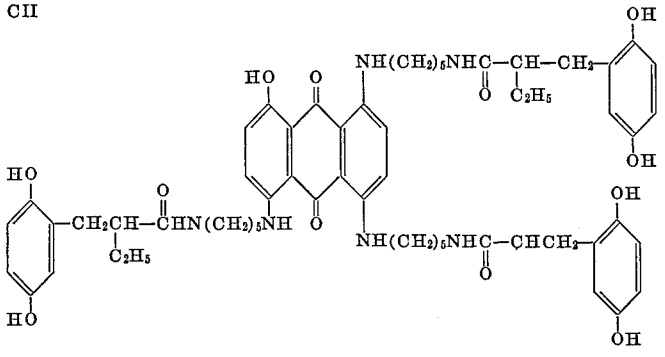
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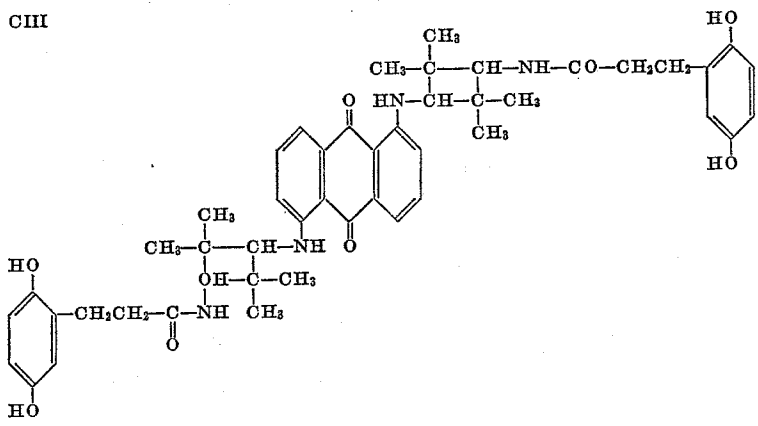
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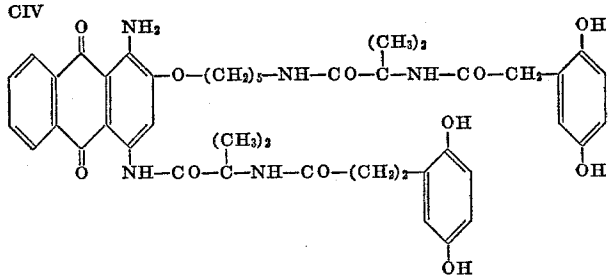
CII



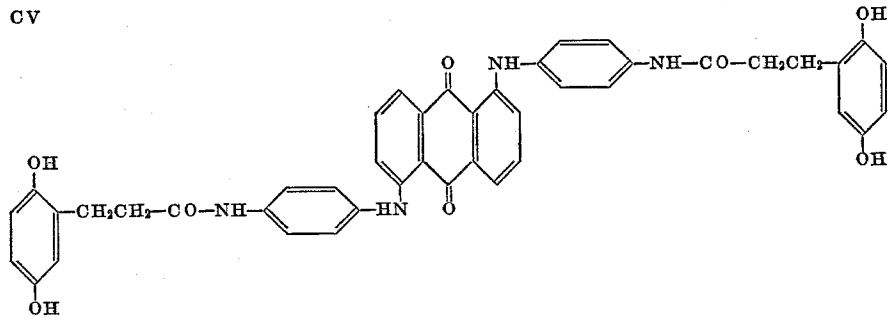
CIII



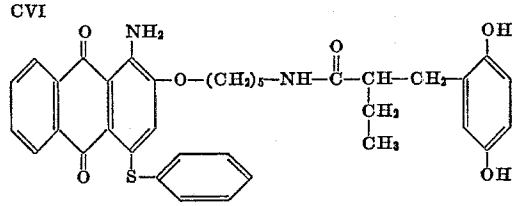
CIV



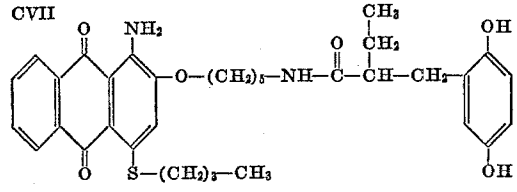
CV



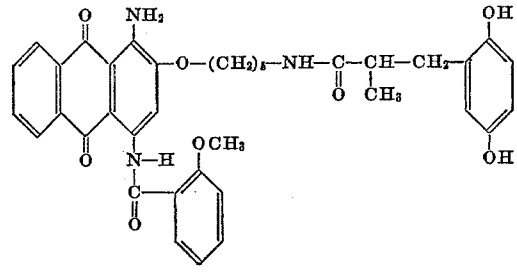
CVI



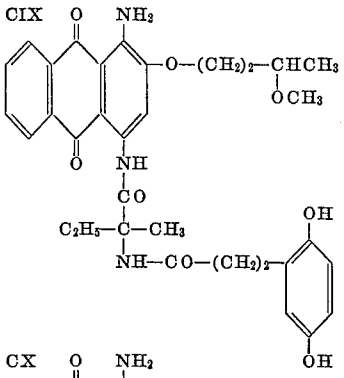
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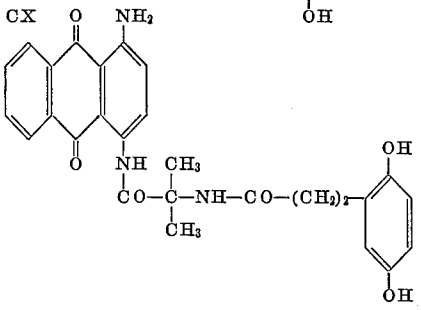
CVIII



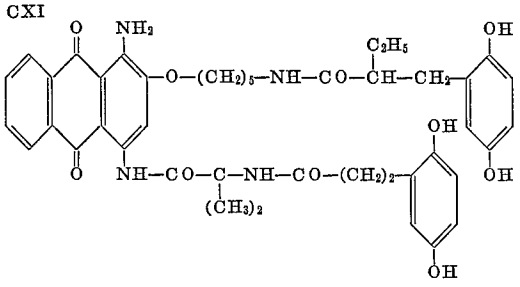
CIX



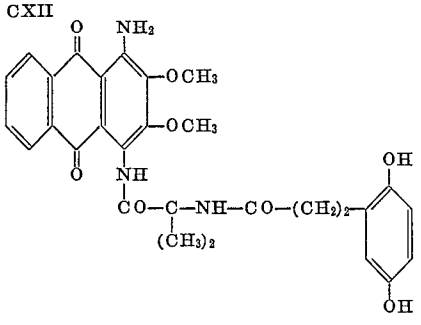
CX



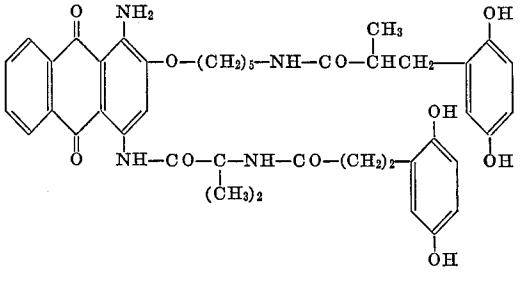
CXI



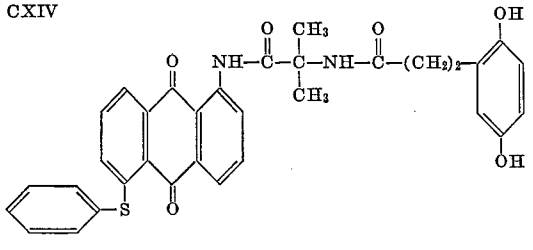
CXII



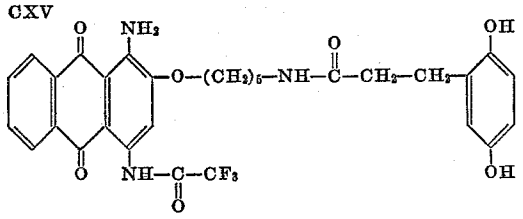
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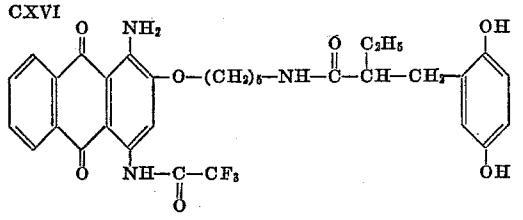
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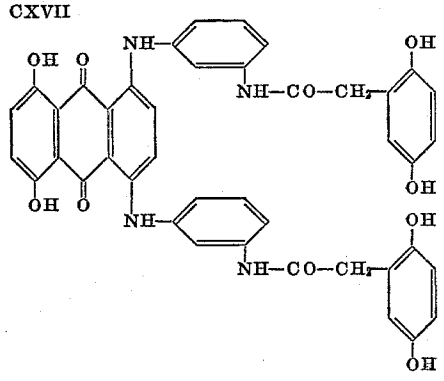
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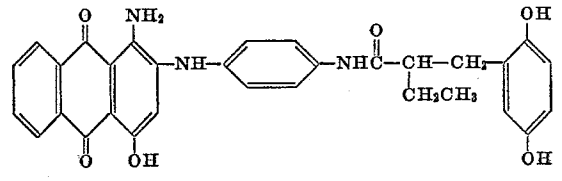
CXVI



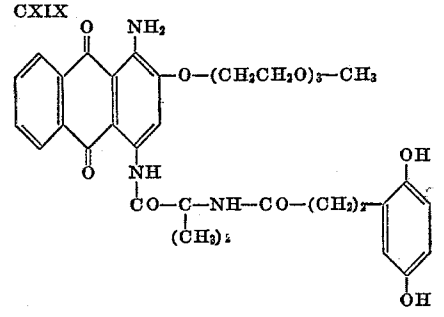
CXVII



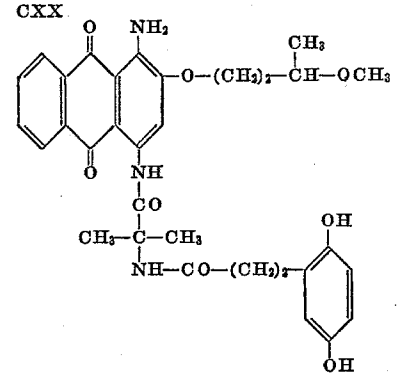
CXVIII



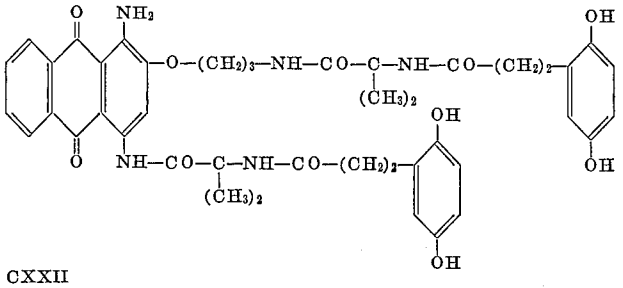
CXIX



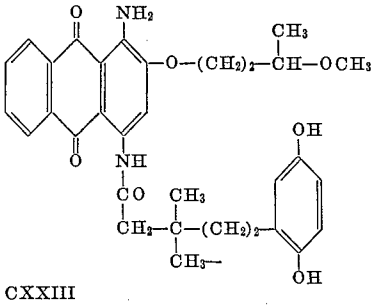
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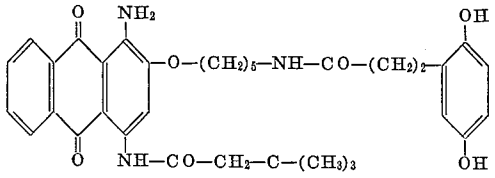
CXXI



CXXII

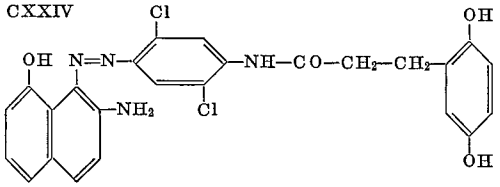


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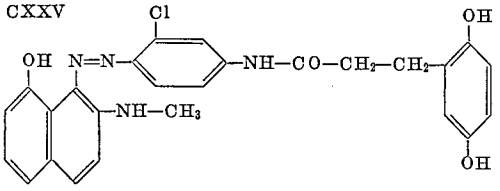


Further in addition to the aforementioned compounds, mention may be made of the following dye developers within the group claimed in the copending Green et al. application, Serial No. 174,248, filed February 19, 1962:

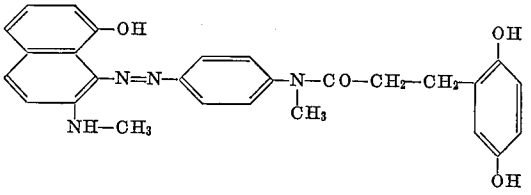
CXXIV



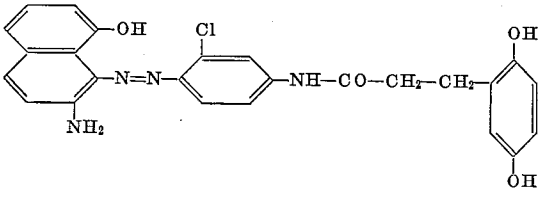
CXXV



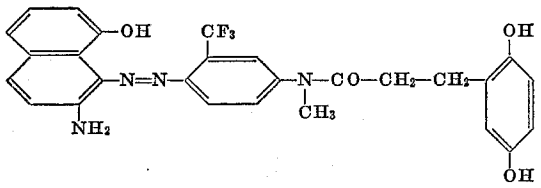
CXXVI



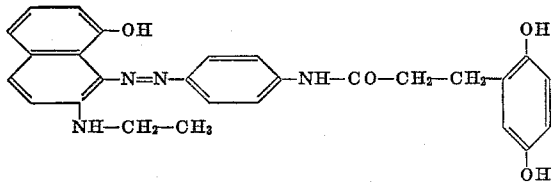
CXXVII



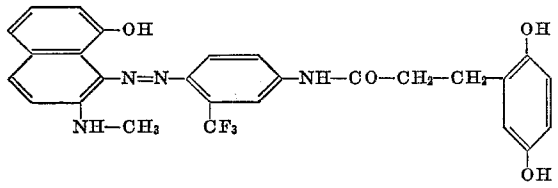
CXXVIII



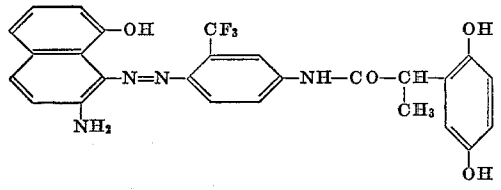
CXXIX



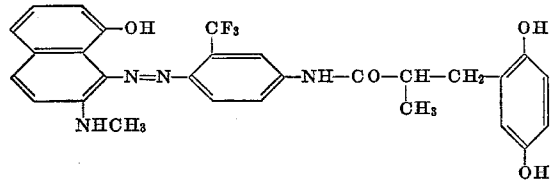
CXXX



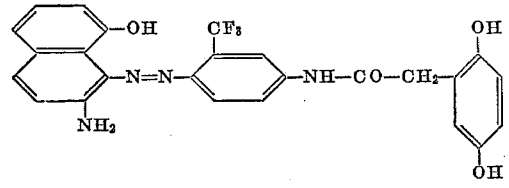
CXXXI



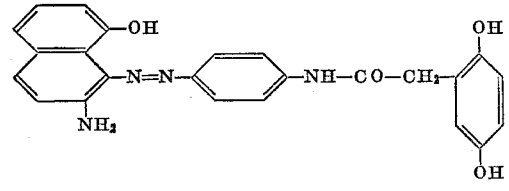
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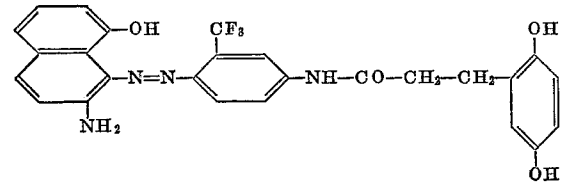
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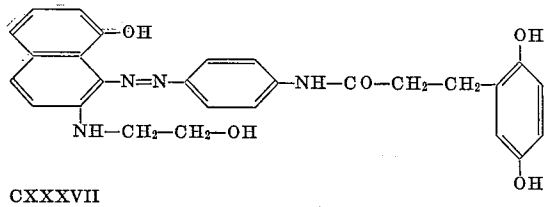
CXXXIV



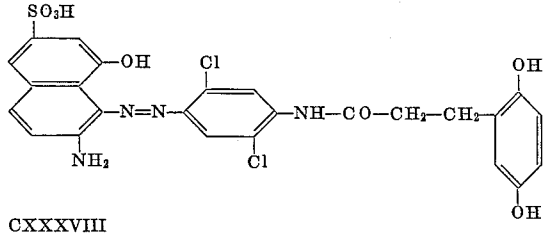
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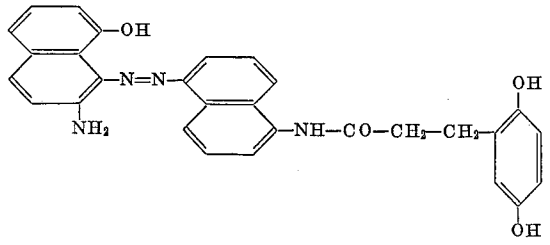
CXXXVI



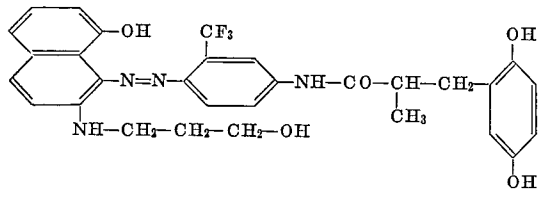
CXXXVII



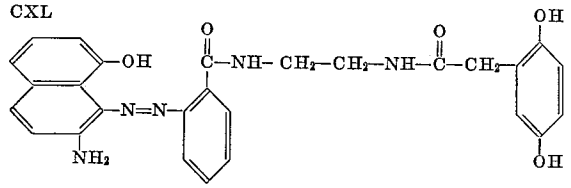
CXXXVIII



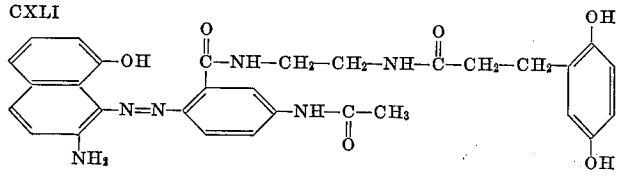
CXXXIX



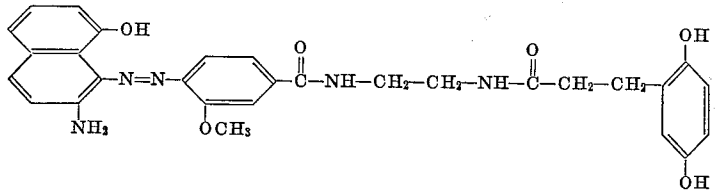
CXL



CXLI

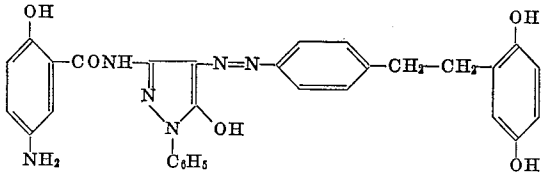


CXLII

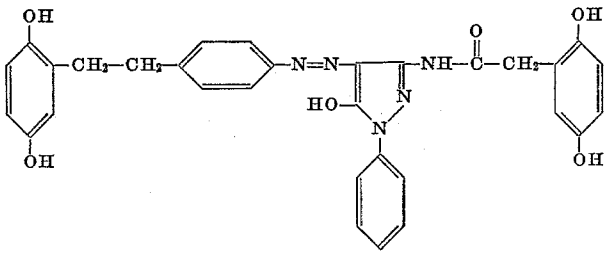


The following dye developers within the group claimed in the Green et al. Patent No. 3,135,734:

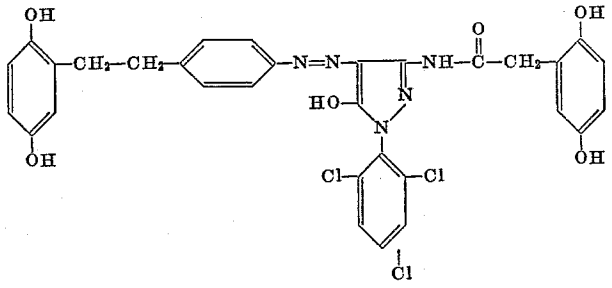
CXLIII



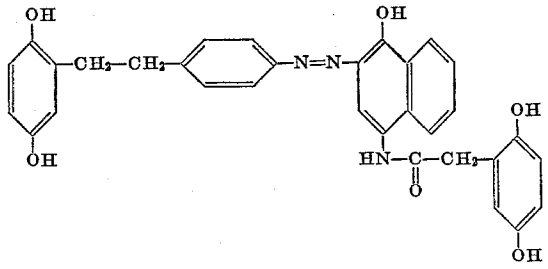
CXLIV



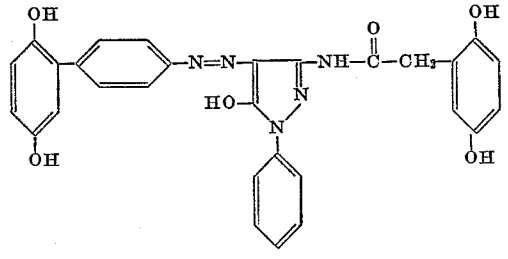
CXLV



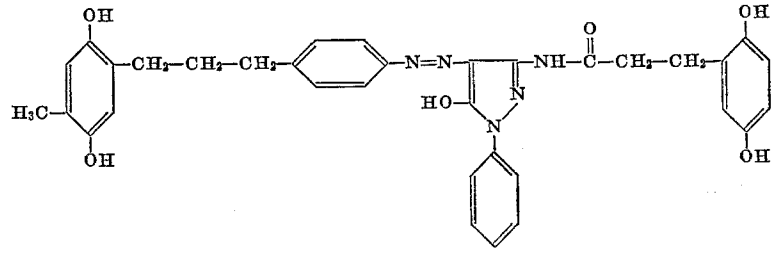
CXLVI



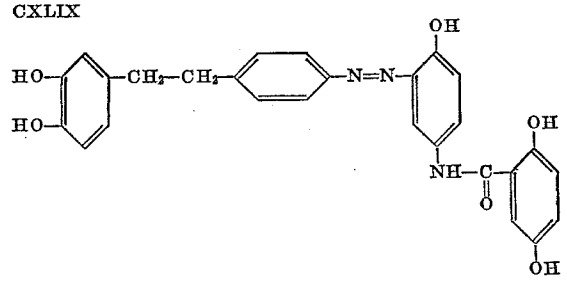
CXLVII



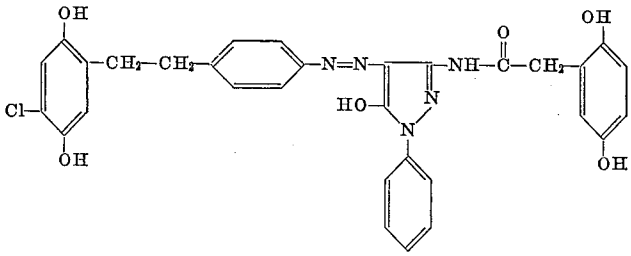
CXLVIII



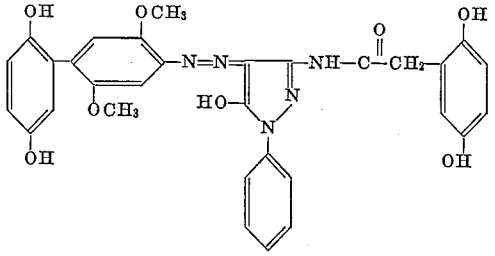
CXLIX



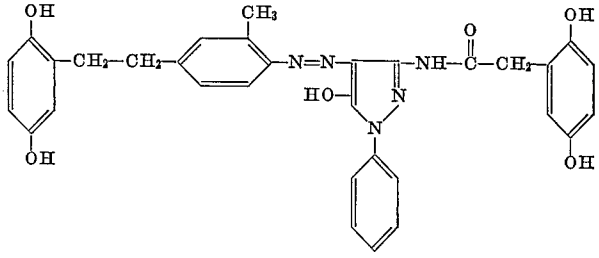
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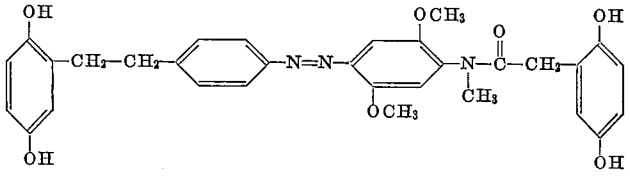
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CLII

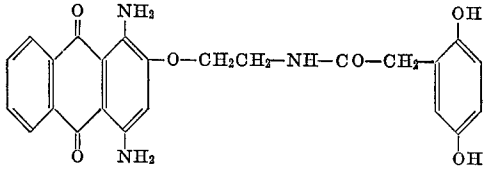


CLIII

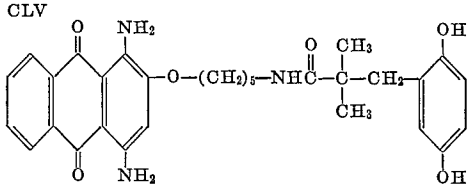


the following dye developers within the group claimed in the copending Downey et al. application Serial No. 152,014, filed November 13, 1961:

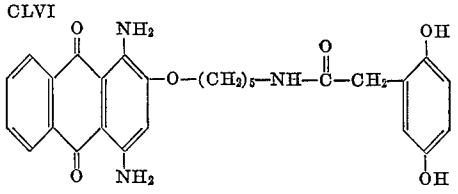
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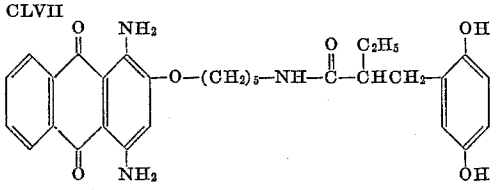
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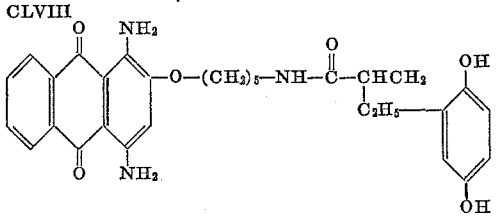
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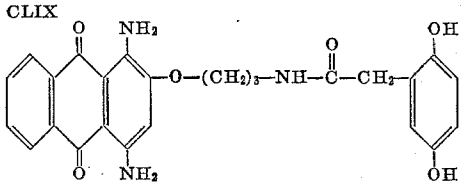
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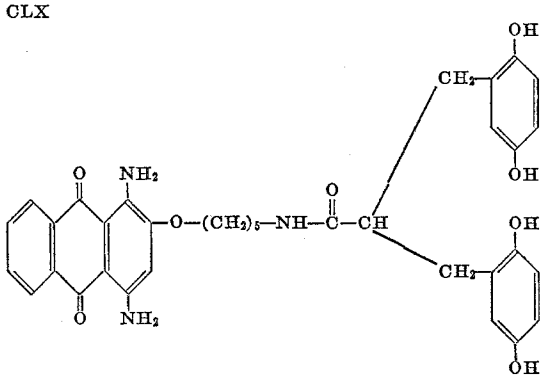
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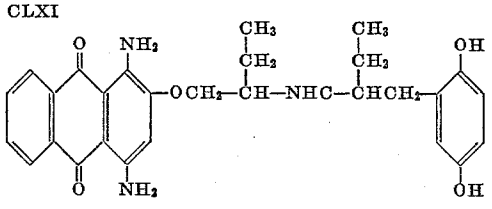
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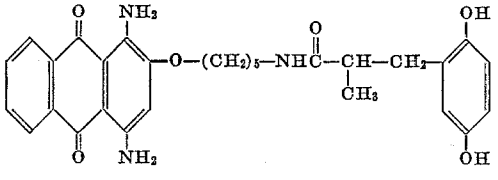
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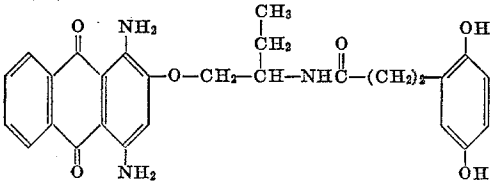
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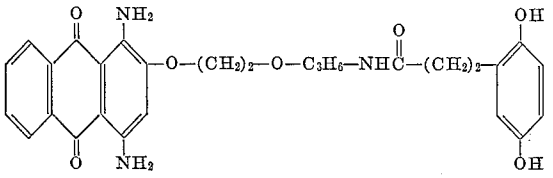
CLXII



CLXIII

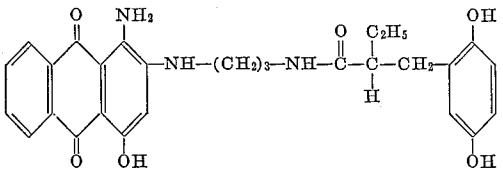


CLXIV

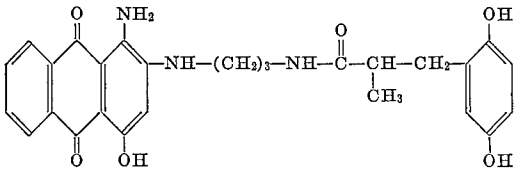


and the following dye developers within the group claimed in the copending Downey et al. application, Serial No. 331,721, filed December 19, 1963:

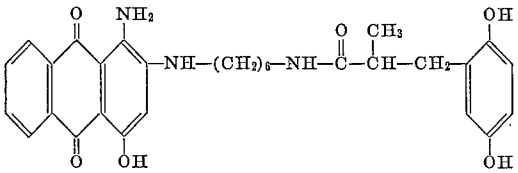
CLXV



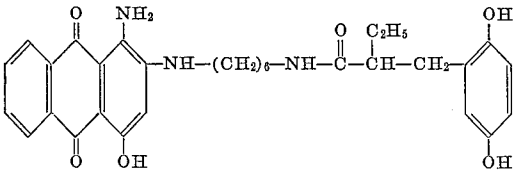
CLXVI



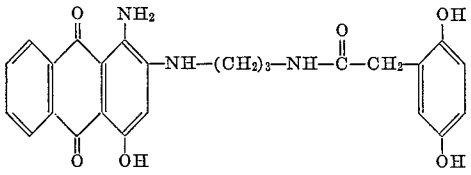
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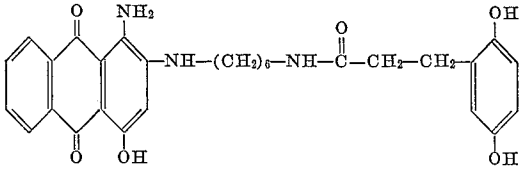
CLXVIII



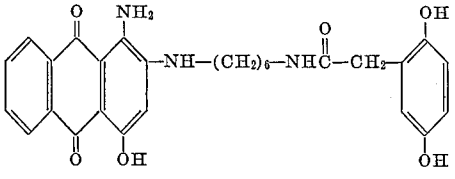
CLXIX



CLXX



CLXXI



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 film units which contain a plurality of photosensitive frames. The photosensitive elements of this invention are especially useful in composite roll film and film pack structures intended for use in a "Polaroid Land Camera" or a similar camera structure such, for example, as the roll film type camera forming the subject matter of U.S. Patent No. 2,435,717, issued to Edwin H. Land on February 10, 1948, or the film pack type camera shown in U.S. Patent No. 2,991,-702, issued to Vaito K. Eloranta on July 11, 1961. In general, such composite roll films comprise a photosensitive roll, a roll of image-receiving material and a plurality of pods containing an aqueous alkaline processing solution. The rolls and pods are so associated with each other that, upon processing, the photosensitive element may be superposed on the image-receiving element and the pods may be ruptured to spread the aqueous alkaline processing solution between the superposed elements. The nature and construction of the pods used in such units are well known to the art. See, for example, U.S. Patents Nos. 2,543,181 and 2,634,886, issued to Edwin H. Land.

It will be noted that the liquid processing composition may contain one or more auxiliary or accelerating silver halide developing agents, such as p-methylaminophenol (Metol); 2,4-diaminophenol (Amidol); benzylaminophenol; hydroquinones; 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, and now U.S. Patent No. 3,173,-786.

The dye developers of this invention may be used also in conventional photographic processes, such as tray or tank development of conventional photosenistive 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 autocoupling 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. Particularly useful are the image-receiving elements described and claimed in the copending application of Edwin H. Land, Serial No. 234,864, filed November 1, 1962. 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.

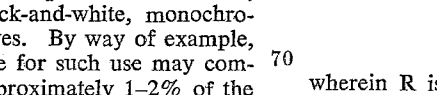
The novel dye developers herein disclosed are also suitable for use as dyes for textile fibres, such as nylon.

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

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

What is claimed is:

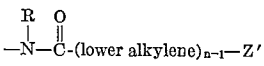
1. A compound selected from the group consisting of anthraquinone monoazo, and disazo dyes characterized in that they contain essentially not less than one and not more than two groups of the formula:



wherein R is selected from the group consisting of hydrogen and lower alkyl radicals, n is a positive integer from one to two, and Z' is a benzene nucleus substituted by at least two members of the group consisting of hydroxyl and amino groups in one of the ortho- and para-

positions with respect to one another, said Z' providing the only benzene nucleus in said compound so substituted by at least two members of said group.

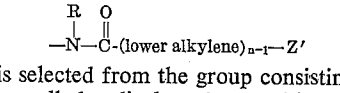
2. A dye selected from the group consisting of mono and disazo dyes characterized in that they contain essentially not less than one and not more than two groups of the formula:



wherein R is selected from the group consisting of hydrogen and lower alkyl radicals, n is a positive integer from one to two, and Z' is a benzene nucleus substituted by at least two members of the group consisting of hydroxyl and amino groups in one of the ortho- and para-positions with respect to one another, said nitrogen atom

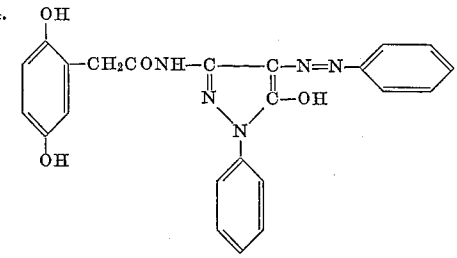
being bonded to a carbon atom of said dye molecule, said Z' providing the only benzene nucleus in said dye so substituted by at least two members of said group.

3. An anthraquinone dye having at least one and not more than two groups of the formula:

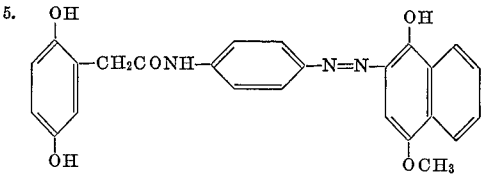


wherein R is selected from the group consisting of hydrogen and lower alkyl radicals, n is a positive integer from one to two, and Z' is a radical comprising a benzene nucleus substituted by at least two members of the group consisting of hydroxyl and amino groups in one of the ortho- and para-positions with respect to one another, each said group being in a substituent linked to a nuclear carbon atom of said anthraquinone nucleus.

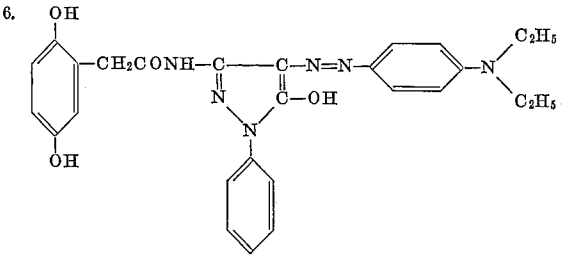
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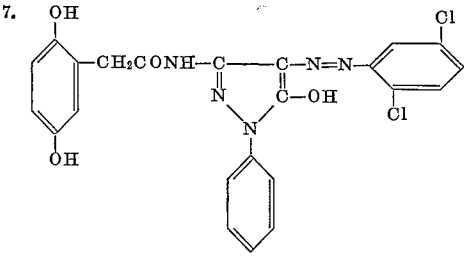
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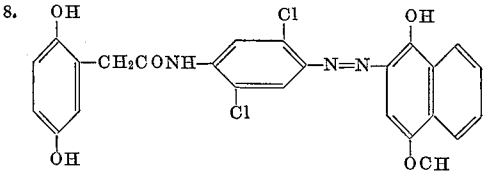
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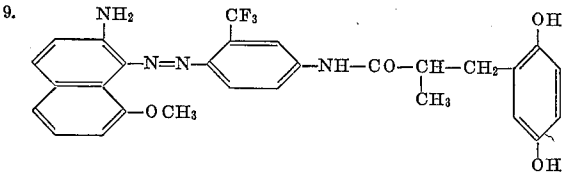
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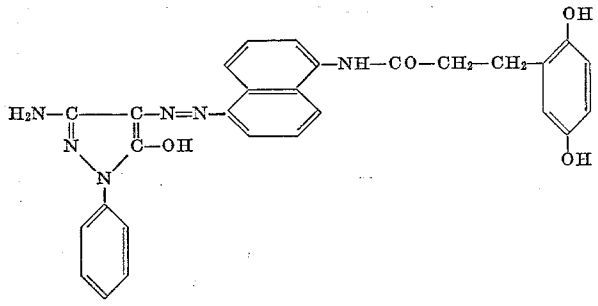
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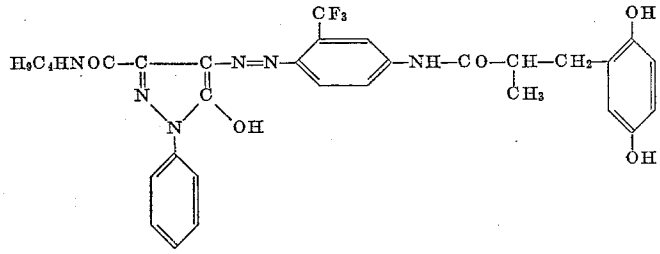
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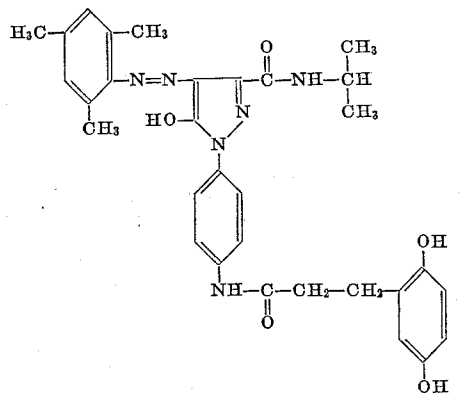
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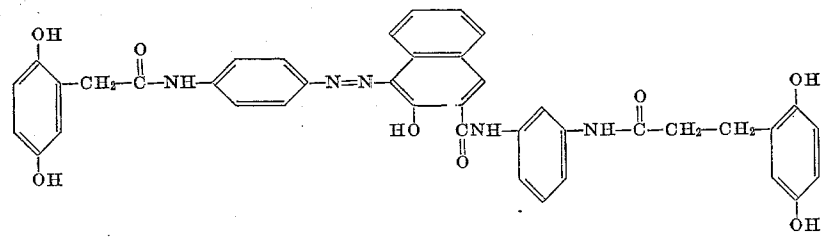
11.



12.



13.



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1,047,620	12/1958	Germany.

CHARLES B. PARKER, *Primary Examiner.*

F. D. HIGEL, *Assistant Examiner.*