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p-DIHYDROXYPHENYL SULFAMYL AZO AND ANTHRAQUINONE DYESTUFFS

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3 Claims. (Cl. 260—195)

This application is a division of our copending application, Serial No. 707,109, filed January 6, 1958, and now abandoned.

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

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

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

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

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 a 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 May 9, 1961 to Howard G. Rogers, discloses diffusion transfer-reversal processes wherein a photographic negative material, such as a photographic element comprising an exposed silver halide emulsion layer containing a latent image, is processed to impart to an image-receiving element a reversed or positive dye image of said latent image by permeating into said emulsion layer a suitable liquid processing composition and bringing said emulsion layer into superposed relationship with an appropriate image-receiving layer. It is an object of this invention to provide additional dye developers suitable for use in such processes.

In carrying out the process of this invention, a photosensitive element containing a silver halide emulsion is exposed and wetted with a liquid processing composition, for example, by immersing, coating, spraying, flowing, etc., in the dark, and the photosensitive element superposed, prior to, during or after wetting, on the sheet-like support element, which may be utilized as an image-receiving element. In a preferred embodiment, the photosensitive element contains a layer of dye developer, and the liquid processing composition is applied to the photosensitive element in a uniform layer as the photosensitive element is brought into superposed position with an image-receiving element. It is also within the scope of this invention to apply the liquid processing composition prior to exposure, in accordance with the disclosure in the copending U.S. application of Edwin H. Land, Serial No. 498,672, filed April 1, 1955, and now 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 latent image is developed, the oxidation product of the dye developer is immobilized or precipitated in situ with the developed silver, thereby providing an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the dye developer upon oxidation, and especially as regards its solubility in alkaline 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 or element, said transfer substantially excluding silver or oxidized dye developer. Under certain circumstances, the layer of the liquid processing composition may be utilized as the image-receiving layer. The latter element receives a depthwise diffusion, from the emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide a reversed or positive, colored image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer to provide a pH affording the desired color. 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. Imbibition periods of approximately one minute have been found to give good results, but this contact period may be adjusted where necessary to compensate for variations in temperature or other conditions. The desired positive image is revealed by stripping the image-receiving element from the photosensitive element at the end of the imbibition period.

The dye developers of this invention may be utilized in the photosensitive element, for example in, on or behind the silver halide emulsion, or they may be utilized in the image-receiving element or in the liquid processing composition. In a preferred embodiment, a coating or layer of the dye developer is placed behind the silver halide emulsion, i.e., on the side of the emulsion adapted to be located most distant from the photographed subject when the emulsion is exposed and preferably also adapted to be most distant from the image-receiving element when in superposed relationship therewith. Placing the dye developer behind the emulsion layer, as in the preferred embodiment, has the advantage of providing increased contrast in the positive image, and also minimizes any light-filtering action by the colored dye developer. In this preferred embodiment, the layer of dye developer may be applied by using a coating solution containing about 0.5 to 8%, by weight, of the dye developer. Similar concentrations may be used if the dye developer is utilized as a component of the liquid processing composition. Concentrations as low as 0.2% in the liquid processing composition being suitable in certain instances.

The liquid processing composition above referred to comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or

sodium carbonate, and may contain the dye developer. In some instances, it may contain a small amount of a conventional developing agent. If the liquid processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin, uniform layer, it may also include a viscosity-increasing compound constituting film-forming material of the type which, when said composition is spread and dried, will form a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric, water-soluble ether inert to an alkali solution, as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected when left in solution for a long period of time may also be used.

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

(A) $$[Z-Y-\underset{\displaystyle R}{\underset{|}{N}}-SO_2-]_pX$$

wherein Z is an o-dihydroxyphenyl or a p-dihydroxyphenyl group and the halogen and alkyl substituted derivatives thereof; Y is a covalent bond or a divalent radical; R is hydrogen or a lower alkyl group; *p* is 1 or 2; and X is the residue of a dye molecule, preferably the residue of an azo or anthraquinone dye molecule.

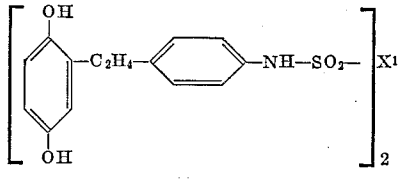
It will be apparent that the novel dye developers of this invention may also be characterized as dyes that contain not less than one and not more than two groups selected from those represented by the formula:

)B) $$Z-Y-\underset{\displaystyle R}{\underset{|}{N}}-SO_2-$$

wherein Z, Y and R have the same significance as previously noted.

In a preferred embodiment, Z is a p-dihydroxyphenyl group; Y is an ethylphenyl group; R is hydrogen; *p* is 2; and X^1 is the residue of an azo or anthraquinone dye molecule; and such dye developers may be represented by formula:

C)



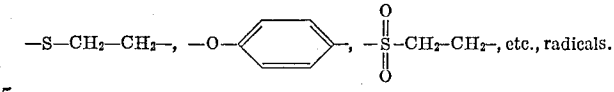
As used herein with reference to X, the expression "residue of a dye molecule" is intended to signify the atoms necessary to complete a chromophoric system. Thus, X may be referred to as a dye radical.

As examples of divalent radicals, signified by the term Y in Formula A, suitable for use in the practice of this invention, mention may be made of: divalent organic radicals such as, e.g., alkylene radicals, preferably lower

alkylene radicals, such as ethylene, isopropylene, etc., arylene radicals, such as phenylene, etc., alkarylene radicals, preferably lower alkphenylene radicals, such as ethylphenyl, acyl radicals such as

$$-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-, \text{ etc.}$$

divalent inorganic radicals such as, e.g., thio, oxy, sulfonyl, etc., radicals; and divalent radicals which contain both hetero and carbon atoms as constituent components of said radicals such as, e.g.,



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

(D) $$Z-Y-\underset{\displaystyle R}{\underset{|}{N}}-H$$

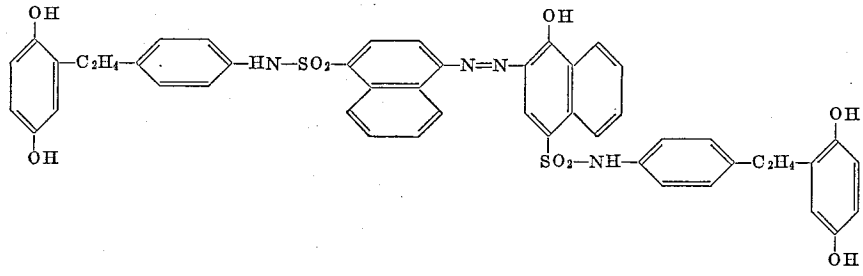
wherein Z, Y, and R have the same meaning as above, such as for example, amino-hydroquinone, amino-ethyl-hydroquinone, amino-phenyl-hydroquinone, amino-phenethyl-thio-hydroquinone, etc.; with a sulfonyl chloride derivative of a dye, i.e., of the formula:

(E) $$[Cl-SO_2-]_pX$$

wherein X and *p* have the same meaning as above.

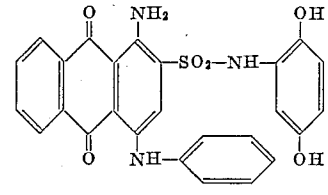
As examples of suitable dye developers within the scope of this invention, mention may be made of the following:

(F)



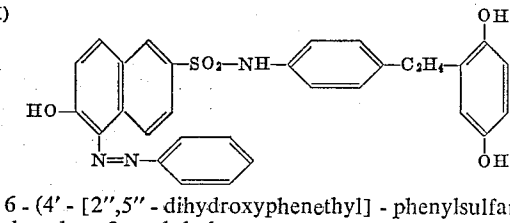
4,4' - bis - (4'' - [2''',5''' - dihydroxyphenethyl]-phenylsulfamyl) - 1' - hydroxy - 1,2' - azonaphthalene.

(G)



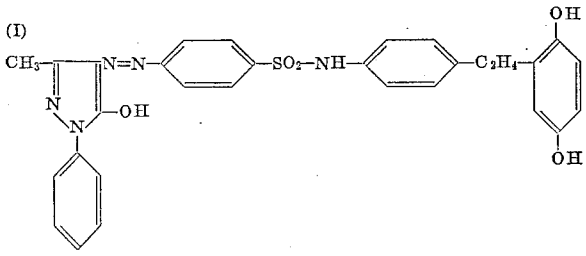
1 - amino - 4 - anilino - 2 - hydroquinonylsulfamyl-anthraquinone.

(H)



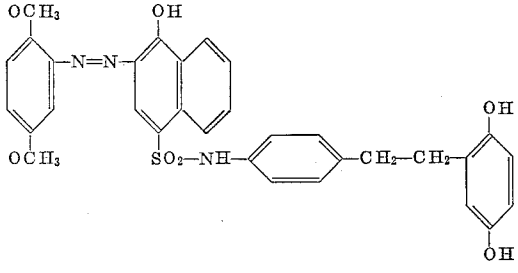
6 - (4' - [2'',5'' - dihydroxyphenethyl] - phenylsulfamyl)-1-phenylazo-2-naphthol.

(I)



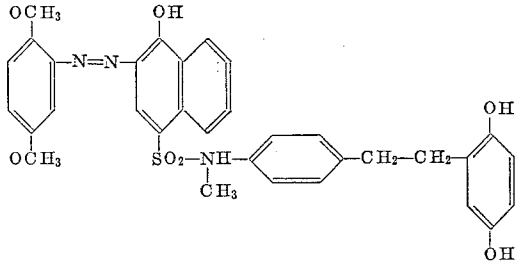
4 - (4' - [4" - (2"',5"' - dihydroxyphenethyl) - phenylsulfamyl]-phenylazo)-3-methyl-1-phenyl-5-pyrazolone.

(J)



4 - (4' - [2",5" - dihydroxyphenethyl] - phenylsulfamyl)-2-(2',5'-dimethoxyphenylazo)-1-naphthol.

(K)



4 - (4' - [2",5" - dihydroxyphenethyl] - N - methylphenylsulfamyl)-2-(2',5'-dimethoxyphenylazo) - 1 - naphthol.

The invention will be illustrated in greater detail in conjunction with the following specific examples which set out representative preparations 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.

Example 1

1 g. of p-aminophenethyl-hydroquinone hydrobromide, prepared according to the procedure disclosed and claimed in U.S. Patent No. 3,019,107, issued January 30, 1962 to Elkan R. Blout, Milton Green, Howard G. Rogers, Myon S. Simon and Robert B. Woodward, and 1.25 g. of 1-hydroxy-1,2'-azonaphthalene-4,4'-bis-sulfonyl chloride, are dissolved in 40 cc. of pyridine. The flask is evacuated, warmed on a steam bath for 2 hours, cooled, and acidified. The resulting solid magenta dye, 4,4'-bis-(4"-[2"',5"'-dihydroxyphenethyl] - phenylsulfamyl) - 1' - hydroxy - 1,2'-azonaphthalene [Formula F], melts at 200 to 204° C. The absorption spectrum of this product exhibits a $\lambda_{max.}$ of 570 mμ in dimethyl formamide.

Analysis for nitrogen:

	Percent
Calculated	6.4
Found	6.5

Example 2

1.7 g. of p-aminophenethyl-hydroquinone-diacetate hydrochloride and 2.0 g. of 2-(2',5'-dimethoxyphenylazo)-1-naphthol-4-sulfonyl chloride are added to 80 cc. of pyridine. The flask is immediately evacuated, warmed on a steam bath for 2 hours and allowed to stand for 12 hours. The contents of the flask are then poured into an excess of ice and hydrochloric acid and the resulting precipitate, 4-(4'-[2",5"-bis-acetoxyphenethyl]-phenylsulfamyl)-2-(2',5'-dimethoxyphenylazo) - 1 - naphthol, separated and dried. The dried precipitate is dissolved in 80 cc. of ethanol. A solution of 1.7 g. of potassium hydroxide in 20 cc. of water is added thereto and the resulting mixture warmed on a steam bath for 3 minutes, acidified with dilute hydrochloric acid and evacuated. The resulting product, 4 - (4'-[2",5" - dihydroxyphenethyl]-phenylsulfamyl)-2-(2',5'-dimethoxyphenylazo) - 1 - naphthol [Formula J], is purified by reprecipitation from methyl Cellosolve with 1% hydrochloric acid and melts above 300° C.

The procedure exemplified in Examples 1 and 2 may be modified by the substitution of the appropriate starting materials where it is desired to synthesize further compounds within Formula 1, for example the specific compounds previously enumerated.

In the following example 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. This example is 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.

Example 3

A photosensitive element is prepared by coating a gelatin-coated film base with a solution containing 3% of 4,4'-bis-(4"-[2"',5"'-dihydroxyphenethyl] - phenylsulfamyl)-1'-hydroxy-1,2'-azonaphthalene, [Formula F as prepared in Example 1], in a 4% solution of cellulose acetate hydrogen phthalate in a 50:50 mixture, by volume, of acetone and tetrahydrofuran. 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:

	Percent
Sodium carboxymethyl cellulose	4.5
1-phenyl-3-pyrazolidone	0.2
Sodium hydroxide	5.0
Potassium bromide	0.5

between said photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element comprises a cellulose acetate-coated baryta paper which has been coated with a solution comprising 6% aqueous polyvinyl alcohol. After an imbition period of approximately one minute, the image-receiving element is separated and contains a magenta positive dye image of the photographed subject.

Example 4

A photosensitive element is prepared by coating a gelatin-coated film base with a solution containing 4% of 4-(4' - [2",5" - dihydroxyphenethyl] - phenylsulfamyl)-2-(2',5'-dimethoxyphenylazo)-1-naphthol, [Formula J as prepared in Example 2], in a 4% solution of cellulose acetate hydrogen phthalate in tetrahydrofuran. 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:

	Percent
Sodium carboxymethyl cellulose	4.25
1-phenyl-3-pyrazolidone	0.6
Sodium hydroxide	1.5
Potassium bromide	0.4

between said photosensitive element and an image-receiving element as said elements are brought into superposed relationship. The image-receiving element comprises a cellulose-coated baryta paper which has been coated with

a solution comprising 10% nylon type F8 (trade name of E. I. du Pont de Nemours & Co., Wilmington, Delaware for N-methoxymethyl polyhexamethylene adipamide) in 80% aqueous ethanol. After an imbition period of approximately one minute, the image-receiving element is separated and contains a magenta positive dye image of the photographed subject.

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

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

It should be noted that the dye developers of this invention are self-sufficient to provide the desired color image and do not depend upon coupling reactions to produce the desired color. They thus provide a complete departure from conventional photographic color processes in which the color is produced by a coupling reaction involving the oxidized developing agent.

Dyes utilized to provide the dye portion of the dye developers of this invention should not, as for example, sulfide dyes, possess constituents which are harmful to photographic materials such as silver halide. In the event the dye portion of the dye developer is of a nature which tends to desensitize silver halide, suitable precautions, such as those mentioned in U.S. Patent No. 3,019,-124, issued January 30, 1962 to Howard G. Rogers, should be utilized for controlling this undesirable condition.

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

It will be apparent that, by appropriate selection of the image-receiving element from among suitable known opaque and transparent materials, it is possible to obtain either a colored positive reflection print or a colored positive transparency. Likewise, the inventive concepts herein set forth are adaptable for multicolor work by the use of special photographic materials, for example, film materials of the type containing two or more photosensitized elements associated with an appropriate number of image-receiving elements and adapted to be treated with one or more liquid processing compositions, appropriate dye developers suitable to impart the desired subtractive colors being incorporated in the photosensitized elements or in the liquid processing compositions. Examples of such photographic materials are disclosed in U.S. Patent No. 2,647,049 to Edwin H. Land on July 28, 1953.

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

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

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

What is claimed is:

1. A compound of the formula:



wherein Z is p-dihydroxyphenyl; Y is selected from the group consisting of a covalent bond and lower alkylene, phenylene, and lower alkphenylene radicals; R is selected from the group consisting of hydrogen and lower alkyl groups; *p* is a positive integer from 1 to 2, inclusive; and X is the radical of a dye molecule selected from the group consisting of azo and anthraquinone dyes, each



radical being directly bonded to a ring carbon atom of a separate ring of said dye radical X, said ring being selected from the group consisting of benzene, naphthalene, pyrazolone, and anthraquinone rings.

2. As a compound, 4-4'-bis-(4''-[2''',5'''-dihydroxyphenethyl] - phenylsulfamyl) - 1' - hydroxy-1,2'-azonaphthalene.

3. As a compound, 4-(4'-[2'',5''-dihydroxyphenethyl]-phenylsulfamyl) - 2-(2',5' - dimethoxyphenylazo)-1-naphthol.

No references cited.

CHARLES B. PARKER, *Primary Examiner.*