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2,701,766

DEVELOPERS FOR AND METHOD OF PRODUCING PHENAZONIUM DYESTUFF IMAGES WITH p-DIALKYLAMINOANILINE DEVELOPING AGENTS

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This invention relates to the production of phenazonium dyestuff images by color development with p-dialkylaminoanilines, and particularly to 6-substituted-8-hydroxycinchoninic acids as color forming couplers therefor.

The formation of colored photographic images by coupling the development product of an aromatic amino developing agent with color forming or coupling compounds is well known, and is generally referred to as color forming development. In these methods the subtractive process of color image formation is ordinarily used and the image dyes are intended to be of the complementary or secondary colors, cyan, or blue-green, and magenta and yellow. The dyes produced by coupling are azomethines, indamines, or indophenols, depending upon the composition of the coupler and of the developer. The couplers which produce magenta dyes are ordinarily pyrazolones or cyanoacetyl compounds. The coupler or color former may be present in the emulsion or in the developing solution which during the development process couples with the oxidation product of the aromatic amino developer to form a dye image in the emulsion. The developed emulsion may then be bleached and fixed for removal of the silver image leaving the color image in the emulsion.

It is known that 8-hydroxyquinolines, including 5,7-dibromo-8-hydroxyquinoline, are utilized with the usual p-phenylenediamine type developers to produce quinonimines. The colors formed by these compounds on coupling with the oxidation product of the developer are generally cyan with the tone ranging from blue to blue-green. When the 5,7-dibromo derivative is reacted with the oxidation products of a p-phenylenediamine type developer, the bromine atom in the coupling position, to wit, para to the phenolic hydroxyl group, is eliminated. The bromine atom in the 7-position is retained and serves to accentuate the color of the cyan dye formed.

United States Patent 2,486,440, issued November 1, 1949, describes the production of blue, cyan, purple, purplish-blue, and red phenazonium dyestuff images by color developing an exposed silver halide emulsion with a color developer comprising a developer of the aromatic triamine type in the presence of 8-hydroxyquinoline as the color former.

The phenazonium dye images produced in this way are extremely desirable from the standpoint of transmission spectra and stability. However, some of the phenazonium dyes of such images are only formed by a special after-treatment with acids or acid reacting solutions, i. e., acid cuprous chloride solutions of the green or yellow dye images, presumably of a quinonimine, resulting from the color forming development step. The value of the phenazonium dye as a photographic image is, therefore, somewhat offset by the fact that additional time and chemicals are necessary in order to obtain the image thereof.

Tulagin and Coles describe in their United States Patent 2,524,741, issued October 3, 1950, the direct production of such phenazonium dyestuff images by the color forming development step, i. e., without an additional after-treatment, by employing a 1,2,4-triaminobenzene developer and an 8-hydroxyquinoline (including 8-hydroxycinchoninic acid) as the color former containing in the 6-position of the quinoline ring a substituent, such as halogen, nitro, sulfonic acid, or arsonic acid radical

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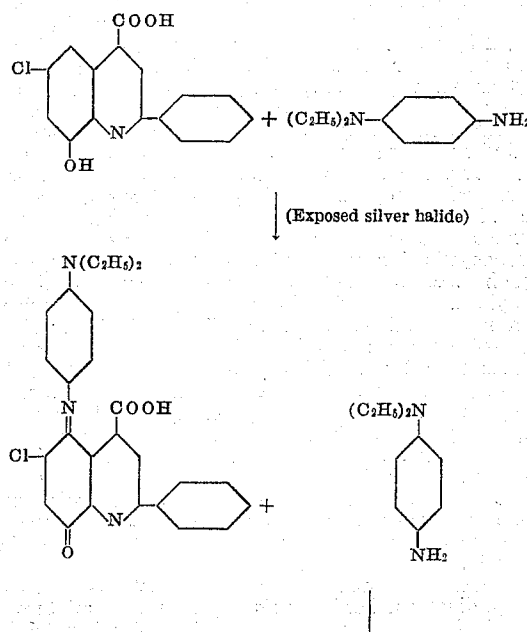
which is eliminated during the color forming development as a negative ion.

In the coupling of a 6-halo-8-hydroxyquinoline or a 6-halo-8-hydroxycinchoninic acid as a color former and a 1,2,4-triaminobenzene as a developer, the originally formed quinonimine ring closes through elimination of the substituent group in the 6-position to form a magenta azine dye. In this process, the halogen atom present in the 6-position is designed to function only as a specific means of insuring and facilitating azine dye formation. The azine ring is formed by the interaction of one molecule of oxidized 1,2,4-triaminobenzene developer. The halogen atom present in the 7-position of 8-hydroxyquinolines of the prior art serves solely to accentuate the color of the quinonimine image formed. The halogen atom in the 5-position of such compounds is eliminated during color coupling and otherwise serves no particular purpose.

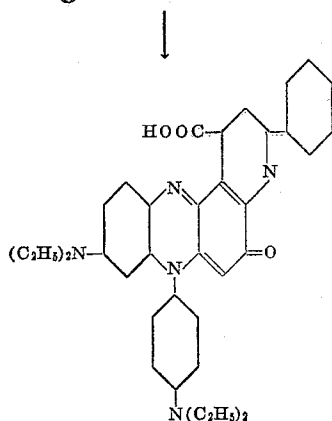
I have discovered that contrary to all expectation, 6-substituted-8-hydroxycinchoninic acids when coupled with the oxidation product of a p-dialkylaminoaniline developer yield azine magenta dye images in the silver halide emulsion. Instead of yielding the expected cyan dye images, strangely enough, the color changes quite rapidly to azine magenta. This is attributable to the fact that two molecules of the color developer enter into the dye forming reaction as soon as the color former is treated in situ with a developable silver image as will be illustrated hereinafter.

This discovery leads to the conclusion that when one molecular equivalent of a 6-substituted-8-hydroxycinchoninic acid is coupled with one molecular equivalent of the oxidation product of p-dialkylaminoaniline, coupling takes place in the 5-position of the said acid, i. e., para to the phenolic hydroxyl group of said acid, to yield the expected (quinonimine) cyan dye. With an additional molecular equivalent of the p-dialkylaminoaniline, the quinonimine intermediate undergoes ring closure to a magenta (azine) dye. During the latter reaction, the substituted group, i. e., chlorine, bromine, or sulfo, in the 6-position of the quinonimine intermediate is replaced by a p-dialkylaminoanilino group which together with the adjacent indamino group forms an azine ring.

The following series of reaction with 2-phenyl-6-chloro-8-hydroxycinchoninic acid as the color former and p-diethylaminoaniline as the developer are offered as a possible and tentative explanation of the formation of the azine dye.



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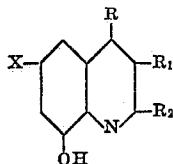


The azine dyes obtained in this manner are superior spectrophotometrically, and in resistance to acid and light fading, to quinonimine dyes prepared from 8-hydroxyquinolines and 5,7-dibromo-8-hydroxyquinolines and to azomethines prepared from pyrazolones.

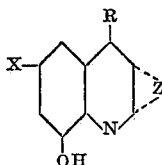
The utilization of 6-substituted-8-hydroxycinchoninic acids as color formers in the production of phenazonium dyestuff images in the presence of p-dialkylaminoaniline developers, constitutes the purpose and objects of the present invention.

Other objects and advantages will become apparent from the following description.

The 6-substituted-8-hydroxycinchoninic acids contemplated herein are characterized by the following general formula:



and



wherein R represents $-\text{COOH}$, $-\text{CONH}_2$, or $-\text{CONHR}_3$ in which R_3 is an alkyl radical of not more than 26 carbon atoms, such as from methyl up to and including hexacosyl radical, a sulfonated aliphatic radical containing at least 10 carbon atoms or a sulfonated aromatic radical substituted by an aliphatic radical containing at least 5 carbon atoms, R_1 represents either hydrogen, allyl, a lower alkyl group, e. g., methyl, ethyl, propyl, isopropyl, and the like, or a carboxyalkyl group, e. g., carboxymethyl, carboxyethyl, carboxypropyl, and the like, R_2 represents an allyl or lower alkyl group of the same value as R_1 , an aryl group, e. g., phenyl, naphthyl, diphenyl, etc., or a heterocyclic group, e. g., thienyl, furyl, pyrrol, and the like, X represents either chlorine, bromine, or sulfo groups, and Z represents the atoms necessary to complete a carbocyclic ring system of 5 to 10 carbon atoms, e. g., trimethylene, tetramethylene, methyl substituted trimethylene, benzotrimethylene, benztetramethylene, naphthotetramethylene, and the like. Said lower alkyl, aryl, and heterocyclic radicals given as values for R_2 may be substituted by alkali insensitive groups, such as halogen, e. g., chlorine, bromine, iodine, etc., alkyl, e. g., methyl, ethyl, propyl, etc., aryl, e. g., phenyl, naphthyl, etc., alkoxy, e. g., methoxy, ethoxy, propoxy, etc., aryloxy, e. g., phenoxy, naphthoxy, etc., amino, nitro, sulfonic acid, carboxylic acid and the like.

The compounds characterized by the foregoing formulae are prepared according to the method described in United States Patent 2,579,420, issued on December 18, 1951.

In general, the method consists of selectively hydrolyzing 6,8-dihalocinchoninic acids by heating a mixture of the acid in an aqueous solution of an alkali metal hy-

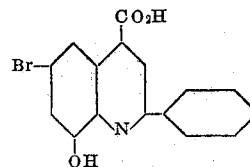
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dride or carbonate of 5 to 20% concentration in an amount corresponding to at least three chemical equivalents per chemical equivalent of 6,8-dichlorocinchoninic acid at a temperature ranging from 50° to 175° C. in the presence of a copper catalyst until solution of the acid occurs. After filtering the reaction mixture, the filtrate is acidified with acetic acid and the crude product collected. The product may be purified by crystallization from acetic acid or mixtures of dimethylformamide and acetic acid.

The 6-bromo derivatives of 8-hydroxycinchoninic acid can be prepared according to the general procedure of the Doebner-Miller reaction. For example, the compound of Illustration 1 is obtained by treating 2-amino-5-bromophenol with benzaldehyde and pyruvic acid in a suitable solvent.

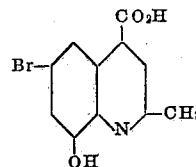
Examples of compounds embraced by the above formulae are the following:

(1)



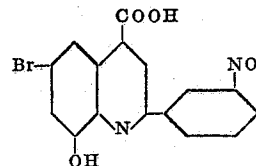
2-phenyl-6-bromo-8-hydroxycinchoninic acid

(2)



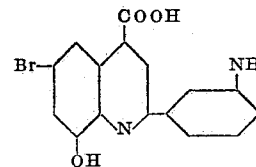
2-methyl-6-bromo-8-hydroxycinchoninic acid

(3)



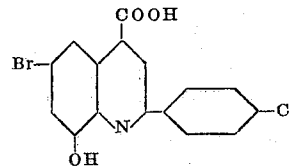
2-(3'-nitrophenyl)-6-bromo-8-hydroxycinchoninic acid

(4)



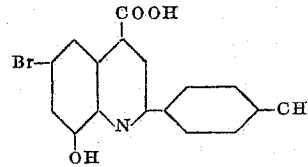
2-(3'-aminophenyl)-6-bromo-8-hydroxycinchoninic acid

(5)



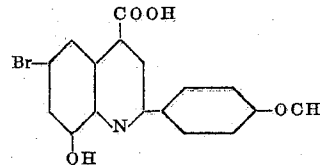
2-(4'-chlorophenyl)-6-bromo-8-hydroxycinchoninic acid

(6)

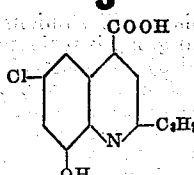
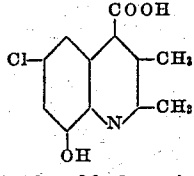
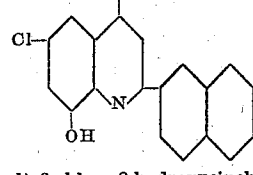
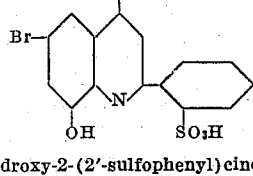
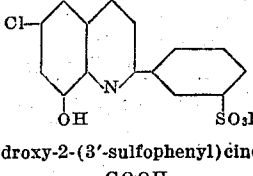
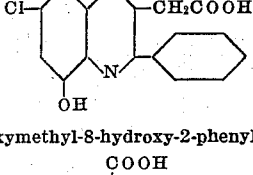
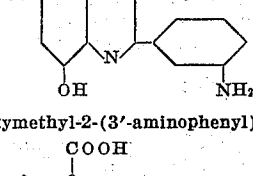
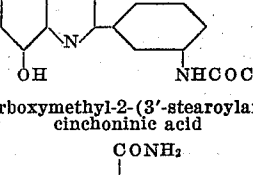
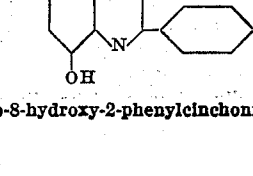
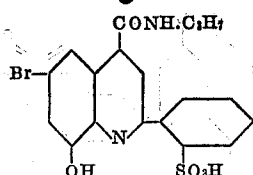
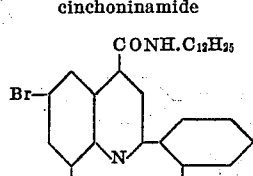
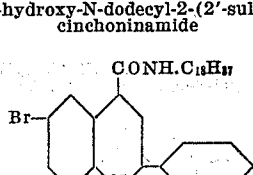
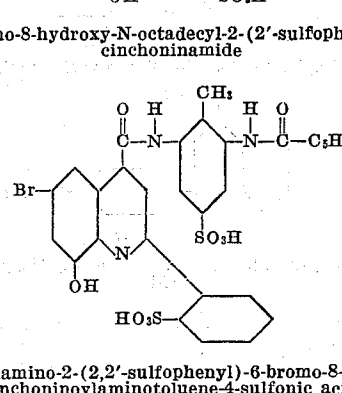
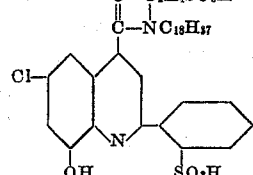
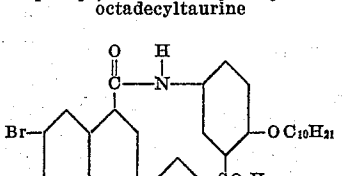
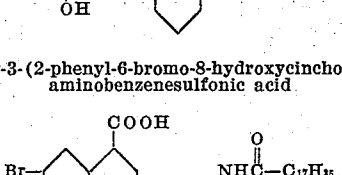


2-(p-tolyl)-6-bromo-8-hydroxycinchoninic acid

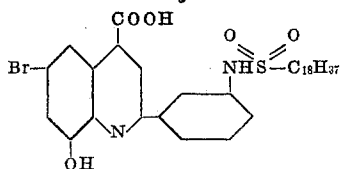
(7)



2-(4'-methoxyphenyl)-6-bromo-8-hydroxycinchoninic acid

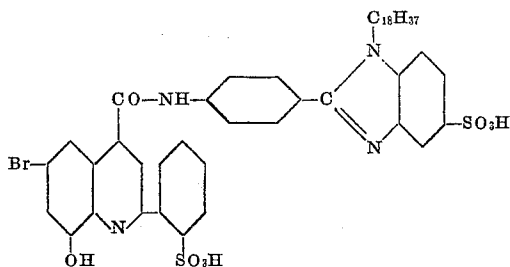
- (8) **5**

 2-propyl-6-chloro-8-hydroxycinchoninic acid
- (9) **10**

 2,3-dimethyl-6-chloro-8-hydroxycinchoninic acid
- (10) **15**

 2-(β-naphthyl)-6-chloro-8-hydroxycinchoninic acid
- (11) **20**

 6-bromo-8-hydroxy-2-(2'-sulfophenyl)cinchoninic acid
- (12) **25**

 6-chloro-8-hydroxy-2-(3'-sulfophenyl)cinchoninic acid
- (13) **30**

 6-chloro-3-carboxymethyl-8-hydroxy-2-phenylcinchoninic acid
- (14) **35**

 6-chloro-3-carboxymethyl-2-(3'-aminophenyl)cinchoninic acid
- (15) **40**

 6-chloro-3-carboxymethyl-2-(3'-stearylaminophenyl)cinchoninic acid
- (16) **45**

 6-chloro-8-hydroxy-2-phenylcinchoninamide
- (17) **50**

 6-bromo-8-hydroxy-N-(n-propyl)-2-(2'-sulfophenyl)cinchoninamide
- (18) **55**

 6-bromo-8-hydroxy-N-dodecyl-2-(2'-sulfophenyl)cinchoninamide
- (19) **60**

 6-bromo-8-hydroxy-N-octadecyl-2-(2'-sulfophenyl)cinchoninamide
- (20) **65**

 6-caproylamino-2-(2,2'-sulfophenyl)-6-bromo-8-hydroxycinchoninoylaminotoluene-4-sulfonic acid
- (21) **70**

 2-(2'-sulfophenyl)-6-chloro-8-hydroxycinchoninoyl-octadecyltaurine
- (22) **75**

 6-deoxy-3-(2-phenyl-6-bromo-8-hydroxycinchoninoyl)-aminobenzenesulfonic acid
- (23) **80**

 2-(3'-stearyl-amino-2'-sulfophenyl)-6-bromo-8-hydroxycinchoninic acid

(24)



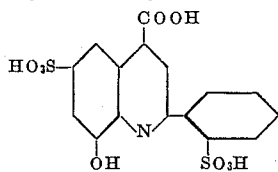
2-(3'-octadecanesulfonamidophenyl)-6-bromo-8-hydroxy-cinchoninic acid

(25)



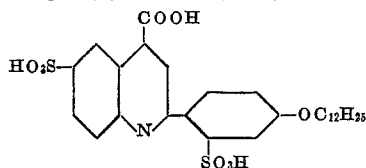
2-[4-(6-bromo-8-hydroxy-2-(2'-sulfophenyl)-cinchoninoyl)-aminophenyl]-1-octadecyl-5-sulfobenzimidazole

(26)



2-(2'-sulfophenyl)-6-sulfo-8-hydroxycinchoninic acid

(27)



2-(4'-dodecoxy-2'-sulfophenyl)-6-sulfo-8-hydroxycinchoninic acid

The compounds of the general formulae wherein R is carboxyalkyl as shown by illustrations 13 to 15 are prepared by conventional methods. For example, compound 13 is prepared by reacting 5-chloro-7-bromoisoatin with benzoylpropionic acid to form the 6-chloro-3-carboxymethyl-8-bromo-2-phenylcinchoninic acid. This step is followed by an alkaline hydrolysis which accomplishes the replacement of the bromine atom by a hydroxyl group. Compound 14 is prepared in an analogous manner with the exception that 3-nitrobenzoylpropionic acid is used in place of benzoylpropionic acid and the alkaline hydrolysis is followed by a reduction of the nitro group. The resulting amino derivative is readily converted into compound 15 by reacting it with stearylchloride.

Compound 16 is prepared by reacting 6-chloro-8-acetoxy-2-phenylcinchoninic acid with thionyl chloride. The resulting acid chloride is converted into the amide by treatment with aqueous ammonia which simultaneously splits off the acetyl group to give the final hydroxy derivative.

The compounds of the above general formulae wherein R is represented by CONHR₃, as shown by illustrations 17 to 22, are readily prepared by methods conventional in the art. For instance, compound 20 is obtained by treating equimolecular quantities of 2-phenyl-6-bromo-8-hydroxycinchoninic acid and 6-amino-2-stearylaminotoluene-4-sulfonic acid in pyridine solution with phosphorus trichloride. Compounds 17, 18, 19, 21, and 22 are prepared by similar procedures while employing the appropriate intermediates.

Compounds 23 and 24 are prepared by reacting compound 4 in pyridine with a fatty acid chloride or an alkyl sulfonyl chloride of 10 to 18 carbon atoms, such as, for example, octadecanoyl chloride, octadecanesulfonyl chloride, and the like.

Compound 25 was prepared by reacting under anhydrous conditions, 6-bromo-8-hydroxy-2-(2'-sulfophenyl)-cinchoninic acid and 2-(4'-aminophenyl)-1-octadecyl-5-sulfobenzimidazole in the presence of phosphorous trichloride and pyridine.

Compounds 26 and 27, and particularly those char-

acterized by formulae of illustrations 1 to 25 in which the chloro or bromo group is replaced by a sulfo group, are readily prepared by conventional methods. For example, compounds 26 and 27 are prepared by refluxing 1 molar equivalent of 3-sulfo-6-aminophenol and 1.1 molar equivalent of an o-sulfobenzaldehyde with approximately 2 molar equivalents of pyruvic acid in methanol for several hours.

The compounds listed above may be added to the p-dialkylaminoaniline developer, provided that they are not fast to diffusion in gelatin, i. e., those of the general formulae wherein R₃ of —CONHR₃ is an alkyl, sulfonated alkyl, and sulfonated aromatic radical substituted by an alkyl radical of not more than 5 carbon atoms, or to the silver halide emulsion in the form of an alkaline solution. Those compounds containing the long aliphatic chain are non-migratory when located in photographic emulsions. The other compounds, however, may be employed either in the developer or in the emulsion, although it is preferred that they be added to the developer.

When incorporating the compounds fast to diffusion into photographic silver halide emulsions or developers, it is preferred that the compound be first dissolved or dispersed in an alkaline solution, such as alcoholic sodium or potassium hydroxide or an aqueous solution of the same alkali and of the same concentration. The alkali solution containing the compound is diluted with color developer and the exposed film color developed, or the alkali solution added to a gelatino silver halide emulsion and the emulsion coated on a film base.

After color forming development, the film is then processed by the usual treating baths, one of which may be alkaline, to produce a magenta phenazonium dye image. The alkali solution or the presence of alkali in one of the treating baths is not necessary to produce the magenta dye image; it causes the magenta dye image to be formed more quickly. A small amount of dipotassium monosodium ferricyanide added to the alkaline solution appears to accelerate the change from the blue-green color formed immediately following color forming development to the magenta color. An alkaline hypo or an alkaline hardener solution will serve the same purpose.

The aqueous alkali, such as sodium or potassium hydroxide, may be used if desired at any stage subsequent to color forming development. The concentration depends on the desired rate of magenta color formation and the resistance of the colloidal carrier to alkali treatment and may be as high as 2 N, provided that swelling repressors, such as sodium sulfate, are used with higher alkali concentrations. Concentrations ranging from 0.05 N to 0.4 N of sodium or potassium hydroxide are generally preferred. In lieu of an aqueous alkali solution, the sodium or potassium hydroxide may be added to the usual hardener bath, e. g., formaldehyde bath, bleach, or hypo bath, in amounts ranging from 8 to 25 grams per liter.

The color developers which are utilized for color development of the magenta dye image, as stated, are of the p-dialkylaminoaniline type, a large number of which is well known to the photographic art. Suitable developers of this type are, for example:

- 4-dimethylaminoaniline
- 4-diethylaminoaniline
- 4-dipropylaminoaniline
- 4-(N-methyl-N-hydroxyethylamino)aniline
- 4-(N-ethyl-N-hydroxyethylamino)aniline
- 4-(N,N-dihydroxyethylamino)aniline

The reaction products of 4-alkylaminoaniline and ethylene oxide described in United States Patent 2,163,166, and the sulfonamido derivatives of p-phenylenediamine, such as N-β-methanesulfonamidoethyl-4-amino-aniline, N-ethyl-β-methanesulfonamido-ethyl-4-aminoaniline, and the like, described in United States Patent 2,193,015, may also be employed as developing agents.

The foregoing developing agents are characterized by the presence of a free or primary amino group in the phenyl nucleus which enables the oxidation product of the developer to couple with the color formers to form a dye image in the emulsion adjacent to the individual particles of the silver image. The silver image may be

removed by bleaching in the well known manner to leave the color image in the emulsion.

A suitable developing solution is prepared as follows:

	Grams
p-Aminodiethylaniline -----	2.0
Sodium carbonate (anhydrous) -----	50.0
Sodium sulfite (anhydrous) -----	2.0
Potassium bromide -----	0.2
Water to make 1 liter.	

The exposed silver halide emulsions are developed in the above solution in the usual manner. A solution or suspension of the color former is only added to the developing solution where the color former is not present in the silver halide emulsion.

Many specific objects, features, and advantages of my invention will become apparent to those skilled in the art from the following examples. These examples are not to be considered as limiting my invention but are merely illustrative of the methods of carrying it out.

Example I

0.25 gram of 2 phenyl-6-chloro-8-hydroxycinchoninic acid was moistened with methanol and treated with a few drops of N-sodium hydroxide to yield a light yellow solution. This solution was diluted to 20 mls. with a color developer as prepared above. An exposed film strip was placed in the color developer solution for 10 minutes. The developer solution was decanted and the strip treated for 6 minutes with a formaldehyde hardening bath containing 14.4 grams of sodium hydroxide per liter. The processing was completed in the usual manner including the customary bleaching, fixing, and washing steps, except that the washing was not prolonged. A magenta phenazonium dye image was obtained which showed an absorption peak of 553 mμ, and possessed excellent stability against fading by light and exposure to acid vapors.

Example II

0.3 gram of 2-propyl-6-bromo-8-hydroxycinchoninic acid was dissolved in a few drops of N-sodium hydroxide. The solution was diluted with 20 mls. of p-dialkylaminoaniline developer and a flashed film strip processed as described in Example I. A magenta phenazonium dye image of excellent transmission spectra and stability was obtained.

Example III

Example I was repeated with the exception that after color development, the film was immersed for 3 minutes in a hardener of the following composition:

Sodium carbonate (monohydrate) -----	grams.. 10
Sodium sulfate -----	do. 45
Formalin (40%) -----	mls. 8
Water to make 1 liter.	

The hardened film was then immersed for a few minutes in 0.3 N sodium hydroxide. By further processing the film in the usual manner, a magenta phenazonium dye image of excellent transmission spectra and acid stability was obtained.

Example IV

16 grams of 6-chloro-3-carboxymethyl-8-hydroxy-2-(3'-stearoylamino)phenylcinchoninic acid were dissolved in 300 mls. of aqueous alcoholic N-potassium hydroxide and the solution added to 1 kg. of a melted gelatino silver iodobromide emulsion. The emulsion was coated on a film base.

The emulsion was then exposed and color developed with a p-dialkylaminoaniline developer and the color developed film hardened with the hardener of Example I and the processing completed in the usual manner. A magenta phenazonium dye image of excellent transmission spectra and acid stability was obtained.

Example V

Example IV was repeated with the exception that after color development, the film was immersed for 3 minutes in a hardener of the following composition:

Sodium carbonate (monohydrate) -----	grams.. 10
Sodium sulfate -----	do. 45
Formalin (40%) -----	mls. 8
Water to make 1 liter.	

By further processing the film in the usual manner, a magenta phenazonium dye image of excellent transmission spectra and acid stability was obtained.

Example VI

A sodium hydroxide solution containing 18 grams of 6-bromo-8-hydroxy-2-(2'-sulfophenyl)-N-octadecylcinchoninamide was added to 1 kg. of a melted gelatino silver iodobromide emulsion and the emulsion coated on a film base. By further processing the film as in Example IV or V, a magenta phenazonium dye image of excellent transmission spectra and acid stability was obtained.

Example VII

Example I was repeated with the exception that 2-phenyl-6-chloro-8-hydroxycinchoninic acid was replaced by an equivalent amount of 2-(β-naphthyl)-6-chloro-8-hydroxycinchoninic acid. A magenta phenazonium dye image of excellent transmission spectra and acid stability was obtained.

Example VIII

Example IV was repeated with the exception that 2-[4-(6-bromo-8-hydroxy-2-(2'-sulfophenyl)-cinchoninoyl)aminophenyl]-1-octadecyl-5-sulfo-benzimidazole was used in place of 6-chloro-3-carboxymethyl-8-hydroxy-2-(3'-stearoylamino)phenylcinchoninic acid. A magenta phenazonium dye image of excellent transmission spectra and acid stability was obtained.

The formation of phenazonium dye images with p-dialkylamino developers and 6-halo-8-hydroxycinchoninic acids can also be utilized for the formation of reversal images as illustrated by the following examples.

Example IX

A film strip was exposed in a sensitometer and developed for 15 minutes in a black and white developer having the following composition:

	Grams
p-Methylaminophenol sulfate -----	3
Sodium sulfite -----	50
Hydroquinone -----	6
Sodium carbonate (monohydrate) -----	40
Sodium thiocyanate -----	2
Potassium bromide -----	2
Water to make 1 liter.	

The black and white developed film strip was washed for 2 minutes, exposed to white light for 1 minute and color developed for 10 minutes in the color forming developer of Example I.

The film strip was washed and immersed for 4 minutes in a hardener having the following composition:

Sodium carbonate (monohydrate) -----	grams.. 5
Sodium sulfate -----	do. 45
Formalin (40%) -----	mls. 8
Water to make 1 liter.	

After the customary bleaching, fixing, and washing operations, a reversal magenta phenazonium dye image was obtained.

Example X

A film base was coated with the color former containing the emulsion of Example IV. After drying, a strip was sensitometrically exposed and developed for 12 minutes in the black and white developer described in Example IX. This developer is incapable of reacting or coupling with the non-diffusing color former but causes the formation of a negative black and white image. The negatively developed film was washed, flashed, and developed in a second developer having the following composition:

	Grams
p-Aminodiethylaniline -----	4
Sodium bisulfite -----	2
Sodium carbonate (monohydrate) -----	60
Potassium bromide -----	1
Water to make 1 liter.	

The color developed film was washed and immersed for 3 minutes in a hardener of the following composition:

Formalin (40%) -----	mls. 6
Sodium sulfate -----	grams.. 40
Sodium hydroxide -----	do. 16
Water to make 1 liter.	

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The hardened film was washed, bleached, fixed, and washed in the conventional manner. A reversal phenazonium dye image was obtained.

Example XI

Example IX was repeated with the exception that the 2-phenyl-6-chloro-8-hydroxycinchoninic acid in the color forming developer was replaced by an equivalent amount of 2-phenyl-6-sulfo-8-hydroxycinchoninic acid.

Example XII

18 grams of 2-(4'-dodecoxy-2'-sulfophenyl)-6-sulfo-8-hydroxycinchoninic acid dispersed in 60 mls. of N-potassium hydroxide solution and further diluted with 250 mls. of water were added to 1 kilogram of a melted gelatino silver iodobromide emulsion. The emulsion was coated on a film base. A film strip cut from this coating was exposed in a sensitometer and developed for 15 minutes in a black and white developer having the following composition:

	Grams
p-Methylaminophenol sulfate	3
Sodium sulfite	50
Hydroquinone	6
Sodium carbonate (monohydrate)	40
Sodium thiocyanate	2
Potassium bromide	2
Water to make 1 liter.	

The black and white developed film strip was short-stopped, washed for 2 minutes, exposed to white light for 1 minute and color developed for 10 minutes in a color developer having the following composition:

	Grams
p-Aminodiethylaniline	2.0
Sodium carbonate (anhydrous)	50.0
Sodium sulfite (anhydrous)	2.0
Potassium bromide	0.2
Water to make 1 liter.	

The film strip was washed and immersed for 5 minutes in a hardener having the following composition:

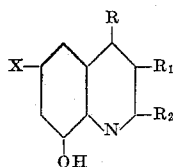
Sodium hydroxide	grams-- 25
Sodium sulfate	do----- 50
Formalin (40%)	mls--- 8
Water to make 1 liter.	

After the customary bleaching, fixing, and washing operations, a reversal magenta phenazonium dye image was obtained.

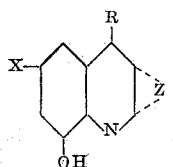
This application is a continuation-in-part of my application Serial No. 180,504, filed on August 19, 1950, now abandoned.

I claim:

1. The method of producing magenta phenazonium dyestuff images in a gelatino silver halide emulsion layer which comprises exposing the layer and developing it with an N,N-dialkyl-p-phenylenediamine developing agent containing only the two amino groups in the presence of a phenazonium dye coupler compound selected from the class consisting of those corresponding to the following formulae:



and



wherein R represents a member of the class consisting of —COOH, —CONH₂, and —CONHR₃ in which R₃ is a member selected from alkyl radicals of not more than 26

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carbon atoms, sulfonated alkyl radicals containing at least 10 carbon atoms, and sulfonated aromatic radicals substituted by an aliphatic radical containing at least 5 carbon atoms, R₁ is a member selected from the class consisting of hydrogen, carboxyalkyl, allyl, and lower alkyl, R₂ represents a member selected from the class consisting of allyl, lower alkyl, aryl, and heterocyclic groups, X represents a member selected from the class consisting of halogen and sulfo groups, and Z represents the atoms necessary to complete a carbocyclic ring system of 5 to 10 carbon atoms.

2. The method as defined in claim 1, wherein the phenazonium coupler compound is 2-phenyl-6-chloro-8-hydroxycinchoninic acid.

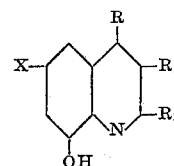
3. The method as defined in claim 1, wherein the phenazonium coupler compound is 2-propyl-6-bromo-8-hydroxycinchoninic acid.

4. The method as defined in claim 1, wherein the phenazonium coupler compound is 6-chloro-3-carboxymethyl-8-hydroxy-2-(3'-stearoylamino-phenyl)cinchoninic acid.

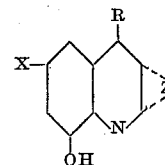
5. The method as defined in claim 1, wherein the phenazonium coupler compound is 6-bromo-8-hydroxy-2-(2'-sulfophenyl)-N-octadecylcinchoninamide.

6. The method as defined in claim 1, wherein the phenazonium coupler compound is 2-[4-(6-bromo-8-hydroxy-2-(2'-sulfophenyl)cinchoninoyl)amino-phenyl]-1-octadecyl-5-sulfobenzimidazole.

7. A color forming photographic developer comprising an N,N-dialkyl-p-phenylenediamine developing agent containing only the two amino groups and a phenazonium dye coupler compound selected from the class consisting of those corresponding to the following formulae:



and



wherein R represents a member of the class consisting of —COOH, —CONH₂, and —CONHR₃ in which R₃ is a member selected from alkyl radicals of not more than 5 carbon atoms, sulfonated aliphatic radicals containing at least 5 carbon atoms, and sulfonated aromatic radicals substituted by an aliphatic radical containing at least 5 carbon atoms, R₁ is a member selected from the class consisting of hydrogen, carboxyalkyl, allyl, and lower alkyl, R₂ represents a member selected from the class consisting of allyl, lower alkyl, aryl, and heterocyclic groups, X represents a member selected from the class consisting of halogen and sulfo groups, and Z represents the atoms necessary to complete a carbocyclic ring system of 5 to 10 carbon atoms.

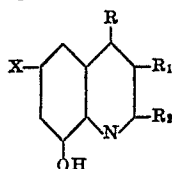
8. A color forming photographic developer comprising an N,N-dialkyl-p-phenylenediamine developing agent containing only the two amino groups and 2-phenyl-6-chloro-8-hydroxycinchoninic acid as a phenazonium dye-stuff coupler compound.

9. A color forming photographic developer comprising an N,N-dialkyl-p-phenylenediamine developing agent containing only the two amino groups and 2-propyl-6-bromo-8-hydroxycinchoninic acid as a phenazonium dye-stuff coupler compound.

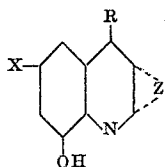
10. The method of producing reversal magenta phenazonium dyestuff images in a gelatino silver halide emulsion layer which comprises exposing the layer, developing it in a black and white developer, exposing the residual silver halide and developing it with an N,N-dialkyl-p-phenylenediamine developing agent containing only the two amino groups in the presence of a phenazonium

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dye coupler compound selected from the class consisting of those corresponding to the following formulae: and



and



wherein R represents a member of the class consisting of —COOH, —CONH₂, and —CONHR₃ in which R₃ is a member selected from alkyl radicals of not more than 26 carbon atoms, sulfonated alkyl radicals containing at least 10 carbon atoms, and sulfonated aromatic radicals substituted by an aliphatic radical containing at least 5 carbon atoms, R₁ is a member selected from the class consisting of hydrogen, carboxyalkyl, allyl, and lower alkyl, R₂ represents a member selected from the class consisting of allyl, lower alkyl, aryl, and heterocyclic groups, X represents a member selected from the class consisting of halogen and sulfo groups, and Z represents the atoms necessary to complete a carbocyclic ring system of 5 to 10 carbon atoms.

11. The method as defined in claim 10, wherein the phenazonium coupler compound is 2-phenyl-6-chloro-8-hydroxycinchoninic acid.

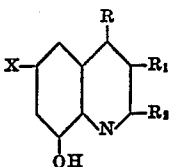
12. The method as defined in claim 10, wherein the phenazonium coupler compound is 2-propyl-6-bromo-8-hydroxycinchoninic acid.

13. The method as defined in claim 10, wherein the phenazonium coupler compound is 6-chloro-3-carboxymethyl-8-hydroxy-2-(3'-stearoylamino-phenyl)cinchoninic acid.

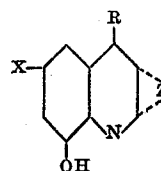
14. The method as defined in claim 10, wherein the phenazonium coupler compound is 6-bromo-8-hydroxy-2-(2'-sulfophenyl)-N-octadecylcinchoninamide.

15. The method as defined in claim 10, wherein the phenazonium coupler compound is 2-[4-(6-bromo-8-hydroxy-2-(2'-sulfophenyl)cinchoninoyl)aminophenyl]-1-octadecyl-5-sulfobenzimidazole.

16. The method of producing reversal magenta phenazonium dye images in a gelatino silver halide emulsion layer containing a phenazonium dye coupler compound selected from the class consisting of those corresponding to the following formulae:



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wherein R represents a member of the class consisting of —COOH, —CONH₂, and —CONHR₃ in which R₃ is a member selected from alkyl radicals of not more than 26 carbon atoms, sulfonated alkyl radicals containing at least 10 carbon atoms, and sulfonated aromatic radicals substituted by an aliphatic radical containing at least 5 carbon atoms, R₁ is a member selected from the class consisting of hydrogen, carboxyalkyl, allyl, and lower alkyl, R₂ represents a member selected from the class consisting of allyl, lower alkyl, aryl, and heterocyclic groups, X represents a member selected from the class consisting of halogen and sulfo groups, and Z represents the atoms necessary to complete a carbocyclic ring system of 5 to 10 carbon atoms, which comprises exposing said layers in a black and white developer incapable of coupling with said coupler compound, exposing the undeveloped silver halide and developing the layer with an N,N-dialkyl-p-phenylenediamine developing agent containing only the two amino groups.

17. The method according to claim 16 wherein the phenazonium coupler compound is 6-bromo-8-hydroxy-2-(2'-sulfophenyl)-N-octadecylcinchoninamide.

18. The method according to claim 16 wherein the phenazonium coupler compound is 2-[4-(6-bromo-8-hydroxy-2-(2'-sulfophenyl)cinchoninoyl)aminophenyl]-1-octadecyl-5-sulfobenzimidazole.

19. The method according to claim 16 wherein the phenazonium coupler compound is 6-chloro-3-carboxymethyl-8-hydroxy-2-(3'-stearoylamino-phenyl)cinchoninic acid.

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