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COLOR DEVELOPERS FOR THE PRODUCTION OF AZINE DYE IMAGES

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13 Claims. (Cl. 95—88)

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The present invention relates to the production of azine dye images by color forming development while employing as the color forming developer derivatives of 2,4-diamino aniline in which the amino group in the 2-position is substituted by an aliphatically linked hydrophilic group.

This application is a continuation-in-part of my application Serial No. 793,532, filed December 23, 1947, now abandoned, entitled "Color Developers for the Production of Phenazonium Dyestuff Images."

In the copending application Serial No. 640,382, filed on January 10, 1946, by Willy A. Schmidt and Vsevolod Tulagin, now U. S. P. 2,486,440, there is described the production of azine dye images by color forming development while utilizing inter alia as the color developer derivatives of 2,4-diamino-aniline. While these color developers have been found to be effective in producing the desired dyestuff images in the presence of the usual color forming components, it is noted that they have a tendency to be adsorbed to silver halide grains of the photographic emulsions, thereby making it difficult to effect the complete removal thereof from the emulsion by washing after development. Furthermore, said compounds have been observed to cause stain in the reduction of silver halides, particularly when such reduction takes place in the absence of a color former.

Difficulties have also been encountered in the production of yellow dye images by the utilization of the aforestated developers. Experience has shown that when using such developers with color formers generally employed for the production of yellow azomethine images, i. e., open chain keto methylene compounds, magenta images rather than yellow images ensue. These magenta images may be subsequently converted into yellow images but only by a separate step involving a treatment with an alkali.

It has now been discovered that the production of azine dye images can be effectively carried out without the aforenoted objections if there be employed as color developers derivatives of 2,4-diamino anilines in which the amino group in the 2-position is substituted by an aliphatically linked hydrophilic group such as hydroxy, carboxy or sulfo. Inasmuch as said compounds are capable of effecting the reduction of silver halides including latent images without the formation of

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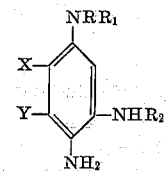
stain, they may also be employed as developers for black and white images.

These developers also have the unique property of yielding yellow dye images directly when employed to develop a developable silver halide emulsion in the presence of an open chain keto methylene compound. They are therefore admirably suited for the production in one development step of azine dye images in the three subtractive colors.

Developers utilizing such compounds and their employment particularly in the production of azine dye images constitute the purposes and object of the present invention.

The derivatives of 2,4-diamino aniline contemplated for use herein as developers are typified by the following structural formula:



wherein R is hydrogen or alkyl, i. e., methyl, ethyl, propyl, butyl, amyl or the like and R_1 is an aliphatic radical such as alkyl as above, carboxy alkyl, such as carboxy methyl, carboxy ethyl, and the like; hydroxy alkyl, such as hydroxy ethyl, hydroxy propyl, and the like, aryl, such as phenyl, toluyl and the like; carboxy alkyl aryl, such as carboxy methyl phenyl, carboxy ethyl phenyl, and the like, carboxy alkoxy aryl, such as carboxy methoxy phenyl, carboxy ethoxyphenyl; hydroxy alkyl aryl, such as hydroxy methyl phenyl, hydroxy ethyl phenyl, and the like; and hydroxy alkoxy aryl, such as hydroxy methoxy phenyl, hydroxy ethoxy phenyl and the like, R_2 is an alkyl group substituted by a hydrophilic group such as carboxy alkyl, such as carboxy methyl, carboxy ethyl and the like; hydroxy alkyl, such as hydroxy ethyl, hydroxy propyl, and the like; sulfo alkyl such as, sulfomethyl, sulfoethyl, sulfopropyl, sulfobutyl and the like and X and Y are hydrogen, alkyl as above, sulfo or carboxy, or together represent the atoms necessary to complete a six-membered isocyclic ring system such as benzo and the like. It is to be observed that in the above compounds the substituent groups repre-

sented by R_1 and R_2 have a carbon atom thereof directly linked to the amino nitrogen atom. In other words, such compounds are true amines. Preferably the compounds which are utilized are the N-substituted 4,6-diamino-metanilic acids, in which case Y is hydrogen and X is sulfo.

Examples of compounds illustrative of those within the general formula are the following:

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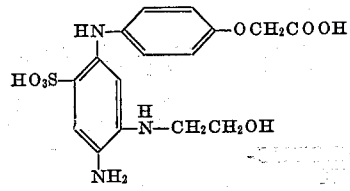

4-(β-hydroxyethylamino)-6-(4'-carboxy-methoxy phenylamino) metanilic acid

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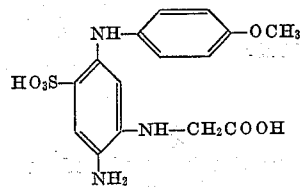

4-(carboxymethylamino)-6-(4'-methoxy phenylamino)-metanilic acid

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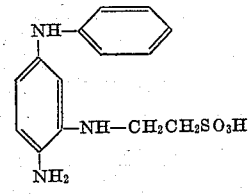
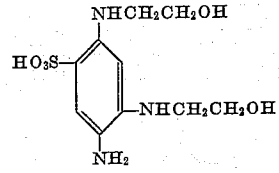


2-(β-sulfoethylamino)-4-phenylamino aniline



4,6-di(β-hydroxyethylamino)-metanilic acid

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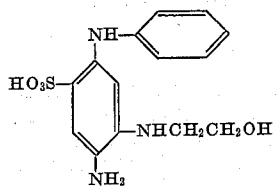

4-(β-hydroxyethylamino)-6-phenylamino-metanilic acid

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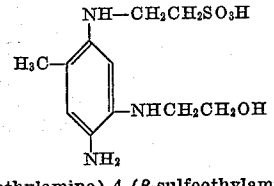

2-(β-hydroxyethylamino)-4-(β-sulfoethylamino)-5-methyl aniline

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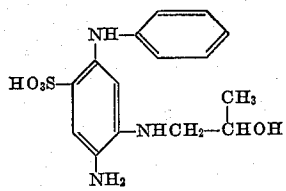

4-(β-hydroxy-β-methyl-ethylamino)-6-phenylamino-metanilic acid

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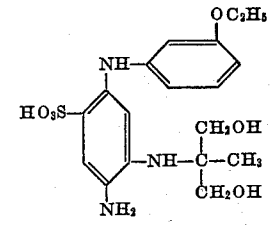

4-(α-di(hydroxymethyl)ethylamino)-6-(3'-ethoxy phenylamino)-metanilic acid

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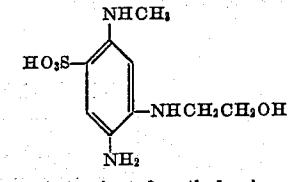

4-(β-hydroxy ethylamino)-6-methylamino-metanilic acid

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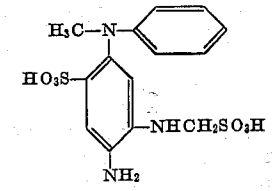


4-(sulfomethylamino)-6-(methyl phenyl amino)-metanilic acid

The aforementioned compounds are prepared by reacting in the proper sequence 2,4-dichloro-5-nitro benzene sodium sulfonate with the amines desired to be introduced into the 2- and 4-positions of the benzene ring, and then effecting reduction of the nitro group to an amino group. The preparation of the compound by the aforesaid method is made possible by the fact that the chlorine atom in the 4-position is more easily replaced by an amino group than the chlorine atom in 2-position. Thus by refluxing the 2,4-dichloro-5-nitro benzene sodium sulfonate with an equivalent of an amine, the chlorine atom in 4-position is selectively replaced by such amine. By subsequently treating the resulting compound with the same or a different amine under more elevated temperatures, i. e., temperature ranging from 110 to 150° C., the chlorine atom in 2-position is replaced by the amine.

The following is a specific illustration of the application of the foregoing general method in the production of 4-(β-hydroxyethylamino)-6-phenyl amino metanilic acid.

Into a 1-liter, 3-necked round-bottom flask equipped with a mechanical stirrer and a reflux condenser was placed 147 parts of the sodium salt of 2,4-dichloro-5-nitro benzene sulfonic acid, 31 parts of ethanolamine and 54 parts of sodium carbonate dissolved in 250 parts of water. After the stirrer was started, the contents of the flask were gently refluxed for 10 hours. 200 cc. of 30% sodium chloride solution were added to the hot reaction mixture and the flask was then cooled in an ice bath. The precipitated orange solid was collected by filtration, washed with a small amount of water, and dried overnight at 80–90° C.

A glass interliner for an Aminco shaking type bomb was charged with 95.6 parts of the 2-chloro-4-(β-hydroxyethylamino)-5-nitro benzene sodium sulfonate (prepared as above), 30 parts of aniline and 34 parts of sodium carbonate dissolved in 200 parts of water. The liner was sealed in the bomb and the bomb shaken at 140° C. for 15 hours. The bomb was cooled and the solid removed from the interliner with small amounts

of hot water. 250 cc. of 30% sodium chloride solution were added with vigorous stirring of the mixture and the whole was then cooled in an ice bath for several hours. The precipitated solid was collected by filtration, washed with 50 parts of water, and then digested with 200 parts of ethanol. The product was again collected on a filter and dried overnight at 60° C. in a vacuum oven.

10 parts of 2-phenylamino-4-(β-hydroxyethyl-amino)-5-nitro benzene sulfonic acid (prepared as above) were added portion-wise to a boiling solution of 40 parts of sodium hydrosulfite in 200 cc. of 10% sodium hydroxide. After reduction is complete, a small amount of decolorizing carbon is added to the solution. The mixture is boiled vigorously for several minutes and then filtered rapidly through a fluted filter. The compound was then isolated from the clear filtrate as the inner salt by acidification with glacial acetic acid. The mixture was cooled in an ice bath for several hours, the inner salt collected on a filter and washed with water. The product was then dried six hours at 65° C. in a vacuum oven and constituted the 4-(β-hydroxyethyl-amino)-6-phenyl amino-metanilic acid.

The same procedure may also be utilized in the preparation of the other compounds noted above while employing amines containing an aliphatically bound hydrophilic group different from that described in the above example. Such other amines are for instance β-sulfoethyl amine (taurine) m-amino-phenoxy-acetic acid, amino acetic acid, p-amino phenyl ethyl alcohol, p-amino phenyl acetic acid, 2-amino-2-methyl-1,3-propanediol and the like.

As stated, the aforementioned derivatives of 2,4-diamino aniline are characterized by their marked ability to effect reduction of silver halides, i. e., latent images, reverse images, bleached images, and the like, without formation of objectionable stain. As a consequence of the reducing power they may be employed for development of black and white images or for the production of color images.

One of the mst notable properties of the aforementioned derivatives of 2,4-diamino aniline, however, is, as stated, their ability to directly yield yellow dye images. This result is achieved when employing the developers to develop a developable silver halide emulsion in the presence of an open chain keto methylene compound even though the emulsion during a subsequent processing step be treated with an acidic bleach bath as is usual in the processing of film to azine dye images. In other words, whereas the formerly employed, 2,4-diamino anilines only yielded yellow images, as the result of a subsequent alkaline treatment, the developers contemplated herein yield such images directly and without such subsequent processing with an alkaline bath. As a consequence such developers very materially contribute to the utilization on a commercial scale of the azine method for processing film in the three subtractive colors.

The yellow dyes obtained by color development with my developers appear to be true azines. Thus they withstand treatment with an acid bisulfite whereas yellow azomethines do not. Furthermore they are not split by strong mineral acids as happens with the yellow azomethines. Such yellow dye images have excellent lightfastness and brilliance and they adequately complement the magenta and cyan dyes produced by the azine methods.

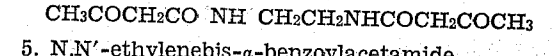
The color formers employed for producing the dye images are those used in the production of color developed images, i. e., those containing aromatic-primary amino, phenolic hydroxyl or active methylene groups.

Examples of such compounds for producing the magenta images are: 3.6-disulfo-8-benzsulfonylamino naphthol-1; 8-benzsulfonylamino-naphthol-1; 8-hydroxy quinoline; naphthsultam acid; 3-sulfo-7-phenylaminonaphthol-1; 1,8-bis-(benzsulfonyl amino)-naphthalene; 6-bromo-8-hydroxy quinoline; 6-sulfo-8-hydroxy quinoline; 2-phenyl-6-bromo-8-hydroxy cinchoninic acid; 6-bromo-8-hydroxy quinaldine; 6-stearoylamino - 2 - (2'-phenyl-6'-bromo-8'-hydroxy cinchoninoyl)-amino toluene-4-sulfonic acid; 2-phenyl-6-chloro-8-hydroxy cinchoninoyl octadecyl taurine, and the like.

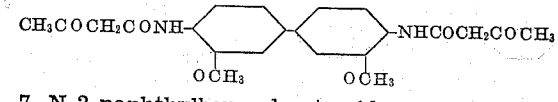
Examples of cyan color formers are: 3-sulfo-6 - aminonaphthol - 1; 3 - sulfo-6-phenyl-amino-naphthol - 1; 3-sulfo-6-(4'-methoxy-phenylamino)-naphthol-1; ethyl urethane of phenyl J acid; 6 - (4' - octadecoxy-phenylamino)-1-naphthol-3-sulfonic acid; 3-sulfo-6-oleylamino-naphthol-1, and the like.

Examples of yellow color forming components are:

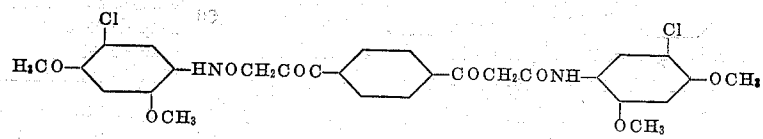
1. Acetoacetanilide.
2. N-1-naphthylacetoacetamide.
3. N-1-naphthyl-α-benzoylacetamide.
4. N,N'-ethylenebisacetoacetamide



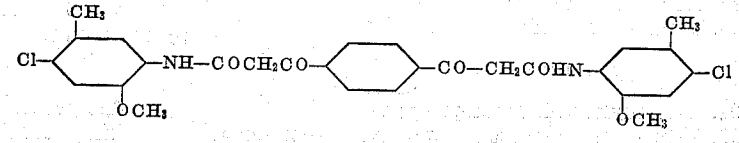
5. N.N'-ethylenebis-α-benzoylacetamide.
6. p.p'-Bi-o-acetoacetaniside



7. N-2-naphthylbenzoylacetamide.
8. p.p'-Biacetoacetanilide.
9. p.p'-Bi-α-benzoylacetanilide.
10. α.α' - Terephthaloylbis-(3-chloro-4.6-dimethoxy-acetanilide).

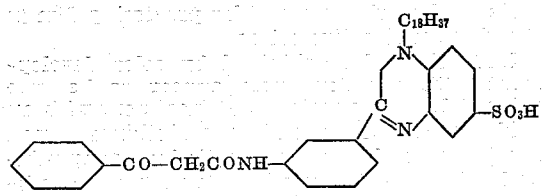


11. α.α' - Terephthaloylbis - (4-chloro-5-methyl-o-acetaniside).



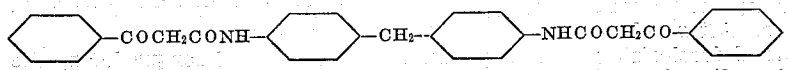
12. α-Benzoylacetanilide.

13. 2-(m-benzoylacetamidophenyl)-1-octadecyl-5-benzimidazolesulfonic acid.



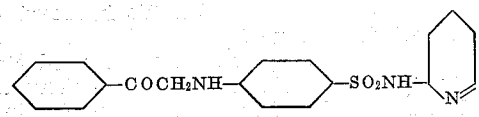
14. o-Acetoacetaniside.

15. 4.4''-methylenebis-α-benzoylacetanilide.

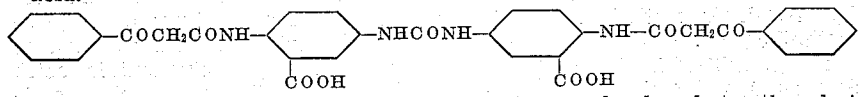


16. o-Phenylacetoacetanilide.

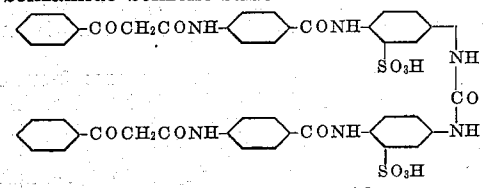
17. 4'-2-pyridylsulfamyl-α-benzoylacetanilide.



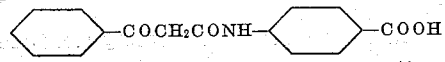
18. 5.5'-ureylenebis-N-benzoylacetyl-anthranilic acid.



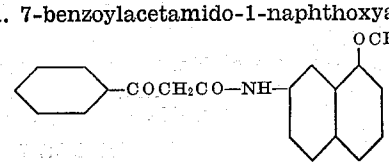
19. 3.3'-ureylenebis-6-p-benzoylacetamido-benzamide-benzene sulfonic acid.



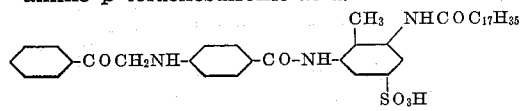
20. p-Benzoylacetamidobenzoic acid.



21. 7-benzoylacetamido-1-naphthoxyacetic acid.

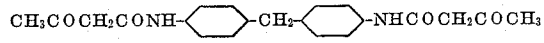


22. 2-p-benzoylacetamidobenzamido-6-stearoylamino-p-toluenesulfonic acid.

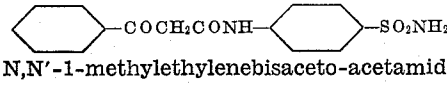


23. α.α'-Terephthaloylbisacetanilide.

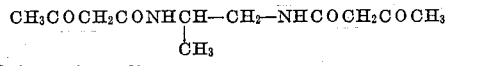
24. 4.4'-methylenebisacetoacetanilide.



25. p-Sulfamylbenzoylacetanilide.



26. N,N'-1-methylethylenebisaceto-acetamide



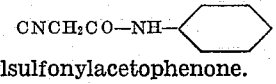
27. 2.4-pentanedione

$CH_3COCH_2COCH_3$

28. 1.3-diphenyl-1.3-propanedione.

29. Benzoylacetonitrile.

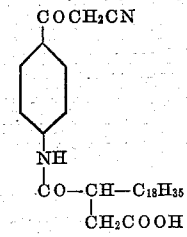
30. Cyanoacetanilide.



31. α-Phenylsulfonylacetophenone.

32. 2-(p-benzoylacetamidophenyl)-1-octadecyl-5-benzimidazolesulfonic acid.

33. p-Cyanoacetyl-3-octadecenylsuccinialic acid.



The process of employing the color developer to produce the azine dye images may be effected in various ways. For instance, a color forming component may be added to the developer containing the diamino aniline derivative. On the other hand, a color former in non-diffusing form may be located in the emulsion and the diamino aniline derivative in the developer. Multi-layer film, each layer containing a non-diffusing color former, may be used and the entire film color developed to the desired subtractive dyestuff images in a single color forming development step using the diamino aniline derivatives as the developer.

While the diamino aniline derivative and an alkali, such as sodium carbonate, sodium hydroxide, or the like, are the essential components of the developer, it is preferred that the developer also contain the usual adjuncts such as an alkali metal bromide, i. e., potassium bromide, sodium bromide, and the like, and an alkali metal sulfite, i. e., sodium sulfite, and the like. If desired there may also be present in the developer a coupling aid in the form of an inorganic or organic base such as pyridine, quinoline, or ammonium hydroxide.

The following exampes will serve to illustrate the invention, but it is to be understood that the invention is not limited thereto:

Example I

A photographic silver bromide emulsion containing per kilo of emulsion .5 part of 3-stearoylamino-5-sulfo-acetoacetanilide as the color former is exposed, the latent image developed in a Metol-Hydroquinone Developer, re-exposed and the residual silver halide developed for 10 minutes in a solution of the following composition:

Potassium carbonate	grams	20
Sodium sulfite	do	60
Ethylene diamine	cc	30
4-(β-hydroxyethylamino)-6-phenylamino-metanilic acid	grams	3
Water	cc	1000

The developed silver images are bleached with potassium ferricyanide and fixed in an acid hardening hypo solution. There is thus obtained a yellow dyestuff image which is stable to acids and alkali oxidizing agents. No difficulty is involved in effecting removal of the developer from the emulsion by the usual washing procedure.

Example II

The procedure is the same as in Example I excepting that the 4-(β-hydroxyethylamino)-6-phenylamino-metanilic acid is replaced by 4-(β-

sulfo-ethylamino)-6-(4'-carboxymethoxy phenylamino)-metanilic acid.

Example III

A photographic silver bromide emulsion is exposed and color developed in a developer having the following composition:

Sodium carbonate monohydrate	grams	60
Potassium bromide	do	2.5
Sodium sulfite	do	40
Pyridine	cc	12
4-carboxymethylamino-6-[4-(β-hydroxyethoxy)]-phenylamino-metanilic acid	grams	4
8-hydroxy quinoline	do	2
Water	cc	1000

After bleaching with ferricyanide bleach and fixing in an acid hardening fixer, there is obtained a magenta azine dye image. No staining is observed, nor is any difficulty met with in the complete removal of the developer from the emulsion by the usual water washing.

Example IV

The procedure is the same as in Example III excepting that the 8-hydroxyquinoline is replaced by the ethyl urethane of phenyl J-acid. By working up the emulsion as in Example III a cyan azine dye image is obtained.

Example V

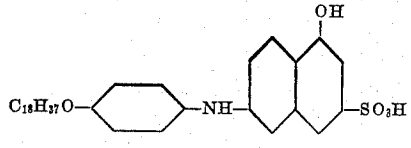
A photographic silver halide emulsion carrying a silver halide image was developed for 15 minutes in a developer of the following composition:

6-phenylamino-4-(β-hydroxyethylamino)-metanilic acid	grams	4
Benzoylacet-2-naphthylamine-5-sulfonamide	grams	3
Sodium sulfite	do	60
Potassium carbonate	do	20
Ethylene diamine	do	30
Water to	cc	1000

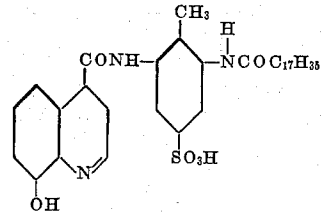
The film, after washing, was bleached in ferricyanide bleach and fixed in acid hardening hypo. There was directly obtained a yellow dye image, no alkaline treatment being necessary.

Example VI

An integral tripack having as the bottom layer a red sensitive emulsion containing as a cyan color former 6-(4'-octadecoxyphenylamino)-1-naphthol-3-sulfonic acid of the formula:



as the middle layer a green sensitive emulsion containing as the magenta color former 2-stearoylamino 6-(8'-hydroxycinchoninylamino)-toluene-4-sulfonic acid acid of the formula:



and as the outermost layer a blue sensitive emulsion containing as the yellow color former

2-(benzoylacetamidophenyl)-1-octadecyl-5-benzimidazole sulfonic acid was exposed, developed in black and white, re-exposed and the residual silver halide developed for 12 minutes in a developer of the following composition:

6-phenylamino-4-(β-hydroxyethylamino)-metanilic acid	grams	8
Potassium carbonate	do	20
Sodium sulfite	do	60
Potassium bromide	do	10
Benzylamine	do	5
Water to	cc	1000

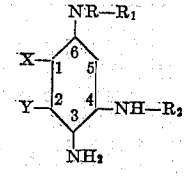
The film after development is washed, bleached in ferricyanide bleach, and fixed in an acid hardening hypo. There was thus obtained a positive dyestuff image in each of the three layers—a cyan dye image in the bottom layer, a magenta dye image in the middle layer, and a brilliant yellow dye image in the top layer.

Similar results are obtained by replacing the metanilic acid derivatives of the above examples by other developers listed hereinabove.

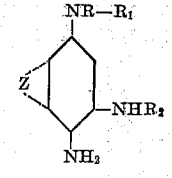
Various modifications of the invention will occur to operators in this field, and I accordingly do not intend to be limited in the patent granted except as necessitated by the appended claims.

I claim:

1. A photographic developer comprising an alkaline aqueous solution of an alkali metal sulfite and a compound selected from the class of the following constitution:



and



wherein R is selected from the class consisting of hydrogen and alkyl, R_1 is selected from the class consisting of alkyl, carboxyalkyl, hydroxyalkyl, aryl, carboxyalkylaryl, carboxyalkoxyaryl, hydroxyalkylaryl and hydroxyalkoxyaryl, R_2 is an alkyl group substituted by a hydroxyl group, X and Y are selected from the class consisting of hydrogen, alkyl, sulfo and carboxy, and Z represents the atoms necessary to complete a 6-membered isocyclic ring.

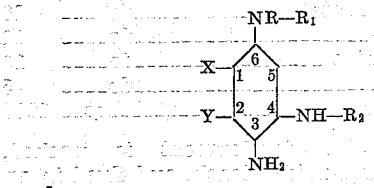
2. The composition as defined in claim 1 wherein Y is hydrogen and X is sulfo.

3. A photographic developer as defined in claim 1 wherein Y is hydrogen and X is sulfo and wherein the developer contains a color former capable of reacting with the oxidation products of a primary aromatic amino developer to form a dye image.

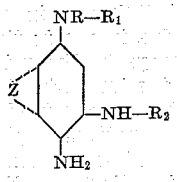
4. A photographic developer for producing azine dyestuff images on color development comprising aqueous alkaline solution of a color former capable of reacting with the oxidation products of a primary aromatic amino developer to form a dye image and 4-(β-hydroxyethylamino)-6-phenylaminometanilic acid.

5. The composition as defined in claim 4 wherein the color former is 8-hydroxyquinoline.

6. The process of producing phenazonium dyestuff images in a developable silver halide emulsion which comprises developing said emulsion in the presence of color forming component with a photographic developer containing as the active developing agent a compound selected from the class consisting of those of the following formula:



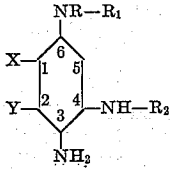
and



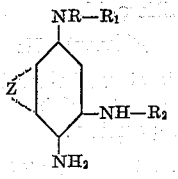
wherein R is selected from the class consisting of hydrogen and alkyl, R_1 is selected from the class consisting of alkyl, carboxyalkyl, hydroxyalkyl, aryl, carboxyalkylaryl, carboxyalkoxyaryl, hydroxyalkylaryl and hydroxyalkoxyaryl, R_2 is an alkyl group substituted by a hydroxyl group, X and Y are selected from the class consisting of hydrogen, alkyl, sulfo and carboxy, and Z represents the atoms necessary to complete a 6-membered isocyclic ring.

7. The process as defined in claim 6 wherein Y is hydrogen and X is sulfo.

8. The process of directly producing yellow dye images resistant to splitting by strong mineral acids which comprises developing a developable silver halide emulsion in the presence of an open chain keto methylene compound with a photographic developer containing as the active developing agent a compound of the following formula:



and



wherein R is selected from the class consisting of hydrogen and alkyl, R_1 is selected from the class of alkyl, carboxyalkyl, hydroxyalkyl, aryl, carboxyalkylaryl, carboxyalkoxyaryl, hydroxyalkylaryl, hydroxyalkoxyaryl, R_2 is an alkyl group substituted by a hydroxyl group, X and Y are selected from the class consisting of hydrogen, alkyl, sulfo and carboxy, and Z represents the atoms necessary to complete a 6-membered isocyclic ring.

9. The process as defined in claim 8 wherein Y is hydrogen and X is sulfo.

10. The process as defined in claim 8 wherein the open chain keto methylene compound contains a benzoylacet radical.

11. The process of directly producing yellow dye images resistant to splitting by strong mineral acids which comprises developing a developable silver halide emulsion in the presence of an open chain keto methylene compound containing a benzoylacet radical with a 4.6 diamino metanilic acid in which the nitrogen atom in the 6-position is substituted by aryl and the nitrogen atom in the 4-position by hydroxy alkyl.

12. The process as defined in claim 11 wherein the 4.6-diaminometanilic acid is 6-phenylamino-4-(β-hydroxyethylamino) metanilic acid.

13. A photographic developer for producing azine dyestuff images on color development comprising an aqueous alkaline solution of 4-(β-hydroxyethylamino)-6-phenylaminometanilic acid, and an alkali metal sulfite.

ROBERT C. GUNTHER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,304,953	Peterson	Dec. 15, 1942
2,489,440	Schmidt et al.	Nov. 1, 1949

FOREIGN PATENTS

Number	Country	Date
553,064	Great Britain	May 6, 1943