May 13, 1952 R. C. GUNTHER ET AL 2,596,926

PREPARATION OF AZINE DYE IMAGES

Filed Dec. 16, 1949

Fig. 2.

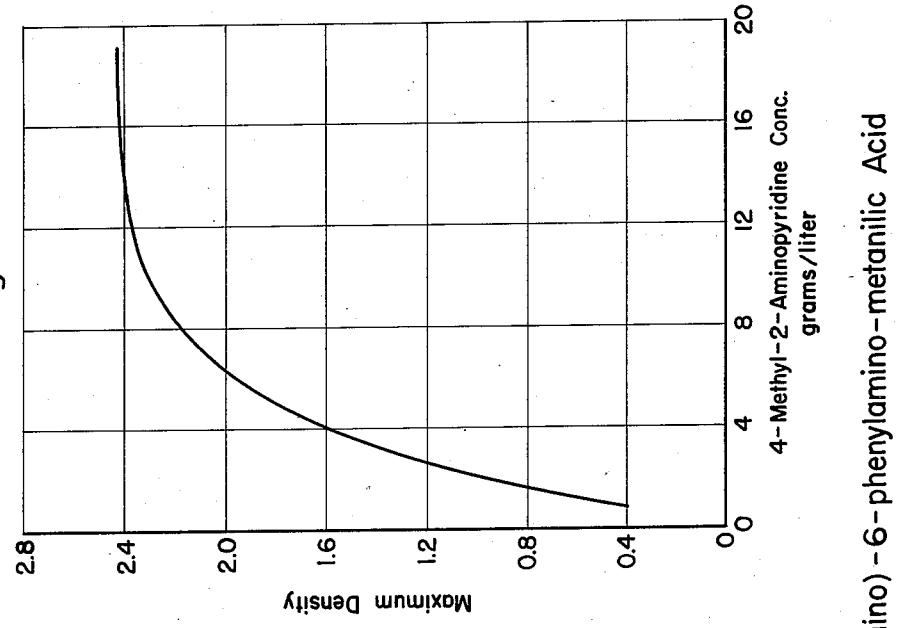
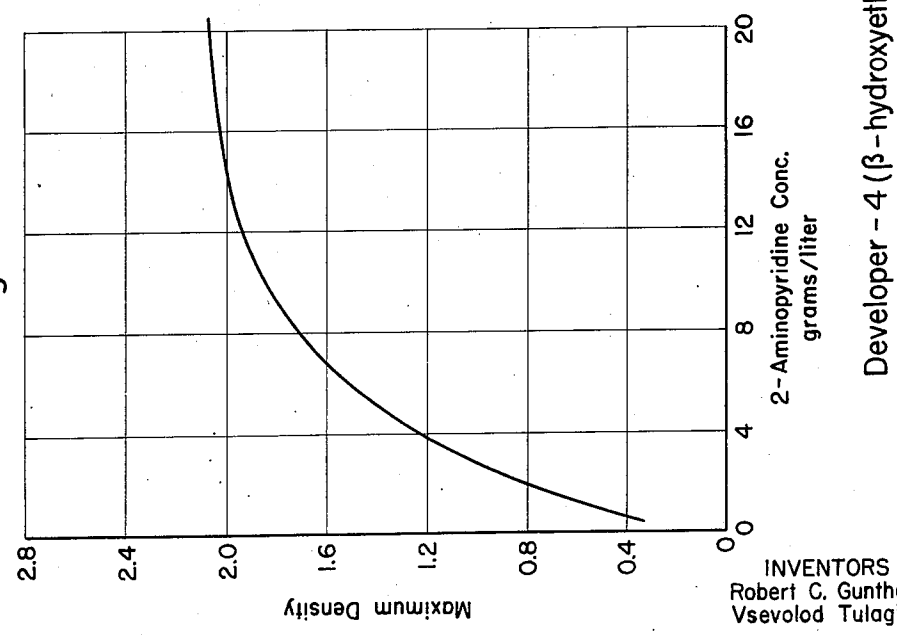


Fig. 1.



Developer - 4 (β-hydroxyethylamino) - 6-phenylamino-metanilic Acid

INVENTORS
Robert C. Gunther
Vsevolod Tulagin

BY

ATTORNEYS

Patented May 13, 1952

2,596,926

UNITED STATES PATENT OFFICE

2,596,926

PREPARATION OF AZINE DYE IMAGES

Robert C. Gunther, Easton, Pa., and Vsevolod Tulagin, Phillipsburg, N. J., assignors to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

Application December 16, 1949, Serial No. 133,464

8 Claims. (Cl. 95—2)

1

The present invention relates to the formation of azine dye images while using color developers insuring the formation of brilliant dye images of proper color rendition.

U. S. Patent 2,486,440 granted to Willy A. Schmidt and Vsevolod Tulagin on November 1, 1949, describes the basic method of producing azine dyestuff images by color developing silver halide emulsions with a 2,4-diamino-aniline in the presence of a color former.

The azine dyes produced by this method have unusual stability, particularly when compared with the quinonimine or azomethine dyes formed while using the older developers of the p-phenylenediamine type.

Despite the many recognized advantages of the azine method, there are certain disadvantages to which considerable study has been given in an effort to effect their elimination. One such disadvantage is the fact that the energy of development and of color coupling is not all that could be desired. A more serious problem, which manifests itself particularly in the development of mutilayer film, is a loss of color rendition in the azine images formed in such material through the phenomenon known as "proximity development."

As is known, the conventional material employed at the present time in color photography is an integral tripack consisting essentially of three superimposed silver halide emulsion layers, the bottom layer being sensitized to red, the middle layer to green, and the top layer to blue. When such a tripack is exposed, the red densities of the picture are recorded in the bottom layer, the green densities in the middle layer, and the blue densities in the top layer. According to customary practice, the image formed in the respective layers is complimentary in color to the light rays for which the particular layer is sensitized.

One of the best modes of constructing such tripacks involves the utilization in each of the three silver halide emulsion layers of a color former which is rendered non-diffusing in the emulsions. Where such tripacks are of the reversible type, they are processed by developing first in a black and white developer, and finally in a color forming developer.

In the color development of such a tripack with a 2,4-diamino-aniline, the color developer reduces in any one layer the silver halide remaining after the first development and is itself oxidized to an active state capable of coupling with the color former present in that layer to

2

form a positive dye image. Consequently in any one layer the amount of dye produced will be a function of the amount of residual silver halide in that layer and the resulting dye will be formed imagewise. Thus in each of the three layers of the tripack, one of the primary color densities (blue in the top layer, green in the middle layer, and red in the bottom layer) is accurately recorded in the form of a positive complimentary dye image.

The coupling reaction between the migratory oxidized developer and the immobile color formers in each layer is normally rapid so that the oxidized developer travels only a very short distance before encountering the color former molecule and coupling therewith. It often happens, however, that some dye may be produced in a particular layer by the coupling of a color former in that layer with an oxidized developer molecule that originated not in that particular layer but in one of the adjacent layers. Typically an oxidized developer molecule originating in the red sensitive layer may "escape" from this layer without coupling and migrate to the green sensitive layer to couple with the color former molecule in that layer. As a result there will be produced in the green sensitive layer a certain amount of magenta dye which records not the green densities of the original picture, but red densities which should have been confined to the bottom or red sensitive layer. This migration of oxidized developer from one layer to an adjacent layer is the phenomenon known as proximity development.

We have now discovered that the development of silver halide emulsions with a 2,4-diamino developer in the presence of a color former may be effected while realizing the advantages of (1) more energetic development of positive silver halide; (2) more energetic color coupling with resultant increase in dye formation efficiency, and (3) more brilliant dye images through improved color rendition (suppression of proximity development), by adding to the 2,4-diamino developer a small quantity of a pyridine derivative. Thus coupling reactions which proceed very slowly or not at all with an ordinary azine developing substance in the conventional carbonate, sulfite and bromide solution, are greatly accelerated by the addition of the pyridine derivative to the solution.

Further, the use of the pyridine derivative in an amount of from 4 grams to 30 grams not only energizes the azine color developer so as to produce a maximum of dye in a minimum of time,

but also produces dye images of exceptional clarity and brilliance.

The improvement in color rendition obtained by the use of the pyridine derivatives is attributable primarily to a suppression of proximity development by the azine developer.

We do not know, nor has it been possible to ascertain, the particular manner in which the pyridine derivative operates to promote this effect. It is known, however, that the action is peculiar to the pyridine derivatives, not even being shared by other heterocyclic nitrogenous bases. Thus we have also employed bases such as piperidine or morpholine, and while finding that these when present in the azine color developer give satisfactory dye density, unlike the pyridine derivatives, the dye formation is accompanied by increased proximity development. The overall effect is a severe loss in color rendition which manifests itself in the final image as a loss in color brilliance.

Nor have we found any other nitrogenous bases capable of operating in the same manner as the pyridine derivatives. Attempts to supplant the pyridine derivatives by aliphatic amines such as ethylenediamine, ethylamine and hexamethylenediamine, led to an effective energizing of azine dye formation. However, as in the case of morpholine, piperidine, and the like, the increased dye formation in each instance was accompanied by a corresponding loss in color brilliance because of a markedly increased proximity development. The action which we have found to be portrayed by the pyridine derivatives are accordingly specific to these particular compounds, and this discovery constitutes a very important part of the invention.

The utilization of pyridine derivatives in azine color developers of the 2,4-diamino-aniline class for the purpose of obtaining more energetic development, more energetic color coupling, and more brilliant dyes through suppression of proximity development, constitute the purposes and objects of our invention.

The 2,4-diamino-anilines which may be employed as the color developers for the contemplated procedure are of the type described in the aforementioned Schmidt and Tulagin Patent No. 2,486,440 and in Gunther application Serial No. 101,913, filed June 28, 1949, and entitled "Color Developers for the Production of Azine Dye Images," now Patent No. 2,570,116.

Specific examples of such developing agents are:

4 - (β - hydroxyethylamino) - 6 - (4' - carboxymethoxy-phenylamino) -metanilic acid.
4-(carboxymethylamino) -6-(4'-methoxy-phenylamino) -metanilic acid.
2-(β-sulfoethylamino) -4-phenylamino-aniline.
4,6-di(β-hydroxyethylamino) -metanilic acid.
4 - (β - hydroxyethylamino) - 6 - phenylamino-metanilic acid.
2 - (β - hydroxyethylamino) - 4 - (β - sulfoethylamino) -5-methyl aniline.
4 - (β-hydroxy-β-methyl-ethylamino) -6-phenylamino-metanilic acid.
4-(α-di(hydroxyethyl) ethylamino) - 6 - (3'-ethoxyphenylamino) -metanilic acid.
4 - (β - hydroxy - ethylamino) - 6 - methylamino-metanilic acid.
4 - (sulfomethylamino) -6-(methylphenylamino) -metanilic acid.

Color formers to be used with the aforementioned developers to give yellow azine dye images are also described in Gunther application Serial No. 101,913. These compounds are typified by the fact that they are open chain keto methylene compounds. Examples of such compounds are:

Acetoacetanilide.
N-1-naphthylacetoacetamide.
N,N'-ethylenebisacetoacetamide.
p,p'-Bi-o-acetoacetaniside.
N-2-naphthylbenzoylacetamide.
p,p'-Biacetoacetanilide.
α,α' - Terephthaloylbis-(3-chloro-4,6-dimethoxy-acetanilide).
α-Benzoylacetanilide.

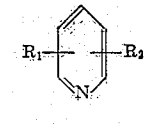
Preferably the color formers utilized contain a group rendering them non-migratory in the emulsion. Examples of such compounds are:
2-(m-benzoylacetamidophenyl) - 1 - octadecyl-5-benzimidazolesulfonic acid.
3,3' - ureylenebis - 5 - p - benzoylacetamidobenzamide-benzene sulfonic acid.
2 - p - benzoylacetamidobenzamido - 6 - stearoylamino-p-toluenesulfonic acid.
2-(p-benzoylacetamidophenyl) - 1 - octadecyl-5-benzimidazolesulfonic acid.
p-Cyanoacetyl-3-octadecenylsuccinalic acid.

Color formers capable of producing magenta dyestuff images are also described in the aforementioned Gunther application as well as in application Serial No. 793,533, filed December 23, 1947 by Tulagin and Coles and entitled "Magenta Colored Phenazonium Dyestuff Images," now Patent No. 2,524,741. Preferably these color formers are: 6-halogen-8-hydroxy quinolines, and particularly those which are non-migratory in the emulsions. Examples of the latter type compounds are:
6-stearoylamino - 2 - (2' - phenyl - 6' - bromo-8'-hydroxy cinchoninoyl) -aminotoluene - 4 - sulfonic acid
2-phenyl-6-chloro-8-hydroxy cinchoninoyl octadecyl taurine
6-decoxy-3-(2-phenyl - 6 - bromo - 8 - hydroxy-cinchoninoyl) -aminobenzene-sulfonic acid
2 - (3-stearoylaminophenyl) -6-bromo-8-hydroxy cinchoninic acid
2 - stearoylamino - 6 - (6 - chloro - 8 - hydroxy-cinchoninoyl) - aminotoluene-4-sulfonic acid, and the like.

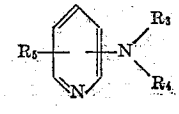
Color formers for the cyan image are also described in the aforesaid Gunther application Serial No. 101,913 and in U. S. Patent 2,445,252, granted July 13, 1948 to Tulagin. Preferably these color formers are aryl-J-acid derivatives, particularly those containing a group rendering the color former non-migratory in the emulsion. Examples of the latter compounds are:

Dodecyl urethane of β-sulfoethyl-J-acid
Tetradecyl urethane of p-anisyl J-acid
2-hexadecyl urethane of phenyl-J-acid
4-stearoylaminophenyl-J-acid, and the like.

The pyridine derivatives that may be utilized in the 2,4-diamino-aniline color developers are those of the following formulae:



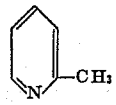
and



wherein R_1 is hydrogen or a lower alkyl group, i. e., methyl, ethyl, propyl or butyl, or a hydroxyalkyl group, such as hydroxymethyl, hydroxyethyl, hydroxypropyl, and the like, R_2 is lower alkyl or hydroxyalkyl as above and R_3, R_4 and R_5 are hydrogen, lower alkyl as above or hydroxyalkyl as above.

Examples of such compounds which we have found to be effective for our purpose are the following:

1.

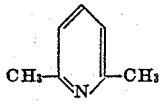


2-methylpyridine (α-picoline)

2.

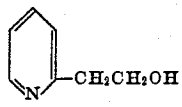
4-methylpyridine (γ-picoline)

3.



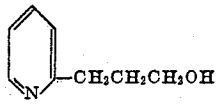
2,6-dimethylpyridine (2,6-lutidine)

4.



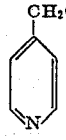
2-β-hydroxyethylpyridine

5.



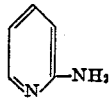
2-γ-hydroxypropylpyridine

6.



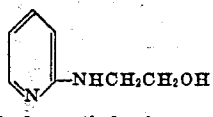
4-γ-hydroxypropylpyridine

7.



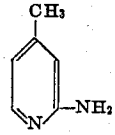
2-aminopyridine

8.



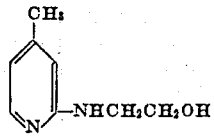
2-β-hydroxyethylamino pyridine

9.



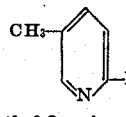
4-methyl-2-aminopyridine

10.



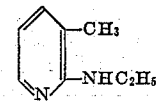
4-methyl-2-β-hydroxyethylamino pyridine

11.



5-methyl-2-aminopyridine

12.



3-methyl-2-ethylaminopyridine

Most of the above compounds are commercially available with the possible exception of those in which the amino group in 2-position is substituted by alkyl or hydroxyalkyl, such as, for example, 3-methyl-2-ethylaminopyridine. These compounds, however, are readily obtained by alkylation of the amino group in 2-position.

It will be observed that pyridine itself is excluded from the scope of the pyridine bases contemplated for use. This is attributable to the fact that pyridine itself is sufficiently volatile to produce toxically hazardous concentrations of its vapors in the confined areas usually used in carrying out photographic processes. Also pyridine is objectionable for use by reason of the peculiar odor which it possesses.

The pyridine bases are added to the developer in an amount ranging from 1 to about 40 grams per liter. The particular quantity will depend upon the developer employed, as well as upon the particular dye density required in the color development.

The color developers contemplated herein in addition to containing the aforementioned 2,4-diamino anilines and the pyridine derivative will also contain the usual adjuncts such as an alkali, i. e., sodium carbonate, a preservative, i. e., sodium sulfite, and a restrainer, i. e., an alkali metal bromide such as potassium bromide, and the like.

The invention may be carried into effect by color development of an exposed silver halide emulsion with the 2,4-diamino anilines while using the color former either in the developer or preferably in non-diffusing form in the silver halide emulsions.

The procedure is applicable to negative, positive or reversible color film, and particularly to such film in the form of the conventional tripack previously described.

The invention is further illustrated by the accompanying self-explanatory drawings, Figures 1 and 2 of which show the effect on the maximum dye density of an azine multilayer type film as described in Examples VI and VII of varying the concentration of 2-aminopyridine and 4-methyl-2-aminopyridine respectively in the color developer employed.

It will be observed that as the concentration of the pyridine base in the color developer is increased from 0 to 20 grams per liter, the maximum dye density increases from about .1 to over 2 units.

The invention is further explained by the following examples but it is to be understood that the invention is not restricted thereto.

Example I

A photographic silver halide emulsion was exposed, developed in a black and white developer, re-exposed and developed for 14 minutes in a bath of the following composition:

4,6-di-(phenylamino) metanilic acid	grams	4.0
p-Anisyl-J-acid	do	1.5
Sodium carbonate, monohydrate	do	20
Sodium sulfite	do	30
Potassium bromide	do	2
5-methyl-2-aminopyridine	do	12
Water to	cc	1000

The film was washed, bleached in a ferricyanide bleach and fixed in an acid-hardening hypo. There was obtained an azine cyan dye image of exceptional density and brilliance.

Example II

The procedure is the same as in Example I excepting that the pyridine is replaced by 4-methyl-2-aminopyridine.

Example III

A multilayer film composed of a red-sensitive bottom layer containing (4-stearoylaminophenyl)-J-acid and a green-sensitive middle layer containing 2 - stearoylamino-6-(6-bromo-8-hydroxycinchoninoyl) aminotoluene-4-sulfonic acid was exposed through a sharp cutting yellow filter, developed in a black and white developer, reexposed, and the residual silver halide developed for 16 minutes in a solution of the following composition:

4-(β-hydroxyethylamino)-6-phenylamino metanilic acid	grams	6.0
Sodium carbonate	do	40
Sodium sulfite	do	40
Potassium bromide	do	5
4 - hydroxypropylpyridine	do	16
Water to	cc	1000

After development the film was washed and bleached in a ferricyanide bleach. After fixing in an acid-hardening hypo, there remained a multi-colored dye image of excellent saturation and brilliance.

Example IV

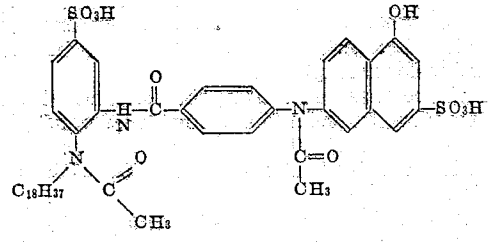
The procedure is the same as in Example III excepting that the 4-hydroxy-propylpyridine is replaced by 2-aminopyridine.

Example V

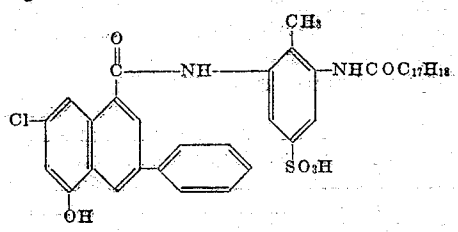
The procedure is the same as in Example III excepting that the 4-hydroxypropylpyridine is replaced by 4-methyl-2-β-hydroxyethylaminopyridine.

Example VI

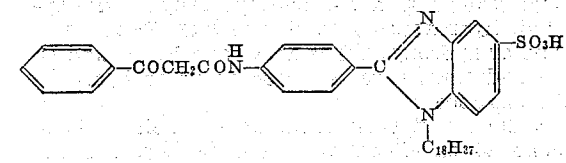
A three layer film composed of a red sensitive bottom layer containing:



6-p-(2-N-octadecylacetamido - 5 - sulfophenylcarbamyl) N-acetylanilino-1-naphthol-3-sulfonic acid, and a green sensitive middle layer containing:



2 - stearoylamino-6 - (6 - chloro - 8 - hydroxy-2-phenylcinchoninyl) amino toluene-4-sulfonic acid, and a blue sensitive emulsion containing:



2-(p-benzoylacetaminophenyl) - 1 - octadecyl-5-benzimidazole sulfonic acid was exposed, developed in a black and white developer, reexposed, and the residual silver halide developed for 18 minutes in a solution of the following composition:

4-(β-hydroxyethylamino)-6-phenylamino metanilic acid	g	5
Sodium carbonate	g	40
Sodium sulfite	g	40
Potassium bromide	g	3
2 - aminopyridine	g	15
Water to	cc	1000

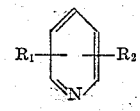
After development the film was washed, bleached in a ferricyanide bleach. After fixing in a 20 per cent sodium thiosulfate solution there remained a tri-colored dye image of superior brilliance and saturation.

Example VII

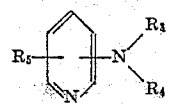
The procedure is the same as in Example VI excepting that the 2-aminopyridine is replaced by 4-methyl-2-amino pyridine.

We claim:

1. In the process of producing brilliant azine dye images through improved color rendition which comprises developing an exposed silver halide emulsion in the presence of a color former capable of reacting with the oxidation products of a 2,4-diaminoaniline to yield an azine dye image with a developing agent containing a 2,4-diamino aniline and a small quantity of a pyridine derivative selected from the class consisting of those of the following formulae:



and

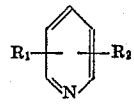


wherein R_1 is selected from the class consisting of hydrogen, lower alkyl and hydroxyalkyl, R_2 is selected from the class consisting of lower alkyl and hydroxyalkyl, and R_3, R_4 and R_5 are a member of the class consisting of hydrogen, hydroxyalkyl and lower alkyl.

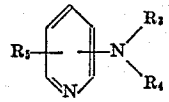
2. The process as defined in claim 1 in which the pyridine derivative is added in an amount of from 1 to 40 grams per liter of solution.

3. In the process of producing subtractively colored azine dye images in a tripack, each silver halide emulsion layer of which is sensitized to one of the primary colors and each silver halide emulsion layer of which contains a color former capable of reacting with the oxidation products of a 2,4-diaminoaniline to yield an azine dye image complimentary in color to the light for which the layer is sensitized by exposing the tripack and developing the same with a color developer containing as the effective de-

veloping agent a 2,4-diamino aniline, the improvement which involves the suppression of proximity development by incorporating in the color developer a pyridine derivative selected from the class consisting of those of the following formulae:



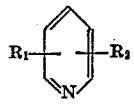
and



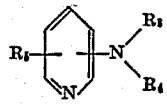
wherein R_1 is selected from the class consisting of hydrogen, lower alkyl and hydroxyalkyl, R_2 is selected from the class consisting of lower alkyl and hydroxyalkyl, and R_3, R_4 and R_5 are a member of the class consisting of hydrogen, hydroxyalkyl and lower alkyl.

4. The process as defined in claim 3 in which the pyridine derivative is added to the color developer in an amount of from 1 to 40 grams per liter of solution.

5. The process of producing azine dye images in a tripack, each silver halide emulsion layer of which is sensitized to one of the primary colors, the red sensitive layer containing an aryl-J-acid non-migratory in the emulsion as a color former, the green sensitive layer containing a 6-halogen-8-hydroxy quinoline non-migratory in the emulsion as a color former, and the blue sensitive layer containing an open chain keto methylene compound non-migratory in the emulsion as a color former, which comprises exposing the tripack and color developing the same with a developer containing a 2,4-diamino aniline and a pyridine derivative selected from the class consisting of those of the following formulae:



and

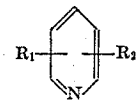


wherein R_1 is selected from the class consisting of hydrogen, lower alkyl and hydroxyalkyl, R_2 is selected from the class consisting of lower alkyl and hydroxyalkyl, and R_3, R_4 and R_5 are a member of the class consisting of hydrogen, hydroxyalkyl and lower alkyl.

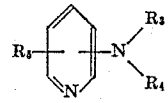
6. The process as defined in claim 5 wherein the pyridine derivative is present in the color developer in an amount of from about 1 to 40 grams per liter.

7. The process as defined in claim 5 wherein the 2,4-diamino aniline is a metanilic acid derivative containing an hydroxyalkylamino group in the 4-position.

8. A color forming developer for the production of brilliant azine dye images comprising an aqueous solution of a 2,4-diamino aniline and a small amount of pyridine derivative selected from the class consisting of those of the following formulae:



and



wherein R_1 is selected from the class consisting of hydrogen, lower alkyl and hydroxyalkyl, R_2 is selected from the class consisting of lower alkyl and hydroxyalkyl, and R_3, R_4 and R_5 are a member of the class consisting of hydrogen, hydroxyalkyl and lower alkyl.

ROBERT C. GUNTHER.
VSEVOLOD TULAGIN.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,486,440	Schmidt	Nov. 1, 1949