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UNITED STATES PATENT OFFICE

2,310,980

REDUCING BATH FOR COLOR PHOTOGRAPHY AND PROCESS OF USING THE SAME

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5 Claims. (Cl. 95—88)

This invention relates to photography. More particularly it relates to reducing compositions for reducing silver salts to metallic silver. Still more particularly it relates to dye generating reducing compositions which are useful in color photography. Still more particularly it relates to aqueous reducing baths containing an aromatic polyamino developing agent having at least one unsubstituted amino group and a nitrogenous base free from ne ative groups and hydroxyl groups attached to carbon atoms. Still more particularly it relates to aqueous reducing baths containing an aromatic polyamino developing agent having at least one unsubstituted amino group and a nitrogenous base free from negative groups and hydroxyl groups attached to carbon, capable of energizing said developing agent so that it no longer acts preferentially on exposed silver salts. The invention also relates to processes of reducing photographic images utilizing the herein-described reducing baths.

This invention has for an object the preparation of active reducing baths from photographic developing agents. A further object is to produce a reducing composition which will reduce metallic salts especially unexposed silver salts of the type used in photographic emulsions to metallic silver. A still further object is to provide an aqueous reducing bath which does not distinguish in its reducing action between unexposed and exposed silver salts in a photographic emulsion. A still further object is to provide a reducing composition which may be used in a reversal process involving no reexposure to light. Another object is to provide a reducing bath which may be used for simultaneously reducing silver salts and forming colored dyes in situ therewith. Another object is to provide an aqueous reducing composition which will increase the effective speed of photographic emulsions in forming colored images, especially reverse images. Other objects include the production of reducing compositions which when used in processes of color-photography result in color photographs of improved quality, saturation of individual color components and brilliancy of individual and combined dye images. A further object is to provide reducing baths which are of general utility in the dyeing arts.

The above and other objects are accomplished by the following invention which comprises a composition containing an aromatic polyamino developing agent containing at least one unsubstituted amino group and a nitrogenous base free from negative groups and hydroxyl groups attached to carbon.

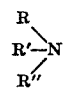
In a more limited sense the invention comprises the preparation and use of an aqueous bath containing an aromatic polyamino developing agent containing at least one unsubstituted amino group and a nitrogenous base free from negative and hydroxyl groups attached to carbon, capable of energizing said developing agent so that it no longer acts preferentially on exposed silver salts.

In a still more limited sense the invention comprises an aqueous reducing bath containing an arylene diamino photographic developing agent and a water-soluble nitrogenous base free from negative groups and hydroxyl attached to carbon, capable of energizing said developing agent so that it no longer distinguishes between exposed and unexposed silver halides in its reducing action.

The energizing agents which change aromatic polyamino developing agents containing at least one unsubstituted amino group and especially those free from negative and hydroxyl groups do not fall into any one specific class of bases but fall within numerous classes. The operative nitrogenous bases as previously stated are free from negative groups such as halogen atoms, e. g. Cl, Br: nitro, SO_3M, COOM wherein M is H or a metal, and hydroxyl groups, attached to carbon. The bases which are water soluble or can be readily dispersed in aqueous systems are most effective. Bases which do not have the above constitution, for example, the alkylol amines, e. g. mono-, di and tri-ethanol amines, do not function in the reducing solutions of the present invention.

An important class of nitrogenous bases which are organic amines may be represented by the general formula:

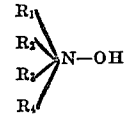
(1)



wherein each R, R' and R'' may be hydrogen, alkyl, cycloalkyl, aryl, aralkyl, or wherein two R's may represent a divalent polymethylene

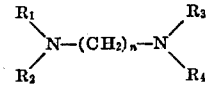
hydrocarbon or R, R' and R'' together may represent a trivalent hydrocarbon radical such as a polymethanyl radical which, with the nitrogen atom, forms an N-heterocyclic nucleus.

Another important class of compounds which are quaternary ammonium bases may be represented by the general formula:

(2) 

wherein each R_1, R_2, R_3 and R_4 may be hydrogen, alkyl, cycloalkyl, aryl, aralkyl, or wherein two R's may represent a divalent polymethylene hydrocarbon radical or three R's may represent a cyclic trivalent hydrocarbon radical such as a polymethenyl radical which with the nitrogen atom forms an N-heterocyclic nucleus.

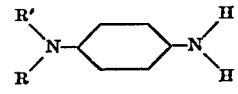
Another important class of compounds which are aliphatic polyamines may be represented by the general formula:

(3) 

wherein each R_1, R_2, R_3 and R_4 may be hydrogen, alkyl, cycloalkyl, aryl, aralkyl, and further characterized in that the methylene groups may be substituted by alkyl, cycloalkyl, aryl and aralkyl groups and at least one of the methylene groups may be substituted by amino groups, and n is 1 to 8.

As examples of suitable alkyl groups which may be present in each of the above formulae mention is made of methyl, ethyl, propyl, isopropyl, n-butyl, tertiary butyl, pentyl, isopentyl, octyl, dodecyl, tetradecyl, octadecyl. Suitable cycloalkyl radicals include cyclobutyl, cyclopentyl, and cycohexyl. Suitable aryl radicals include phenyl, tolyl, α-naphthyl, β-naphthyl, etc. Among the useful aralkyl radicals may be mentioned benzyl, 2-methyl benzyl, naphthyl methyl, etc.

The objects are attained in a refinement of the invention by the preparation of reducing compositions, particularly aqueous baths containing an N-dialkyl phenylene diamine of the general formula:

(4) 

or a water soluble salt thereof, wherein R and R' are the same or different lower alkyl radicals, e. g. methyl and ethyl; and a nitrogenous base free from negative groups and hydroxyl groups and falling within one of the Formulae 1, 2, and 3.

It has been found according to this invention that the arylene diamino compounds, particularly those of the type set forth in Formula 4 above and their water soluble salts become very active reducing agents when they are admixed with nitrogenous bases of the above type especially those falling within one of the Formulae 1, 2 and 3. This discovery is of considerable importance in that it enables the relatively weak reducing agents, namely, the arylene diamino compounds, to be used in a great many arts, wherein only powerful reducing agents have heretofore been used without the attendant disadvantages of the last mentioned agents.

In an important embodiment of the invention the reducing compositions contain in addition to the aromatic polyamino photographic developing agent and nitrogenous base which energizes its reducing powers, a color former which will couple with the products formed during the reducing action to form a dyestuff of the indophenol or azomethine type.

The N-dialkyl p-phenylene diamines, which are rather weak photographic developing agents, when used in conjunction with basic agents herein specified become highly energized and are no longer selective in their reducing action. They lose their ability to differentiate between exposed and unexposed silver halides in their reducing action and no longer act like photographic developing agents. On the contrary, they become overall reducing agents, acting similarly to sodium hydrosulfite, sodium stannite, etc. in regard to silver salt reduction.

In addition to causing weak photographic developing agents, e. g. 1:4-diaminobenzene, 1:4-diamino-naphthalene, p-aminodiethyl aniline, p-aminodiethyltoluidine, etc. to become overall silver halide reducing agents, the addition of the nitrogenous bases free from negative groups and hydroxyl groups vastly increases the dye-forming characteristics of these dye-generating baths which is surprising and unexpected. Thus, it has been found that with a given silver density produced by the conventional type of color-forming developer containing sodium or potassium carbonate as the alkali, a much greater density of dye image is produced with the same silver density by these dye-generating reducing baths. Furthermore, this occurs at the same pH condition of the bath as that containing alkaline carbonates. At least 40%, and sometimes as much as 70% greater dye density for the same amount of reduced silver halides is produced by these dye-generating reducers compared with ordinary carbonate containing color-developers. In addition, the rate of increase in dye-density with alkaline carbonate, or even caustic alkali, containing color-developers rapidly diminishes after 5–8 minutes developing time. With the dye-generating reducers of the present invention, on the other hand, the increase in dye-density continues even after 15 minutes developing time. The specific types of nitrogen bases described above result in three major unexpected and surprising results when used with arylene-diamine developing agents in the presence of quinone-imine, azomethine and azo dye-forming components:

1. Weak photographic developing agents become energetic over-all reducers for silver halides and are no longer photographer developers.

2. For the same amount of silver produced, these dye-generating reducers yield greater amounts of dye.

3. The formation of dye with these dye-generating reducers continues long after the usual color-developers have ceased to produce greater dye density.

The present application is limited to the reducing compositions including those containing color-formers. Processes of producing colored images involving the use of these reducing baths particularly reversal processes and processes involving the use of multi-layer film containing color formers, are claimed in a copending application Serial No. 295,686 of E. Meschter, entitled Color Photography, filed upon an even date herewith.

The present invention will be further illus-

trated but is not intended to be limited by the following examples:

Example I

An aqueous bath of the following composition:

p-Amino-N-diethylaniline	grams	2
Ammonium hydroxide, conc	cc	25
Sodium sulfite, anhy	grams	2
Water to	liter	1

was prepared by adding the ammonia to a solution of the sodium sulfite and then adding the developing agent. Water was then added to make one liter.

An exposed negative film was developed in a metolhydroquinone developer and without fixing, the silver image was removed in a sulfuric acid-potassium dichromate, washed, then treated without re-exposure in the above reducing bath. A reversed image of good quality was readily formed.

Example II

An aqueous bath of the following composition:

p-Aminodiethylaniline	grams	2
Hexamethylenediamine (54% solution)	cc	15
Sodium sulfite, anhy	grams	3
Water to	liter	1

was prepared after the manner set forth in Example I. It had excellent reducing properties for silver halides.

Other reducing baths which have similar properties are set forth in the following examples:

Example III

p-Aminodiethylaniline	grams	3
Ammonium hydroxide, conc	cc	30
Sodium carbonate, anhy	grams	20
Water to	liter	1

Example IV

p-Aminodiethylaniline	grams	3
B-dimethylaminoethylamine	cc	20
Sodium sulfite, anhy	grams	3
Water to	liter	1

Example V

p-Aminodiethylaniline	grams	2
Piperidine	cc	25
Sodium sulfite, anhy	grams	2
Water to	liter	1

Example VI

2-Amino-5-diethylamino-toluene	grams	5
Trimethyl-benzyl-ammonium hydroxide	cc	20
Sodium sulfite, anhy	grams	5
Water to	liter	1

Example VII

4:4-Diaminodiphenylamine	grams	4
Hexamethylenediamine	do	10
Sodium sulfite, anhy	do	2
Water to	liter	1

Example VIII

1:4-Diaminonaphthalene	grams	3
Dimethylcyclohexylamine	cc	30
Sodium sulfite, anhy	grams	3
Water to	liter	1

Example IX

4-Diethylamino-1-naphthylamine	grams	5
B-dimethylaminoethylamine	cc	20
Sodium sulfite, anhy	grams	5
Water to	liter	1

Example X

p-Aminodibutylaniline	grams	3
Hexamethylenediamine	do	20
Sodium sulfite, anhy	do	2
Water to	liter	1

Example XI

p-Aminodiethylaniline	grams	3
Trimethyl-benzyl-ammonium hydroxide	cc	25
Sodium sulfite, anhy	grams	3
Water to	liter	1

When the developing agent is used in the base form it should be incorporated in the solution after the sulfite and nitrogenous base have been added. In the salt form the sulfite is added first, then the developing agent, then the nitrogenous base.

Example XII

A dye forming reducing bath of the following composition:

α-Chlor-ethyl-aceto-acetate	grams	2
p-Amino-N-diethylaniline	do	2
Ammonium hydroxide (conc.)	cc	25
Sodium sulfite, anhy	grams	2
Water to	liter	1

was prepared by the above manner by dissolving the chlorethylacetoacetate in acetone and adding it and the other ingredients to water and bringing the solution up to 1 liter.

A film which had been exposed and developed in a metol-hydroquinone developer and the silver images removed by bleaching was treated in the above solution, whereby a reversed yellow dye and silver images were formed. The silver image was removed in the usual manner, leaving a yellow image.

Example XIII

A dye forming reducing bath of the following composition:

Thioindoxyl-carboxylic acid	grams	2
p-Amino N-diethylaniline	do	3
β-Dimethylaminoethylamine	cc	20
Sodium sulfite, anhy	grams	3
Water to	liter	1

is prepared by adding the thio-indoxyl-carboxylic acid dissolved in 20 ccs. of acetone and the other ingredients to water and bringing the solution to a volume of one liter.

An unexposed reversed silver salt image, when treated in the above solution, forms a magenta dye image in situ with metallic silver. Upon removal of the silver a magenta image of good strength and clarity is obtained.

Example XIV

A dye forming reducing bath of the following composition:

Trichlornaphthol	grams	2
2-amino-5-diethylamino-toluene	do	5
Hexamethylenediamine	do	10
Sodium sulfite, anhy	do	5
Water to	liter	1

is prepared by dissolving the trichlornaphthol in acetone and adding it and the other ingredients to water and bringing the solution to a volume of one liter.

An unexposed reversed silver salt image when treated in the solution forms a blue-green image in situ with metallic silver. Upon removal of the silver a blue-green image of excellent density and clarity was obtained.

In place of the aromatic polyamino developing agents free from nuclear hydroxyl groups set forth in the above examples, may be substituted in whole or in part one or more other specific compounds. Suitable additional compounds of this type, which are known photographic developing agents include:

1:4-diaminobenzene
2:5-diaminotoluene
p-Aminomethyl aniline
p-Aminoethyl aniline
p-Aminodimethyl aniline
p-Aminodiethyl aniline
p-Aminodibutyl aniline
2-amino-5-diethylaminotoluene
2:5-diaminomethoxybenzene
1-amino-4-phenylaminoacetic acid
4:4'-diaminodiphenylamine
2:4-diaminodiphenylamine
4-amino-N-phenylpiperidine
4-amino-N-phenylmorpholine
1:4-diaminonaphthalene
4-aminodiethyl-1-naphthylamine
4-aminophenyl-1:4-naphthalenediamine
1-amino-4-p-aminophenyl-naphthalenediamine

and their water soluble salts, e. g. chloride, sulfate, acetate, oxalate, etc.

Similarly, other basic compounds which cause the above developing agents to become overall reducing agents may be substituted in whole or in part for the specific bases set forth above. Thus, one or more of the following may be used: Lower alkylamines such as mono-, di- and trimethyl, ethyl, n-propyl, n-butyl, etc. amines, which contain no negative groups and hydroxyl groups in the hydrocarbon radicals; straight and branched chain alkyl mono- and poly-amines free from nuclear negative and hydroxy groups, e. g. ethylenediamine, hexamethylene diamine, triaminopropane, β-dimethylamino ethylamine, n-propylamyl hexylamine, tri-n-amylamine, di-iso-amylamine, cyclic and heterocyclic amines, e. g. piperidine, N-methylpiperidine, N-ethylpiperidine, piperazine, N-dimethylcyclohexylamine, N-ethyl-N-methyl cyclohexylamine, n-octyl-pyridinium hydroxide; quaternary N-hydroxides free from nuclear substituted negative groups and hydroxyl groups, e. g.:

Trimethylbenzylammonium hydroxide
Tetramethylammonium hydroxide
n-Dodecyldimethylcyclohexylammonium hydroxide
n-Dodecyltrimethylammonium hydroxide
n-Octadecylbenzyldimethylammonium hydroxide
n-Dodecylphenyldimethylammonium hydroxide

The nitrogenous bases free from negative groups and hydroxyl groups which may be used in practicing this invention are further characterized in that they have an association exponent (pkab) of about 5.00 to about 12.00 and preferably from 9.0 to about 11.40.

The proportions of the components of the reducing solutions may be varied considerably. For instance, the amount of arylene-diamino developing agent may vary from 2 to 12 grams per liter with good results. The amount of alkali metal or ammonium sulfite may vary from 15 to 25 grams per liter of solution. The amount of weak alkali, e. g. sodium carbonate may vary from 0 to 30 grams per liter. With regard to the nitrogenous base free from negative groups and hydroxyl groups, it may vary from 8 to 30 grams or ccs. per liter of solution.

Likewise, other color forming compounds may be substituted for the specific ones set forth in the above examples. As examples of representative suitable color-formers which are soluble or readily dispersible in the reducing solutions are diacylacetamino-aryl-bis-thiazoles of U. S. Patent 2,140,540, of which difuroylacetamino-1,2,4,5-benzo-bis-thiazole is preferred, the acylacetarylides of U. S. Patent 2,108,602, acetyl acetone, benzoyl acetone, B-naphthoyl acetone, acetoacetic esters, ethyl-α-chloroacetoacetate, ethyl-γ-chloroacetoacetate, ethyl malonate, ethyl-p-nitrophenyl-acetate, ethyl acetopropionate, ethyl acetone dicarboxylate, furoylacetic ester, the acylacetamino phenyl morpholines of U. S. Patent 1,133,937, etc.

Suitable magenta color-formers include nitriles, e. g. p-nitrobenzyl cyanide, o-nitrobenzylcyanide, p-toluyl-acetonitrile, ω-cyano-acetyl-dibenzfuran, ω-cyano-acetyl-acenaphthene, 1-ω-cyanoacetylcoumarone, 1:3-di-(ω-cyanoacetyl)-benzene, acyl nitriles, e. g. cyanacetophenone, methoxy-α-naphthoylaceto-nitrile, cyanacetanilides, e. g. 1-cyanacetaminobenzthiazole, etc., pyrazolones, e. g.

Suitable blue-green color formers include phenols, e. g. ortho and meta-chlorophenol, o-bromophenol, o-iodophenol; naphthols, e. g. 2,3,4-trichlornaphthols, 2,6-dibromo-1,5-dihydroxy naphthalene, etc. Other color-formers will be apparent to those skilled in the art.

The energetic dye-generating properties of the reducers described above makes their particularly useful as intensifiers for silver images of too low opacity to make them of satisfactory printing density. This embodiment of the invention is illustrated in the following example:

Example XV

A low opacity silver image is bleached to a reducible silver salt form by a chromic acid and sodium chloride or bromide bleach bath or an alkaline-ferrocyanide bleach. The washed film is treated with a dye-generating reducing bath of the above type which yields a neutral black or grey image. If the intensified image is to be used for printing onto blue-sensitive emulsions a yellow-orange-to-red color-former can be employed.

Intensification processes employing color-forming developers are described in Fischer U. S. Patent 1,079,756 but the process described above constitutes a distinct improvement over the known procedures. A major advantage resides in the substantial increase in image opacity obtained hereby. In addition, the tonal graduations of the image as intensified by the present method do not depart as much from the original tonal scale as by the prior art procedures exemplified in the Fischer patent.

It is to be understood, however, that the dye-forming reducing baths hereof are not limited to photographic uses although such uses are of major importance. On the contrary, they are of considerable utility in the textile and related industries. The production of dye textile materials from natural, chemically modified, artificial and synthetic fibers is facilitated by employing reducing baths as described above. The treatment of cellulose derivatives, for instance, by the use of such baths, is of considerable importance. The dyeing of such materials will be illustrated by the following example:

Example XVI

Equimolecular proportions of p-aminodimethylaniline and 1-naphthol are dissolved in water containing 50 parts per liter of trimethylbenzyl ammonium hydroxide. The naphthoquinoneimide is formed by adding 2 parts of sodium perborate, heating the solution at about 30° C. for 15 minutes with vigorous stirring and then cooling. One part of the naphthoquinoneimide is made into a paste by trituration with 1 to 1.5 parts of sulfite waste liquor of 30 to 40% strength. To this paste is added 2000 parts of warm water and 100 parts of acetate silk are introduced and worked for ½ hour while maintaining the temperature of the dye bath at 60° C. The material is then rinsed and dried. It is found that the depth of color is much greater and the color purity vastly improved by this method over the usual indophenol dyeing methods. The presence of the coupling energizer serving here also to aid in the dye penetration.

In place of the specific color-formers and arylene diamino compounds may be substituted others as described above. Likewise, other nitrogenous bases and other textile materials may be substituted. In a like manner, other oxidizing agents may be substituted for the sodium perborate. Suitable agents include hydrogen peroxide, persulfates, percarbonates, alkali metal peroxides, per-organic acids, e. g. per acetates, per propionates, etc.

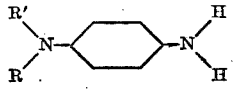
An important advantage of the present invention resides in the fact that the readily available weak arylene diamino types of developing agents may readily be converted into powerful reducing agents in a simple manner and with the aid of inexpensive and readily available additional agents.

A further advantage resides in the fact that a weak developing agent of the arylene diamine type becomes readily converted into an excellent color developing agent producing a much greater dye density for the same amount of reduced silver by the addition of inexpensive and readily available photographic materials. Still other advantages will be apparent to those skilled in the arts of this invention.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments hereof except as defined in the appended claims.

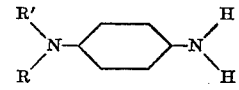
I claim:

1. An aqueous photographic reducing bath containing as the sole type of reducing agent at least one photographic developing agent taken from the group consisting of compounds of the general formula:



wherein R and R' are members of the group consisting of hydrogen and alkyl radicals of 1 to 4 carbon atoms and the water soluble salts thereof and an amount of an aliphatic amine of 1 to 6 carbon atoms free from negative groups and hydroxyl groups attached to carbon sufficient to change the characteristics of the solution so that it no longer distinguishes between exposed and unexposed silver salts, said amount being within the range from 8 ccs. to 30 grams per liter of solution.

2. An aqueous photographic reducing bath comprising as the sole type of reducing agent at least one photographic developing agent taken from the group consisting of compounds of the general formula:



wherein R and R' are hydrogen or an alkyl radical of 1 to 4 carbon atoms, and the water soluble salts thereof, and an aliphatic amine of 1 to 6 carbon atoms free from negative groups and hydroxyl groups attached to carbon in an amount sufficient to change the characteristics of the solution so that it no longer distinguishes between exposed and unexposed silver salts, said amount being within the range from 8 ccs. to 30 grams per liter of solution, and a color-forming compound.

3. An aqueous photographic reducing bath containing as the sole type of reducing agent at least one primary aromatic amino color developing agent, an aliphatic amine of 1–6 carbon atoms which is free from negative groups and hydroxyl groups attached to carbon in an amount sufficient to change the characteristics of the solution so that it no longer distinguishes between exposed and unexposed silver salts, said amount being within the range from 8 cc. to 30 grams per liter of solution, and a color forming compound.

4. An aqueous photographic reducing bath containing as the sole type of reducing agent an aromatic primary amino color developing agent, hexamethylenediamine in an amount sufficient to change the characteristics of the solution so that it no longer distinguishes between exposed and unexposed silver salts, said amount being within the range from 8 cc. to 30 grams per liter of solution, and a color forming compound.

5. An aqueous photographic reducing bath containing as the sole type of reducing agent an aromatic primary amino color developing agent, betadimethylaminoethylamine in an amount sufficient to change the characteristics of the solution so that it no longer distinguishes between exposed and unexposed silver salts, said amount being within the range from 8 cc. to 30 grams per liter of solution, and a color forming compound.

EMERY MESCHTER.

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CERTIFICATE OF CORRECTION.

Patent No. 2,310,980. February 16, 1943.

EMERY MESCHTER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, second column, line 18, for the patent number "1,133,937" read --2,133,937--; and line 35, for "their" read --them--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of April, A. D. 1943.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

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