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PHOTOGRAPHIC REVERSAL PROCESS OF PRODUCING DYE IMAGES WITHOUT RE-EXPOSURE

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5 Claims. (Cl. 95—88)

This invention relates to photographic processes. More particularly it relates to photographic reversal processes involving the production of dyestuff images. Still more particularly it relates to processes for obtaining direct positive dye images and silver images by reversal methods.

This invention has for an object the provision of a reversal method for producing black-and-white positives of good quality. A further object is the provision of such a process involving the use of readily available organic chemicals. A still further object is to provide a black-and-white reversal process which obviates the use of odoriferous sulfur compounds. A still further object is the provision of a reversal process for producing black-and-white dyestuff images suitable for processing sub-standard size film. Other objects include the provision of a black-and-white reversal process of increased dye density which involves a minimum number of steps and a general advance in the art.

The above objects are accomplished by the following invention which comprises the use of an aqueous reducing 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 the presence of a black color former for developing residual or reversed images.

In a more limited sense the invention comprises the formation of black and white reversed dyestuff images by the use of an aqueous reducing bath containing an arylene diamino photographic developing agent and a nitrogenous base free from negative groups and hydroxyl groups attached to carbon, in the presence of a black color-former for developing the residual or reversed image.

In a still more limited sense the invention comprises the formation of black and white reversed dyestuff images by the use of an aqueous reducing bath containing an arylene diamino developing agent free from nuclear hydroxyl groups 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 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:

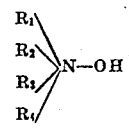
(1)



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 polymethenyl 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:

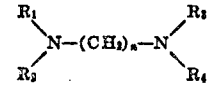
(2)



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 cyclohexyl. 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 that reducing solutions of the above type produce excellent black-and-white reversed dyestuff images if a black color former is present during the reduction step. The color-former may be present in the emulsion layer or in the aqueous reducing bath, but is preferably in the layer.

Because of the activity of the reducing baths, it is not necessary to re-expose the photographic element after the first development or formation of the negative images. The elimination of this step presents a distinct advantage in that it saves processing time, cuts down the size of the processing apparatus, etc.

Due to the energetic dye-producing action of the reducers shown above, the density of dye image is considerably greater, per density of silver produced, than with ordinary color-forming developers. Accordingly, the amount of silver halides need not be as great to produce a satisfactory dye density and thus the total coating weight of the emulsion layer can be materially reduced over that required for films to be processed by ordinary reversal processes.

The invention will be further illustrated but is not intended to be limited by the following examples:

Example I

A film element provided with a panchromatized silver halide emulsion layer coating of about 80 milligrams per 100 square centimeters and containing about 15 grams of β-naphthol as a black color former per kilogram of emulsion is processed after exposure as follows:

1. Develop 8 minutes in a metol-hydroquinone positive type developer.
2. Wash.
3. Reduce residual silver salts by treatment for 12 minutes in:

2-amino-5-diethylaminotoluene-2HCl ..... grams.. 6
B-dimethylaminoethylamine ..... cc.. 20
Sodium sulfite, anhy ..... grams.. 5
Water to ..... liter.. 1

4. Wash.
5. Bleach silver images in 4% alkaline potassium ferricyanide.
6. Wash.
7. Fix in:

Sodium thiosulfate, $7H_2O$ ..... grams.. 300
Potassium alum ..... do.... 20
Water to ..... liter.. 1

8. Wash and dry.

In place of the specific reducing baths set forth above in Step 3 may be substituted any one of the following baths with equally good results.

Bath A

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

Bath B

p-aminodiethylaniline ..... grams.. 2
Hexamethylenediamine ..... cc.. 15
Sodium sulfite, anhy ..... grams.. 3
Water to ..... liter.. 1

Bath C

p-aminodiethylaniline ..... grams.. 3
Ammonium hydroxide, conc ..... cc.. 30
Sodium carbonate, anhy ..... grams.. 2
Water to ..... liter.. 1

Bath D

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

Bath E

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

Bath F

2-amino-5-diethylamino-toluene ..... grams.. 5
Trimethylbenzyl-ammonium hydroxide.. cc.. 20
Sodium sulfite, anhy ..... grams.. 5
Water to ..... liter.. 1

Bath G

4:4-diaminodiphenylamine ..... grams.. 4
Hexamethylenediamine ..... cc.. 10
Sodium sulfite, anhy ..... grams.. 2
Water to ..... liter.. 1

Bath H

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

Bath I

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

Bath J

p-aminodibutylaniline	grams	3
Hexamethylenediamine	cc	20
Sodium sulfite, anhy	grams	2
Water to	liter	1

Bath K

p-aminodiethylaniline	grams	3
Trimethylbenzyl-ammonium hydroxide	cc	25
Sodium sulfite, anhy	grams	3
Water to	liter	1

Example II

To one kilogram of panchromatized silver gelatino bromide emulsion are added 20 grams of a mixture composed of 9 parts by weight of m-dodecyl-aminophenyl-hydroxynaphtho-thiazole sulfonic acid and 1 part by weight of 1-(m-stearoyl-aminophenyl)-3-methyl-5-pyrazolone dissolved in sodium hydroxide-alcohol solution. A 90 mg. coating of this neutral color-forming emulsion is coated on subbed cellulose acetate film base, exposed and processed as described under Example I. Dye-forming bath B is used to reduce the reversed image in step 3 of the process.

The simplified reversal process introduced by the present invention also makes possible an economical method for the production of enlarged black and white prints from colored transparencies. Recently several commercial films have become available for the production of colored transparencies. It is ofttimes desirable to produce enlarged prints from such positive color transparencies but the required process of making an intermediate negative and projection-printing from this is costly if only a few prints are desired. The other method involving the reversal of printing paper by known methods does not yield satisfactory results. The above disadvantages are overcome by this invention. The following example illustrates this embodiment hereof.

Example III

A silver chloro-bromide or chloride projection paper is bathed in a solution composed of 8 milligrams of pinacyanol, C. I. 808, and 6 milligrams of pinaflavol, C. I. 808A dissolved in a mixture of 650 cc. water and 350 cc. ethyl alcohol and containing 15 drops of concentrated ammonium hydroxide. After sensitizing for 4 minutes at 70° F., the paper is washed for five minutes in running water and then dried. The colored positive transparency is then enlarged directly on to the sensitized projection paper. The print is developed 1½ to 3 minutes in

Sodium sulfite	grams	50.0
Hydroquinone	do	25.0
Boric acid	do	5.0
Potassium bromide	do	2.5
Sodium hydroxide	do	25.0
Water to	liter	1

then washed. The reversed image is reduced by treatment for 3–5 minutes in

2-amino-5-diethylamino-toluene	grams	5
Trimethyl-benzyl ammonium hydroxide	cc	20
Sodium sulfite, anhydride	grams	8
Water to	liter	1

to which add

	Grams
2-5-dimethylbenzoxazole	4
Ethyl alcohol	100

In place of 2-5-dimethylbenzoxazole, which produces a bluish-black image, 2-methylbenzoxazole and 2-5-dimethylbenzo-thiazole can be used to produce brownish-black images. Similarly, other reducing baths, e. g. A. or C to K may be resorted to with similar results.

The low coating weight of emulsion on sensitized papers has, in the past, seriously militated against their successful use in reversal processes. The characteristic of the dye-forming reducers to produce extremely heavy deposits of dye-image for relatively low density of silver deposits, now makes it possible to employ the economical projection papers for rapid reversal processes yielding positive prints.

The color formers, as previously stated, may be placed in the aqueous baths instead of emulsion with similar results. They may be added in a solvent such as ethyl or methyl alcohol or acetone to which may be added alkali, e. g. sodium hydroxide.

In place of the specific black color former set forth in the previous example other black color formers may be substituted. Thus suitable additional blank color-formers include N-dodecyl-1:2-hydroxy-naphthoic acid-2-amino carbazole, meta-dodecoylaminophenyl - hydroxynaphthothiazole sulfonic acid mixed with 10% of 1(m-stearoylaminophenyl)-3-methyl-5 - pyrazolone; 4-(a-hydroxynaphthoyl)-4'-(p - nitro-benzoyl-acetyl)-di-chloro-benzidide (for emulsions); for developer use:—beta-naphthol diketohydrindene, 2-5-dimethylbenzoxazole, 2-methyl-benzoxazole, 2-5-dimethylbenzothiazole.

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
p-Aminophenyl-1:4-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, especially hydroxyl groups in the hydrocarbon radicals;

straight and branched chain alkyl mono- and poly-amines free from nuclear negative, especially hydroxy groups, e. g. ethylenediamine, hexamethylene diamine, triamino-propane, B-dimethylamino ethylamine, n-propyl-amyl hexylamine, tri-n-amylamine, di-iso-amylamine, cyclic and heterocyclic amines, e. g. piperidine, methylpiperidine, ethylpiperidine, piperazine, N-dimethylcyclohexylamine, N - ethyl - N - methyl cyclohexylamine, n-octyl-pyridinium hydroxide; quaternary n-hydroxides free from nuclear substituted negative groups especially 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 5 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 litter of solution.

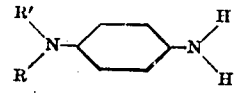
The numerous advantages of this invention should be apparent to those skilled in the art. The reversal methods hereof represent a definite improvement over the art in that the residual silver image does not need to be removed. The reversal system involves only 8 steps and produces black images. Prior reversal processes involving the use of sodium hydrosulfite have various shortcomings and do not produce black images.

A further advantage is concerned with the fact that due to its energetic dye-producing action, the density of dye images is considerably greater, per density of silver produced than with ordinary color-forming developers. This means the amount of silver halides in the emulsion can be materially reduced resulting in an economical manufacturing improvement over films for ordinary reversal methods. This economy feature is borne out by the above examples. The coating weight of negative films for reversal processes is usually about 105 to 115 mgs., that is this amount of dried gelatino-silver halide emulsion covers 100 square centimeters. By the present invention coating weights of 80 mgs. are practical.

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 the invention is not to be limited to the specific embodiments herein except as defined by the appended claims.

I claim:

1. A photographic reversal process comprising developing a photographic element containing a latent image in silver halides in an ordinary developer to produce a negative image and developing the residual silver halide image without re-exposure in the presence of a black color former with an aqueous reducing solution containing a compound 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 aliphatic amine of 1 to 6 carbon atoms 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; said base being free from negative groups and hydroxyl groups attached to carbon.

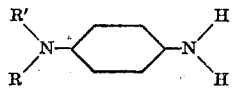
2. A photographic reversal process which comprises developing a photographic element containing at least one latent image layer in silver halides in an ordinary developer to produce a negative image and developing the residual silver halide image without re-exposure in the presence of a black color former with an aqueous reducing solution containing as the sole type of reducing agent at least one primary aromatic polyamino color developing agent, and an aliphatic amine of 1–6 carbon atoms 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 of from 8 cc. to 30 grams per liter of the solution, said amine being free from negative groups and hydroxyl groups attached to carbon.

3. A photographic reversal process which comprises developing a photographic element containing at least one latent image layer in silver halides in an ordinary developer to produce a negative image and developing the residual silver halide image without re-exposure in the presence of a black color former with an aqueous reducing solution containing as the sole type of reducing agent at least one primary aromatic polyamino color developing agent and 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 of from 8 cc. to 30 grams per liter of solution.

4. A photographic reversal process which comprises developing a photographic element containing at least one latent image layer in silver halides in an ordinary developer to produce a negative image and developing the residual silver halide image without re-exposure in the presence of a black color former with an aqueous reducing solution containing as the sole type of reducing agent at least one primary aromatic polyamino color developing agent, and beta-dimethylaminoethylamine 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 of from 8 cc. to 30 grams per liter of solution.

5. A photographic reversal process comprising developing a photographic element containing a latent image in silver halides in an ordinary developer to produce a negative image and developing the residual silver halide image without re-exposure in the presence of a black color former

with an aqueous reducing solution containing a compound 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 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 of from 8 cc. to 30 grams per liter of solution.

EMERY MESCHTER.