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PROCESSES OF COLOR DEVELOPMENT

Emery Meschter, Milltown, N. J., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to photography. More particularly it relates to processes of color photography wherein dyestuff images are produced by the color coupling development of silver salt images. 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 heterocyclic nitrogenous base free from negative groups and hydroxyl groups attached to carbon atoms. In one of its aspects it relates to aqueous reducing baths containing an aromatic polyamino developing agent having at least one unsubstituted amino group and a heterocyclic 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, including photographic reversal processes.

This invention has for an object the preparation of active color coupling reducing baths from photographic developing agents. A further object is to produce a color coupling 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 layer. A still further object is to provide a reducing composition which may be used in a reversal process which requires no reexposure to light. Another object is to provide a reversal process which requires 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 developing or reducing compositions which when used in color coupling development 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 hereindescribed invention which comprises the development of silver salt images with a primary aromatic amino developing agent in the presence of (1) a compound which couples with

the oxidation product of the developing agent on photographic development to produce a dyestuff and (2) a heterocyclic nitrogenous base free from negative groups and hydroxyl groups attached to acyclic carbon.

In a more limited sense the invention comprises the preparation and use for color coupling development of an aqueous bath containing an aromatic polyamino developing agent having at least one unsubstituted amino group and a strong heterocyclic nitrogenous base free from negative and hydroxyl groups attached to carbon.

To be more specific the heterocyclic bases comprehended have such a basicity that they are capable of fogging a photographic silver halide layer. They have a basicity materially greater than pyridine possessing an association exponent greater than 9.00, e. g. from 9.00 to 12.00. The association exponent being the pK_{ab} value which is derived from the formula:

$$pK_{ab} = -\log \frac{K_b}{K_w}$$

where K_b and K_w are the dissociation constants for the base and water respectively.

It has been found that when such heterocyclic nitrogenous bases are used in photographic developing solutions for the color coupling development of silver salt images that the color coupling is enhanced and the efficiency of dye production is materially increased. Coupling reactions which proceed only slowly with an ordinary color developer and exposed silver bromide, for instance, are greatly accelerated. The amount of dye formed is much greater in proportion to the amount of silver produced than when the heterocyclic nitrogenous bases are not used.

When the heterocyclic nitrogenous bases are used in an amount of from 8 grams to 30 grams or 8 ccs. to 30 ccs. in the case of a liquid, per liter of solution, the bases are capable of energizing the aromatic primary amino color developing agents so that they no longer act preferentially on exposed silver salts. This property is of value in a reversal process wherein a dye image is formed in the second development step since it is not necessary to re-expose the element to light. The primary and secondary silver images can be removed after the second color forming development step. The heterocyclic nitrogenous bases are particularly useful with arylenediamino color developing agents having at least one unsubstituted amino group.

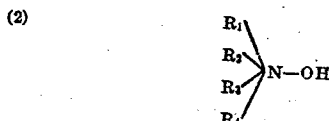
The present application is directed to an invention divided out of my copending applications, Serial Nos. 295,685, 295,686, and 295,687, now U. S. Patents Nos. 2,310,980, 2,310,981, and 2,310,982, respectively, and is a continuation in part of such applications.

The heterocyclic nitrogen bases having an as-

sociation exponent greater than 9.00 as previously stated are free from negative groups such as halogen atoms e. g. Cl and Br; nitro, SO_3M , wherein M is hydrogen or a metal, and hydroxyl groups attached to carbon. The heterocyclic nitrogenous bases may for example contain at least one heterocyclic nitrogen atom and 4 or 5 carbon atoms, and have the general formula:

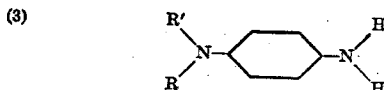


wherein two of the R's constitute a divalent hydrocarbon radical which form a heterocyclic nucleus with the nitrogen atom and the other R is hydrogen or a lower alkyl or cycloalkyl radical, or three of the R's may represent a single substituted polymethylene radical which with the nitrogen atom forms a heterocyclic nucleus of the general formula:



wherein two of the R's represent a divalent hydrocarbon or substituted hydrocarbon radical and the remaining R's constitute alkyl or cyclo alkyl groups or three R's represent a single polyvalent hydrocarbon radical which with the nitrogen atom forms an N-heterocyclic ring and the remaining R is alkyl or cycloalkyl.

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:



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 heterocyclic nitrogenous base free from negative groups and hydroxyl groups attached to carbon and falling within one of the Formulae 1 and 2.

It has been found according to this invention that the aryleno diamino compounds, particularly those of the type set forth in Formula 3 above and their water soluble salts become very active reducing agents when they are admixed with nitrogenous bases of the above type especially those which are free from intracyclic double bonds. This discovery is of considerable importance in that it enables the relatively weak reducing agents, namely, the aryleno 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 utilizing the invention the reducing compositions may 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 quinoneimine dyestuff including a dyestuff of the indophenol, indoaniline and indamine class or of the azomethine type. The color formers, however, may be present in the photographic elements treated as immobile or non-diffusing dye intermediates.

The N-dialkyl p-phenylene diamines, which are

rather weak photographic developing agents, when used in conjunction with heterocyclic basic agents herein specified in amounts from 8 grams or ccs. to 30 grams or ccs. per liter of solution become highly energized and are no longer selective in their reducing action. They lose their ability to readily differentiate between exposed and unexposed silver halides in their reducing action and no longer act completely like selective 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 heterocyclic 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 30% 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 aryleno-diamine developing agents in the presence of quinoneimine, azomethine and azo dye-forming components:

1. Weak photographic developing agents become energetic overall reducers for silver halides and are no longer photographic 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.

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

Example I

A dye forming reducing bath of the following composition:

A-chloroethyl-acetoacetate	grams	2
p-Amino-N-diethylaniline	do	2
Piperidine	cc	25
Sodium sulfite, anhy	grams	2
Water to	liter	1

was prepared by the above manner by dissolving the chloroethyl-acetoacetate 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 metolhydroquinone 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 II

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

An unexposed reversed silver salt image layer of a photographic element, when treated in the solution, forms a yellow image in situ with metallic silver. Upon removal of the silver a yellow image of excellent density and clarity was obtained.

When trichloronaphthol is substituted for the alpha chloroethyl-acetoacetate of Example II a blue-green image is formed in situ with the metallic silver. The trichloronaphthol can be dissolved in acetone and thus incorporated into the developer solution. Similarly, when the thioindoxyl-carboxylic acid is substituted a magenta image of good strength and clarity is formed.

In place of the aromatic color developing agents set forth in the above examples may be substituted a large number of other such specific compounds. Suitable additional color coupling developing agents include:

1:4-diaminobenzene
2:5-diaminotoluene
p-Aminoethyl aniline
p-Aminomethyl 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 heterocyclic nitrogen bases which enhance the color coupling reaction may be substituted for the piperidine of the above examples.

Suitable additional compounds include the substituted piperidines wherein the nucleus or the nitrogen atom contains an innocuous substituent which does not interfere with a color coupling reaction between the development products and the color former. Among the useful substituents are lower alkyl groups forming compounds such as N-methylpiperidine, N-ethylpiperidine, alpha-methylpiperidine, alpha-ethyl-piperidine, 2-hydroxy-3-ethyl-piperidine, 1-n-butyl-2-methylpiperidine, etc. Still other useful bases include morpholine and piperazine. The saturated heterocyclic amines are preferred.

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. (if a liquid) 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 diacetylacetoamino-aryl-bis-thiazoles of U. S. Patent 2,140,540, of which difuroylacetamino-1,2,4,5-benzo-bis-thiazole is preferred, the acylacetarilides of U. S. Patent 2,108,602, acetyl, acetone, benzoyl acetone, B-naphthoyl acetone, acetoacetic esters, ethyl-alpha-chloroacetoacetate, ethyl-gamma-chloroacetoacetate, ethyl malonate, ethyl-p-nitrophenyl-acetate, ethyl acetopropionate, ethyl acetone dicarboxylate, furoylacetic ester, the acylacetamino phenyl morpholines of U. S. Patent 2,133,937, etc.

Suitable magenta color formers include nitriles, e. g., p-nitrobenzyl cyanide, o-nitro-benzylcyanide, p-toluy-acetonitrile, w-cyanoacetyl-dibenzfuran, w-cyanoacetyl-acenaphthene, 1-w-cyanoacetylcoumarone, 1,3-di-(w-cyanoacetyl)-benzene, acyl nitriles, e. g., cyanacetophenone, methoxy-alpha-naphthoylacetone, cyanacetanilides, e. g., 1-cyanacet-aminobenzthiazole, etc., pyrazolones, e. g., 1-phenyl-3-furyl-5-pyrazolone, 1-phenyl-3-carboxylic acid-5-pyrazolone, 1-phenyl-3-hydroxy-5-imino-pyrazolone, 1-(8'-quinolyl)-3-methyl-5-pyrazolone, 1-phenyl-3-methyl-5-thiopyrazolone, etc.

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

The energetic dye-generating properties of the reducers described above makes them 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 III

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-ferricyanide 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 dyed 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 IV

Equimolecular proportions of p-aminodimethylaniline and 1-naphthol are dissolved in water containing 50 parts per liter of piperidine. 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 naphthoquinone-imide 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 80° 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 serves 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, perorganic acids, e. g., peracetates, perpropionates, etc.

While the above examples are concerned with color developer solutions wherein the dye intermediate or color formers are in the treating solution, the invention is not limited to that aspect. On the contrary, the color formers may be used in water permeable layers or strata. To be more specific, color formers of the immobile or non-diffusing types, including those which are substantive to water permeable colloid binding agents, such as gelatin. The color formers can be incorporated in gelatino-silver halide emulsions, for example, or in separate color yielding layers or strata in operative association with such layers. Color formers which yield various colors, e. g., blue-green, yellow, magenta, and composite colors, such as black, may be used in accordance with the teachings of this invention. Single layer and multi-layer elements containing immobile color formers are comprehended.

One embodiment of the invention is therefore concerned with the use of aqueous baths of the above type containing a heterocyclic nitrogen base but free from color formers, for the treatment of multi-layer film composed of three superposed differentially sensitized silver halide emulsion layers containing immobile color former compounds which form colors complementary in color to the employed sensitivity range of the respective emulsion layers. This embodiment will be more fully described below.

The reversal process of this invention may be used with a wide variety of different types of film structure. The processes, however, all involve the development of a latent image or series of partial latent images corresponding to a scene in-

cluding colored scenes, in an ordinary non-color forming photographic developer. The residual silver salts represent a reversed image since they are the counterpart residue of a given amount of silver halide coating, a certain portion of which has been employed to produce a metallic silver image corresponding to the latent image. The residual silver salts or reversed image can first be freed of the initially developed silver image by means of the well known bleaching and clearing baths but are preferably directly treated in the dye generating reducing baths described herein in the presence of color formers, especially those capable of forming indophenol or azomethine dyes.

The reversal processes hereof as previously stated, are of utility in the processing of multi-layer film, including mono- and multipacks composed of differentially color sensitive photographic emulsion layers. They are of especial utility in processing mono-packs comprising at least three differentially color sensitive silver halide emulsion layers, each containing immobile color formers, which are borne by a transparent base member. One of the layers may be placed on one side of the base and two on the other. The layers may be separated by clear layers, e. g., colloid layers such as gelatin which may prevent migration of color formers, sensitizers, which may be dyed to act as temporary filter layers.

A preferred embodiment of the invention involves the reversal processing of multilayer film which is differentially color sensitized and contains light barrier layers and especially treatment of such film wherein the respective color sensitive layers contain a color former which forms upon development a dye complementary in color to the sensitivity of the respective emulsion layer.

Photographic and film elements of the type just described are claimed in U. S. P. 2,191,502 and Serial No. 287,154, filed July 28, 1939, now U. S. Patent 2,266,441. In such films at least one emulsion layer is protected from the action of light after the first development of a reversal process due to the fact that a layer of pre-fogged silver gelatino halide emulsion is interposed between at least two differentially color sensitized emulsion layers.

Example V

A monopack comprising a cellulose acetate film base suitably subbed is coated with a gelatino silver bromide emulsion sensitized to red so as to exhibit very little sensitivity in the green spectral region by means of a green blind sensitizing dye, e. g., pinacyanol. To this blue-red sensitive emulsion layer is added 15 grams of a non-migratory blue-green color former, e. g., a salicylaldehyde-o-sulfobenzaldehyde acetal of polyvinyl alcohol per 1000 grams of emulsion. Over this blue-red sensitive layer is coated another silver halide emulsion layer which is sensitized to the blue-green region of the spectrum with a sensitizing dye, e. g., erythrosin, and contains a magenta (minus green) color former, e. g., 1-(m-stearoylamino-phenyl)-3-methyl-5-pyrazolone. Over the last mentioned layer is coated a layer of gelatin solution containing a removable yellow filter dye, e. g., Tartrazine C. I. 640. Over the yellow filter layer is coated a blue sensitive silver halide emulsion containing a yellow color former, e. g., furoylacetbenzoylacet-benzidide.

The above described film element is exposed to a colored object scene whereby latent images representing different color component aspects in the different sensitive layers are formed as is

known in the art. See, for instance, Schinzel Austrian Patent No. 42,478. The film is then processed by the following steps:

1. Develop 10 minutes in an ordinary metolhydroquinone positive developer.
2. Wash 10 minutes.
3. Reduce residual silver salts by treating for 15 minutes in a dye generating reducer of the following formula:

Sodium sulfite, anhydrous	grams	1.0
p-Aminodiethyl aniline dihydrochloride	grams	2.0
Piperidine	cc	20
Water to	liter	1
4. Wash 10 minutes.
5. Bleach 7 minutes in a solution containing 3½% by weight of potassium ferricyanide and made alkaline with ammonium hydroxide or sodium carbonate.
6. Rinse.
7. Remove bleached silver in a 25% solution of hypo (crystalline sodium thiosulfate).
8. Wash 15 minutes and dry.

In place of the specific dye forming reducing baths of the preceding examples may be substituted a wide variety of reducing baths having the above described characteristics. Thus any of the baths described in the aforesaid application may be substituted with similar result.

Similarly, various other immobile color formers may be substituted for the specific color formers set forth in the above examples. Color formers which give excellent results include non-migratory yellow color formers, which may be used in the blue-sensitive layer, as follows: diacylacetamino-aryl-bis-thiazoles of U. S. Patent 2,140,540, of which difuroylacetamino-1,2,4,5-benzo-bis-thiazole and di-acetoacetamino-1,2,4,5-benzo-bis-thiazole are especially useful as are 2-hydroxy-3-naphthoylamino-benzoyl-acetanilide, sodium stearoylamino-benzoyl-acetanilide-p-carboxylate, p-caproylamino, benzoylamino salicylic acid, furoylacet-p-amino phenyl amyl ether (U. S. P. 2,184,303), and di-picolinoyl-acet benzidine.

Suitable non-migratory magenta color formers which are especially useful are 1-(3'-sulfo-phenyl)-3-(4"-stearyl-amino phenyl)-3-(4"-dodecoylamino-phenyl)-5-pyrazolone, 4,4'-bis-(3"-methyl pyrazolonyl-1")-diphenyl (described in U. S. P. 2,200,924), 4,4'-methylene-bis-(m-stearylaminophenyl)-methyl pyrazolone, and 4,4'-o-sulfo-benzylidene-bis-(phenyl methyl pyrazolone) (described in U. S. P. 2,294,909).

Suitable non-migratory blue-green color formers of especial utility include 4,4'-di-(1-hydroxy-2-naphthoyl-amino) diphenyl, 1-hydroxy-2-carboxy-5-dodecoylamino naphthalene, 1-N stearyl-4-N-(1'-oxy-2"-naphthoyl) - phenylenediamine sodium sulfonate, resorcinol mono-n-dodecyl ether (described in U. S. P. 2,166,181), product of p-hydroxybenzoic acid and formaldehyde (described in McQueen, Serial No. 261,794, filed March 14, 1939, now U. S. Patent 2,323,481), product of polyvinyl alcohol and salicylaldehyde (described in Dorough and McQueen, Serial No. 233,480, filed October 5, 1938, now U. S. Patent 2,310,943 granted February 16, 1943).

Example VI

A multilayer film so disposed that light after passing through an optical aperture is first incident on a blue sensitive silver halide emulsion containing a yellow filter dye such as Luxol Fast

Yellow T, then a pre-fogged emulsion layer, then a green sensitive emulsion, another pre-fogged emulsion layer containing a soluble red dye, e. g., carmosine M, then a red sensitive silver halide emulsion, and finally the base. The amount of silver salt in the pre-fogged layers and the fogging exposure given the layers is such that upon the first development of the layers a light barrier layer will be formed therein so that substantially less than 1% of light will be transmitted by either of them.

In using this film, it is exposed normally in a camera, and then developed in a non-color forming developer. After development and washing the film contains three color separation negative image layers bearing both silver and unexposed, undeveloped, silver salt images, and two layers of metallic silver. The film is now preferably exposed through the base with a red or white printing light which exposes only the silver salt image remaining in the red sensitive layer. The red light does not substantially affect the other two layers because of their lack of sensitivity to the red light used as the printing light, and secondly, the black metallic silver barrier layer prevents substantially all of the printing light from passing through to the outer layers.

The film is now developed in a color-forming developer of the following composition:

2:3:4-trichlor-alpha-naphthol	grams	2
2-amino-5-diethylaminotoluene	do	5
Potassium carbonate	ccs	10
Sodium sulfite, anhy	grams	5
Water to	liter	1

prepared by dissolving the trichloronaphthol in alcohol and adding the other ingredients to water and bringing the solution up to one liter, whereby a blue-green (minus-yellow) dye image and silver image is formed. The film is then thoroughly washed.

The top or blue sensitive layer is then exposed to a blue or preferably a white printing light. This printing light does not affect the middle layer because of the metallic silver barrier layer between the top and middle layers. The entire film is then treated with a yellow (minus-blue) color forming developer of the following composition:

Potassium carbonate	grams	40
Sodium sulfite, anhy	do	5
Diethyl-paraphenylenediamine hydrochloride	do	3
Water to	liter	1

to which is added the following solution:

Benzoyl acetone—3 grams dissolved in 25 cc. of ethyl alcohol.

After development, the blue sensitive layer will contain both metallic silver and yellow dye images. It is then thoroughly washed.

The green sensitive middle layer on both sides of which are black, metallic silver barrier layers, remains. This layer is treated in a dye forming reducing bath of the type herein described containing an arylene diamino compound and a nitrogenous base and a magenta color former. A suitable bath is composed of:

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

Example VII

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

1. Develop 8 minutes in a metol-borax, fine-grain type developer.
2. Wash.
3. Reduce residual silver salts by treatment for 12 minutes in:

2-amino-5-diethylaminotoluene-2HCl	grams	6
Piperidine	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 ₂ O	grams	300
Potassium alum	do.	20
Water to	liter	1
8. Wash and dry.

If the fine-grain images are satisfactory in density as they are being washed in step No. 4, the silver images are allowed to remain and the film is simply dried after step No. 4. If, on the other hand, they appear too dense, the transmission of the images can be increased by removing the silver images, or a portion thereof, by bleaching and fixing as described in steps 5, 6 and 7 above.

Example VIII

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-hydroxynaphthol-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 but substituting N-methyl piperidine in the reducing bath to reduce the reversed image.

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 oftentimes 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 IX

A silver chlorobromide 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 min-

utes 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
Piperazine	cc.	20
Sodium sulfite, anhydride	grams	8
Water to	liter	1

to which add

2-5-dimethylbenzoxazole	grams	4
Ethyl alcohol	do.	100

If the image is too dark, all or a portion of the silver image can be removed by the steps indicated under Example I. 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.

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.

The present invention provides an improvement over previous suggestions for reversal development, wherein residual silver halides are chemically exposed by means of sulfur bearing compounds such as thiourea, allyl thiourea, etc., since these proposals incur the need for additional tubes or tanks in processing machines, more wash water consumption and an extended total processing time. Furthermore, such compounds are undesirable because of their objectionable odor.

A further advantage resides in the fact that a much greater density of dye image is produced with the same silver density as compared with the usual color developers containing alkaline carbonates as pH regulators.

An additional advantage resides in the fact that a very great increase in the coupling velocity of color formers is obtained by the use of the baths containing arylene diamino compounds and certain nitrogenous bases as energizers. Still other advantages will be apparent to those skilled in the art.

The numerous advantages of this invention should be apparent to those skilled in the art. The reversal methods hereof wherein black dye images are produced represent a definite improvement over the art in that the silver image does not need to be removed. The reversal sys-

tem involves only 8 steps and produces good 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 color forming photographic developer comprising a primary aromatic amino developing agent, a compound which couples with the oxidation product of the developing agent on photographic development to produce a dyestuff image and a heterocyclic nitrogenous base free from negative groups and hydroxyl groups attached to acyclic carbon.

2. A color forming photographic developer comprising a primary aromatic amino developing agent, a compound which couples with the oxidation product of the developing agent on photographic development to produce a dyestuff image and a heterocyclic nitrogenous base having an association exponent greater than 9.00.

3. A color forming photographic developer comprising a primary aromatic amino developing agent, a compound which couples with the oxidation product of the developing agent on photographic development to produce a dyestuff image and a heterocyclic nitrogenous base having an association exponent greater than 9.00 in an amount of 8 grams to 30 grams per liter of solution.

4. A color forming photographic developer comprising a color coupling primary aromatic amino developing agent, a compound which couples with the oxidation product of the developing agent on photographic development of a silver salt image to produce a dyestuff image and a saturated heterocyclic amine having an association exponent greater than 9.00.

5. A color forming photographic developer comprising a color coupling primary aromatic amino developing agent, a compound which couples with the oxidation product of the developing agent on photographic development of a silver salt image to produce a dyestuff image and a piperidine base having an association exponent greater than 9.00.

6. The process which comprises developing a photographic element containing a reducible silver salt image with a photographic developer

solution comprising a primary aromatic amino color developing agent in the presence of a heterocyclic nitrogenous base free from negative groups and hydroxyl groups attached to acyclic carbon and a color former.

7. The process which comprises developing a photographic element containing a reducible silver salt image with a photographic developer solution comprising a primary aromatic amino color developing agent in the presence of a saturated heterocyclic amine and a color former.

8. A photographic reversal process which comprises developing a photographic element containing a latent silver halide image in an ordinary developer to produce a negative image and developing the reversal silver halide image without re-exposure with an aqueous reducing bath containing a primary aromatic amino color developing agent in the presence of a heterocyclic nitrogenous base free from negative groups and hydroxyl groups attached to acyclic carbon and a color former.

9. A photographic reversal process which comprises developing a photographic element containing a latent silver halide image in an ordinary developer to produce a negative image and developing the reversal silver halide image without re-exposure with an aqueous reducing bath containing a primary aromatic amino color developing agent in the presence of a saturated heterocyclic amine having an association exponent greater than 9.00 and a color former.

10. A photographic reversal process which comprises developing a photographic element containing a latent silver halide image in an ordinary developer to produce a negative image and developing the reversal silver halide image without re-exposure with an aqueous reducing bath containing a primary aromatic amino color developing agent in the presence of a piperidine base having an association exponent greater than 9.00.

11. A photographic reversal process which comprises developing a photographic element containing a latent silver halide image in an ordinary developer to produce a negative image and developing the reversal silver halide image without re-exposure with an aqueous reducing bath containing a primary aromatic amino color developing agent in the presence of piperidine and a color former.

12. A color forming photographic developer comprising a primary aromatic amino developing agent, a compound which couples with the oxidation product of that developing agent on photographic development of a silver salt image to produce a dyestuff image and piperidine.

13. A color forming photographic developer comprising a primary aromatic amino developing agent, a compound which couples with the oxidation product of that developing agent on photographic development of a silver salt image to produce a dyestuff image and piperazine.

14. A color forming photographic developer comprising a primary aromatic amino developing agent, a compound which couples with the oxidation product of that developing agent on photographic development of a silver salt image to produce a dyestuff image and morpholine.

EMERY MESCHTER.