

[54] REVERSAL COLOR PHOTOGRAPHIC PROCESSES

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[58] Field of Search96/22, 55, 66 R

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[57] ABSTRACT

Color reversal processes comprising a negative silver development step, followed by reversal color development with an aqueous alkaline color developing composition containing a 3-alkyl-N-alkyl-N-alkoxyalkyl-p-phenylenediamine or a 3-alkoxy-N-alkyl-N-alkoxyalkyl-p-phenylenediamine color developing agent advantageously produce color image reproductions that are superior to those produced by prior art processes by enhancing interlayer and intralayer interimage effects produced in the negative development step, thus giving more complete correction for unwanted absorptions of the dyes, as well as (1) reducing color contamination of dye images caused by color fog, (2) increasing the dye yield per unit of silver, (3) forming dyes of superior light stability, and (4) providing processes that are less sensitive to pH changes.

16 Claims, No Drawings

REVERSAL COLOR PHOTOGRAPHIC PROCESSES

This invention is related to color photography and more particularly to color photographic processing which gives more efficient use of silver in producing higher quality dye images.

In the process of color photography, it is known to use p-phenylenediamine developing agents in conjunction with couplers to produce colored images. A summary of this process is described by Thirtle et al., *Encyclopedia of Chemical Technology*, Vol. 5, pp. 812-845 (1964), John Wiley & Sons, Inc. The color developing agent is oxidized by the silver halide in the presence of a latent image in a photographic element to produce silver metal and oxidized color developing agent. The oxidized color developing agent then couples with color-producing compounds present to produce a dye image-wise with respect to silver development.

Color development of the differently sensitized emulsion layers in color photographic elements containing nondiffusible couplers is advantageously performed in a single color development step to produce a color negative image reproduction when this development step is the first development step, or to produce a color reversal image if a negative black-and-white development step followed by a step in which the residual unexposed and undeveloped silver halide is made developable and then color developed. In reversal color photographic elements that do not contain nondiffusible couplers, diffusible couplers are used in the aqueous alkaline color developer solutions that are used to selectively color develop one silver halide emulsion layer at a time. The reversal processing of such a multicolor, multilayer element (containing no incorporated couplers) requires a negative black-and-white process followed by a step in which residual unexposed and undeveloped silver halide in each emulsion layer is selectively made developable, then that layer is color developed with a color developing solution containing a diffusible coupler that forms a nondiffusible dye that is complementary in color to the light-sensitivity of that layer, then the unexposed and undeveloped silver halide in a second emulsion layer is selectively made developable and color developed with another color developing solution containing a diffusible coupler that forms a nondiffusible dye that is complementary in color to the light-sensitivity of that layer, then the unexposed and undeveloped silver halide in the third emulsion layer is selectively made developable and color developed with another color developing solution containing a diffusible coupler that forms a nondiffusible dye that is complementary in color to the light-sensitivity of that layer. Following completion of the color development, the silver and any residual silver halide are removed by silver bleaching and then fixing the photographic element.

It is known that interlayer and intralayer interimage effects are produced during black-and-white development of a multilayer, multicolor element containing silver bromide emulsion layers in which at least one layer contains at least one mole percent more iodide in mixed silver bromide crystals than iodide in any mixed silver halide crystals in at least one of the other silver halide emulsion layers. The image-wise pattern of iodide ions released by development of the mixed silver halide crystals containing the higher mole percent iodide diffuses to the emulsion layer or emulsion layers that contain mixed silver halide crystals containing a lower mole percent iodide and produces an image-wise inhibition of the latent image development resulting in an increase in residual silver halide in the lower iodide-containing layer according to image development in the higher iodide containing layer. During subsequent color development, the increase in residual silver halide that remained in the lower iodide-containing layer after negative (i.e., black-and-white) development, results in corresponding increases in dye formation. It is known to utilize certain interimage effects to improve color reproduction in subtractive color processes. Reference is made to *Journal of the Optical Society of America*, 42, No. 9, pp. 663-669, September 1952, wherein Hanson and Horton describe the use of interimage effects to correct for unwanted absorptions of photographic dyes. The term "mixed silver ha-

lide," e.g., silver bromide, is to be distinguished from a mixture of silver bromide and silver iodide. It is also known that the presence of certain addenda, e.g., diffusible 4-thiazoline-2-thiones in emulsion layers of a multilayer element during silver image development will cause interimage effects.

Color development processes are desired which will enhance interimage effects and give improved color reproduction.

Color development processes use active aromatic primary amine color developing agents; however, not all silver halide grains containing latent image centers are developed to silver and dye. These so-called "dead grains" are wasted in color photographic development. Color development processes are desired that make more efficient use of latent image-exposed silver halide grains so that the ratio of dye produced to exposed silver halide is larger than the ratio produced in processes known before our invention.

Color development processes are desired that produce less fog or color development in non-image areas while they produce good dye density levels in image areas.

Color development processes are desired that are less sensitive to pH than known processes.

Color development processes are also desired which produce dye images having better stability to prolonged exposure to heat, high humidities and/or light.

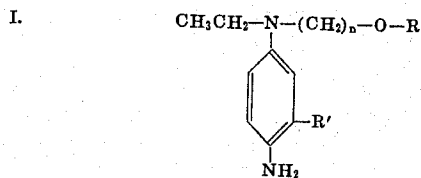
It is, therefore, an object of our invention to provide a novel color development process that produces an enhanced interimage effect.

Another object of our invention is to provide a novel color development process that produces improved color reproduction in subtractive color processes as a result of enhanced interimage effects, as well as lower fog in unexposed areas, higher dye densities in exposed areas, and a color development process that is less sensitive to pH.

Another object of our invention is to provide a novel color development process that produces improved color reproduction by developing substantially all silver halide grains that contain latent images and leaving substantially no "dead silver halide grains."

Still other objects will become apparent from consideration of the following specification and claims.

The above and still other objects of our invention are accomplished by use of our color photographic processes for treating an image-wise exposed multicolor, multilayer photographic element comprising a transparent film support having coated thereon silver halide emulsion layers sensitive to at least two of the red, green and blue areas of the visible spectrum, preferably silver bromide emulsion layers of camera speed. The silver halide emulsion layers are black-and-white developed to silver images in areas of exposure to produce interlayer and intralayer interimage effects. Such interlayer and intralayer interimage effects are substantially enhanced in accordance with the invention by color developing residual undeveloped silver halide in the presence of photographic couplers to form nondiffusible dyes substantially complementary in color to the light sensitivity of the respective silver halide emulsion layers in an aqueous alkaline color developing composition containing a 3-alkyl-N-alkyl-N-alkoxyalkyl-p-phenylenediamine color developing agent or a 3-alkoxy-N-alkyl-N-alkoxyalkyl-p-phenylenediamine color developing agent in which the several alkyl and alkoxy groups are lower alkyl and lower alkoxy groups. These color developing agents used according to our invention include those having the formula:



wherein n is an integer of 2 to 4; R is an alkyl group having one to four carbon atoms, e.g., methyl, ethyl, propyl, butyl, etc.; and R' is an alkyl group having from one to four carbon atoms,

e.g., methyl, ethyl, propyl, butyl, etc., or an alkoxy group having from one to four carbon atoms, e.g., methoxy, ethoxy, propoxy, butoxy, etc.

The photographic couplers present during the color development step are either incorporated in the appropriately sensitized silver halide emulsion layer as nondiffusible couplers, in which case the color development of all three emulsion layers is advantageously accomplished with a single development step with one color developing solution containing a 3-alkyl-N-alkyl-N-alkoxyalkyl-p-phenylenediamine or a 3-alkoxy-N-alkyl-N-alkoxyalkyl-p-phenylenediamine color developing agent; or, diffusible couplers are used in developer solutions, for example, a diffusible cyan-dye-forming coupler is used in a cyan developing composition to color develop the red-sensitive layer, a diffusible yellow-dye-forming coupler is used in a yellow developing composition to color develop the blue-sensitive layer and a diffusible magenta-dye-forming coupler is used in a magenta developing composition to color develop the green-sensitive layer (of an element that contains no nondiffusible couplers) so that at least one of these color developing compositions contains a 3-alkyl-N-alkyl-N-alkoxyalkyl-p-phenylenediamine or a 3-alkoxy-N-alkyl-N-alkoxyalkyl-p-phenylenediamine color developing agent.

Black-and-white development is advantageously done with an aqueous alkaline composition comprising any non-dye-forming silver halide developing agent, preferably at least one of hydroquinone, p-methylaminophenol, 1-phenyl-3-pyrazolidone, 4,4-dimethyl-3-pyrazolidone, etc.

Following the black-and-white development step, the undeveloped silver halide is made developable by any appropriate means, such as, exposure to light, treatment with a chemical fogging agent, e.g., an alkali metal borohydride, an amine borane, etc., prior to or during the color development step. In processing a photographic element that requires the diffusible couplers in separate color developing solutions, the emulsion layers after black-and-white development are sequentially treated in a selective way to make residual silver halide in one emulsion layer at a time developable and then color developed before silver halide in another emulsion layer is made developable, etc. For example, in a black-and-white developed photographic film having coated in succession on a transparent support a red-sensitive emulsion, a green-sensitive emulsion, a bleachable yellow colored filter layer and a blue-sensitive emulsion layer, it is advantageous to selectively re-expose the bottom red-sensitive layer with red light through the support, cyan develop, wash, selectively re-expose the blue-sensitive layer directly with blue light, yellow develop, wash, re-expose the middle green-sensitive layer with white light or make this layer developable with a chemical fogging agent just prior to or during magenta development.

Following completion of color development of the three emulsion layers in an element, the film is washed and the silver and any residual silver halide is removed by treatment with a silver bleach followed by a fixing bath to leave the unobstructed multicolor dye image reproduction in the photographic element. Conventional alkali metal ferricyanide bleach baths and alkali metal thiosulfate fix baths are used advantageously to bleach and then fix the color developed elements.

Typical representative examples of the color developing agents of Formula I are the following:

No.	Color Developing Agent
1.	N-Ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine
2.	N-Ethyl-N-methoxybutyl-3-methyl-p-phenylenediamine
3.	N-Ethyl-N-ethoxyethyl-3-methyl-p-phenylenediamine
4.	N-Ethyl-N-methoxyethyl-3-n-propyl-p-phenylenediamine
5.	N-Ethyl-N-methoxyethyl-3-methoxy-p-phenylenediamine
6.	N-Ethyl-N-butoxyethyl-3-methyl-p-phenylenediamine

These and still other developing agents of Formula I are advantageously used as the free base or as salts of organic or inorganic acids. For example, the hydrochloric acid salts, the sulfuric acid salts, the phosphoric acid salts, the oxalic acid salts, p-toluenesulfonic acid salts, the benzene disulfonic acid salts and the naphthalene disulfonic salts are used to advantage in our process.

The color developing agents of Formula I are used advantageously in aqueous alkaline color developer solutions over a wide range of concentrations, with an operable range of from about 0.5 g/l to about 15 g/l and a preferred range of from about 1.0 g/l to about 12.0 g/l. Other addenda used to advantage in these developer compositions include alkali metal chlorides, alkali metal bromides, alkali metal iodides, alkali metal sulfites, alkali metal sulfates, alkali metal carbonates, alkali metal hydroxides, alkali metal metaborates, alkali metal phosphates, ethylenediamine, citrazinic acid, antifogging agents, e.g., 5-nitrobenzimidazole, etc., an auxiliary developing agent, e.g., 1-phenyl-3-pyrazolidone, a stabilizer for developing agents (e.g., diethyl hydroxylamine, dihydroxyacetone, glycolaldehyde, glyceraldehyde, dihydroxymaleic acid, etc., sodium hexametaphosphate, etc.), etc. A typical color developing composition used in our process for a photographic element that contains incorporated couplers is as follows:

Color Developing Composition I

Benzyl alcohol	0-12 ml.
Alkali metal hexametaphosphate	0-3 g.
Alkali metal sulfite	2-20 g.
Tri alkali metal phosphate ·12H ₂ O	10-60 g.
Alkali metal bromide	0-5 g.
Alkali metal iodide (0.1% soln.)	0-15 ml.
Color developing agent of Formula I	0.5-15 g.
Ethylenediamine sulfate	0-20 g.
Citrazinic acid	0-5 g.
Dithiooctanediol	0-5 g.
Water to	1 l.

and sufficient alkali, e.g., alkali metal hydroxide, alkali metal carbonate, etc., to adjust the pH in the range of from about 10.0 to about 14.0. The alkali metals used to advantage to make the compounds of the color developing composition are sodium, potassium, lithium, etc. Typical color developing compositions used to advantage in processes of our invention for photographic elements that do not contain couplers are as follows:

Cyan and Yellow Color Developing Compositions

Alkali metal hexametaphosphate	0-3 g.
Alkali metal sulfite	3.0-20 g.
Alkali metal bromide	0.2-5 g.
Tri alkali metal phosphate ·12H ₂ O	20.0-60 g.
Alkali metal iodide (0.1% solution)	2.0-50 g.
Color developing agent of Formula I	0.5-10 g.
Antifoggant (1% solution)	1.0-40 ml.
Alkali metal sulfate	0-70 g.
Diffusible coupler	0.5-8 g.
Hexylene glycol	0-20 ml.
Diethyl hydroxylamine (85%)	0.3-10 ml.
Competing coupler (e.g., citrazinic acid)	0-8 g.
Auxiliary developer (e.g., 1-phenyl-3-pyrazolidone)	0.1-2 g.
Alkali to produce a pH in range of	10-14
Water to	1 l.

In this composition, a phenol or naphthol cyan-die-forming coupler is used in cyan developing compositions and an open

chain acyl acetamide type yellow-dye-forming coupler is used in yellow developing compositions. Antifoggants, such as, 5-nitrobenzimidazole, 5-nitrobenzimidazole-6-nitrate, etc., are used to advantage as the antifoggant. Any of the alkalis used in photographic developer solutions are used to advantage in the color developing composition including alkali metal hydroxides, alkali metal carbonates, borax, etc. The alkali metals used to advantage to make the compounds of the cyan and yellow color developing compositions and the following magenta color developing composition are sodium, potassium and lithium.

MAGENTA COLOR DEVELOPING COMPOSITIONS

These are the same as the cyan and yellow developing compositions, except that they do not contain an auxiliary developing agent or any antifogging agent, but they do contain in addition to the components listed above:

Alkali metal thiocyanate	0.3-5 g./l.
Ethylenediamine	1.00-8 ml./l.
A chemical fogging agent for silver halide	0-2 g./l.

Chemical fogging agents used to advantage include the nucleating agents of Hanson et al., U.S. Pat. No. 3,246,987, e.g., the amine boranes (e.g., trimethylamine borane, diethylamine borane, triethylamine borane, tert-butylamine borane, pyridine borane, 2,6-lutidine borane, etc.), the polyamine boranes (e.g., ethylenediamine diborane, hydrazine diborane, etc.), a phosphine borane (e.g., dimethylphosphine borane), an arsine borane (e.g., dimethylarsine borane), a stibene borane (e.g., dimethylstibene borane), a borazine (e.g., borazine, N,N',N''-trimethyl borazine, N,N',N''-trimethoxyborazine, etc.). When no chemical fogging agent is used in the magenta color developing composition, a chemical fogging bath is advantageously used just prior to the magenta color developing composition or, alternatively, the unexposed green-sensitive silver halide emulsion layer is made developable by exposure to light. A typical chemical fogging bath has the composition:

Alkali metal hexametaphosphate	0.6 g.
Alkali metal hydroxide	2.16 g.
Chemical fogging agent for silver halide	0.10 g.
Water to make	1 l.

Any of the chemical fogging agents listed above are used advantageously in this composition.

Any of the well-known diffusible couplers used in the color developer solutions are used to color develop our photographic elements that do not contain incorporated couplers. These couplers include those described by U.S. Pat. Nos. 2,266,452, 2,295,009, 2,313,586, 2,362,598, 2,369,929, 2,772,162, 3,002,836, 2,311,082, 2,353,205, 2,369,489, 2,600,788, 2,343,703, 2,899,306, 2,115,394, 2,108,602, 2,113,330, 2,271,238, 2,289,805, 2,439,352, etc.

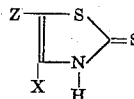
The multicolor, multilayer color photographic elements processed to advantage according to our invention are advantageously coated a wide variety of transparent film supports including cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials as well as glass. The red-, green- and blue-sensitive silver halide emulsion layers are arranged in various orders on the film supports. In a preferred element, a red-sensitized silver halide emulsion layer is advantageously coated over the support, followed in succession by a green-sensitized silver halide emulsion layer and a blue-sensitive silver halide emulsion layer. As has been mentioned before, one type of color photographic elements processed according to our invention contains a nondiffusible cyan-dye-forming coupler in the red-sensitized layer, a nondiffusible magenta-dye-forming

coupler in the green-sensitized layer and a nondiffusible yellow-dye-forming coupler in the blue-sensitive layer, while another type does not contain nondiffusible couplers incorporated in the emulsion layers. Non-sensitive hydrophilic colloid interlayers are advantageously used between one or more of the light-sensitive layers. It is advantageous to have a bleachable yellow-colored filter between the blue-sensitive and green-sensitive layers.

Any of the hydrophilic colloids used in photographic elements are advantageously used in the light-sensitive and non light-sensitive hydrophilic colloid layers of elements processed by our process. Hydrophilic colloids used alone or in combination include both naturally-occurring substances, (such as, proteins, e.g., gelatin, gelatin derivatives, etc., cellulose derivatives, polysaccharides, such as, dextrose, gum arabic and the like) and synthetic polymeric substances, such as, water-soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

Any of the ordinarily employed silver halide developing-out emulsions, e.g., silver chloride, silver chlorobromide, silver chlorobromiodide, silver bromide, silver bromiodide developing-out emulsions are used to advantage in elements processed according to our invention. Particularly useful results are obtained with mixed silver halide emulsions comprising an iodide, e.g., silver bromiodide, silver chlorobromiodide, silver chloriodide, etc., containing mixed silver halide crystals wherein the iodide comprises about 1 to about 20 mole percent of the halide of the mixed silver halide crystals. It is particularly advantageous in photographic elements where interimage effects are desired to have at least one silver halide emulsion layer with mixed crystals having at least 1 mole percent more iodide than any mixed silver halide crystals in at least one of the other silver halide emulsion layers; however, any silver halide emulsion can be used provided the emulsion in at least one layer differs from the emulsion in at least one other layer as to development rate and/or excess of halide in the silver halide.

In addition to, or instead of, the differences in the silver halide emulsion discussed above, certain addenda are advantageously used in one or more of the silver halide emulsion layers to cause interlayer and intralayer interimage effects driving the black-and-white development. For example, diffusible 3-hydrogen substituted 4-thiazoline-2-thiones including those of formula:



wherein X represents alkyl, e.g., methyl or ethyl, an alkyl substituent containing at least one hydroxyl group, e.g., hydroxymethyl, β -hydroxyethyl, gluco or arabino, or an alkyl substituent having at least one carbonyl-containing group, e.g., formyl, carboxyl, ethoxy carbonyl or acetoxy methyl; and Z is independently selected from a value given for X and preferably represents hydrogen. Advantageously, the 4-thiazoline-2-thione compound is one which can enolize to its corresponding mercaptan form at any suitable time, such as, when the 4-thiazoline-2-thione is added to a hydrophilic colloid layer containing light-sensitive silver halide. Representative compounds include 4-thiazoline-4-carboxaldehyde-2-thione, 5-carbomethoxy-4-methyl-4-thiazoline-2-thione, 4-carboxy-4-thiazoline-2-thione, 4-carboxy-5-methyl-4-thiazoline-2-thione, 4-(D-arabino-tetraacetoxybutyl)-4-thiazoline-2-thione, 4-(D-arabino-1,2,3,4-tetrahydroxybutyl)-4-thiazoline-2-thione, 4-hydroxymethyl-4-thiazoline-2-thione, 4-methyl-4-thiazoline-2-thione. These compounds when in solution diffuse through hydrophilic colloid layer of a photographic element in which they are incorporated or to which they are applied in a processing solution prior to silver image development or in the silver image developer itself. These compounds form an immobile complex with silver halide in the emulsion layers and are released from silver halide grains as they are

developed to silver. It is believed that the image-wise release of these compounds during the development of silver halide in one layer inhibits latent image silver halide development in adjacent layers, thus causing "undercut" interimage effects. Undercut interimage effects are characterized by repression of a given color scale produced by a neutral exposure, and the lack of such repression for that color scale in a single color exposure. Undercut interimage effects result in more saturated and brighter dye images and are advantageously measured by procedures described in articles such as by Hanson and Horton, *Journal of the Optical Society of America*, 42, No. 9, pp. 663 - 669, September 1952 and Pinney, "Interimage Effects and Color Reproduction," "The SPSE Reporter," November 1960.

The 3-hydrogen substituted 4-thiazoline-2-thiones are advantageously incorporated in silver halide emulsion layers in the range of from about 5.0 mg to about 500 mg of the addenda per mole of silver and especially in the range of from 100 mg to 200 mg. When the 3-hydrogen substituted 4-thiazoline-2-thione is introduced into the emulsion in a solution such as a black-and-white developer solution during photographic processing, a useful concentration range is from about 0.1 mg to about 1.0 g per liter of solution and, preferably, in the range from about 1.0 mg to 500mg per liter.

Interimage effects produced by any known method during the black-and-white development are enhanced during the color development of our process.

The silver halide emulsions used in elements processed according to our invention are advantageously spectrally sensitized with any of the appropriate cyanines, merocyanines, complex cyanines, complex merocyanines, styryls, hemicyanines, etc. These dyes contain the usual basic nuclei, e.g., thiazole, benzothiazole, naphthothiazole, benzoxazole, naphthoxazole, benzoselenazole, naphthoselenazole, quinoline, etc., or in the case of merocyanine dyes, an acidic nucleus, e.g., hydantoin, 2-thiohydantoin, oxazolidone, pyrazolone, etc. Such dyes are described in the Brooker et al. U.S. Pat. Nos. 2,185,182, 2,241,237; Carroll U.S. Pat. Nos. 2,635,961, 2,652,330; Heseltine and Brooker U.S. Pat. No. 2,666,761; Carroll and Jones U.S. Pat. No. 2,704,715; Brooker and White U.S. Patent No. 2,526,632; Sprague U.S. Pat. No. 2,503,776; Brooker et al. U.S. Pat. No. 2,493,748 and Taber et al., U.S. Pat. No. 3,384,486.

Photographic silver halide emulsions, such as those listed above, can also contain such addenda as chemical sensitizers, e.g., sulfur sensitizers (e.g., allyl thiocarbamide, thiourea, allylthiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.) (see Baldsiefen, U.S. Pat. No. 2,540,685; Damschroder, U.S. Pat. No. 2,597,856 and Yutzy and Leermakers, U.S. Pat. No. 2,597,915), various palladium compounds, such as, palladium chloride (Baldsiefen et al., U.S. Pat. No. 2,540,096), potassium chloropalladate (Stauffer et al. U.S. Pat. No. 2,598,079), etc., or mixtures of such sensitizers; antifoggants, such as, ammonium chloroplatinate (Trivelli and Smith, U.S. Pat. No. 2,566,245), ammonium chloroplatinitite (Trivelli and Smith, U.S. Pat. No. 2,566,263), benzotriazole, nitrobenzimidazole, 5-nitroindazole, benzidine, mercaptans, etc. (see Mees, "The Theory of the Photographic Process," Macmillan Pub., 1942, p. 460), or mixtures thereof; hardeners, such as, formaldehyde or chrome alum (Miller U.S. Pat. No. 1,763,533), glyoxal (Brunken, U.S. Pat. No. 1,870,354), dibromacrolein (Bloch et al. British Pat. No. 406,750), aziridine hardeners of Burness, U.S. Pat. No. 2,964,404; Allen et al., U.S. Pat. No. 2,950,197; Yudelson, U.S. Pat. No. 3,017,280, oxazolium hardeners of VanCampen et al., U.S. Pat. No. 3,316,095, Burness et al., U.S. Pat. No. 3,321,313, vinyl sulfone hardener of Belgian Pat. No. 686,440, etc.

Any of the color-forming couplers used in photographic elements are used to advantage in photographic materials for our process. Included among the phenol and naphthol cyan dye-forming couplers used to advantage are those described by the

following U.S. Pat. Nos. 2,423,730, 2,474,293, 2,521,908, 2,725,291, 2,801,171, 3,253,294, etc. Included among the ketomethylene yellow-dye-forming couplers used to advantage are those described in U.S. Pat. Nos. 2,298,443, 2,778,658, 2,801,171, 2,875,057, 3,253,924, 3,277,155, etc. Included among the 5-pyrazolone magenta dye-forming couplers used to advantage are those described in U.S. Pat. Nos. 2,600,788, 2,801,171, 3,252,924, etc.

Dispersing agents for color-forming couplers and the dispersing techniques used to advantage include those set forth in Jelley et al., U.S. Pat. No. 2,322,027; Mannes et al., U.S. Pat. No. 2,304,940; Fierke et al., U.S. Pat. No. 2,801,171, etc.

In general, the color developing agents of Formula I are prepared by reacting the appropriate ω -alkoxyalkyl chloride or bromide with the appropriate N-ethyl-3-alkylaniline or N-ethyl-3-alkoxyaniline. The tertiary anilines formed by this reaction are then either nitrosated or azo-coupled, followed by catalytic hydrogenation to give the corresponding p-phenylenediamines. Some of the developing agents of Formula I are advantageously isolated as the acid salts.

The di-p-toluenesulfonic acid salt of Color Developing Agent 3 is advantageously prepared by the following sequence of reactions:

(I) N-(β -Ethoxyethyl)-N-ethyl-3-methylaniline: A mixture of 135 g (1 mole) of N-ethyl-3-methylaniline, 153 g (1 mole) of 2-bromoethyl ethyl ether (purified by treatment with sodium bicarbonate and distillation), 88.2 g (1.05 mole) of sodium bicarbonate, 1,100 ml of ethanol and 290 ml of water are refluxed for a total of 64 hours. The ethanol is removed by distillation and the oil layer is extracted with ether; the ether extracts are dried and concentrated, followed by distillation of the residual oil under reduced pressure. After removal of the lower boiling foreruns, the fraction, b.p. 92°-95° C/1mm (overheats readily), is collected. The yield of I is approximately 70 percent.

(II) 4-(2,5-Dichlorophenylazo)-N-(β -ethoxyethyl)-N-ethyl-3-methylaniline: A total of 44 g (0.27 mole) of 2,5-dichloroaniline is dissolved in a mixture of 240 ml concentrated hydrochloric acid and 700 ml of water by heating with stirring on a steam bath. When solution is complete, the reaction mixture is cooled with stirring to 5° C, the hydrochloride salt precipitating out. A solution of 19 g (0.275 mole) of sodium nitrite in 75 ml of water is added dropwise with stirring, keeping the temperature at about 5° C. When complete, stirring is continued for another 20 minutes and the excess nitrous acid destroyed by the addition of sulfamic acid. The cold diazonium solution is filtered and at once added to a cold solution of 56 g (0.27 mole) of I in dilute hydrochloric acid. Considerably more water is added and with stirring a total of 250 g of sodium acetate is added to promote the coupling. After standing for a few hours, the azo dye is filtered off and at once recrystallized from approximately 1,000 ml of ethanol. This is followed by a second recrystallization from 900 ml of ethanol, filtering hot and cooling to about 25° C. The yield of II, m.p. 74.5° - 75.5° C, is 77 percent.

4-Amino-N-(β -ethoxyethyl)-N-ethyl-3-methylaniline, di-p-toluenesulfonic acid salt (Developing Agent 3): Three grams of the azo dye, II, is reduced on a Parr shaker using 300 ml of absolute alcohol and Raney nickel as catalyst. When complete, the catalyst is filtered off and washed on funnel with more ethanol. A solution of 3 g (0.0158 mole) of p-toluenesulfonic acid (hydrate) in 50 ml ethanol is added and the solution is then concentrated to dryness (partial vacuum). The semisolid is then slurried thoroughly with 35 ml of hot isopropyl alcohol, gradually becoming nicely crystalline. The mixture is cooled to about 25° C and allowed to stand undisturbed overnight. The developer salt is filtered off and washed in funnel with small portions of isopropyl alcohol. The yield of Developing Agent 3, m.p. 214°-216° C, is approximately 70 percent.

The di-p-toluenesulfonic acid salt of Color Developing Agent 5 is advantageously prepared similarly to developing agent (3), using N-ethyl-3-methoxyaniline and 2-bromoethyl methyl ether as starting materials.

(III) N-Ethyl-3-methoxy-N-(β -methoxyethyl)-aniline: A mixture of 100 g (0.661 mole) of N-ethyl-3-methoxyaniline, 92 g (0.661 mole) of 2-bromoethyl methyl ether, 55.8 g (0.6665 mole) of sodium bicarbonate, 1,000 ml of ethanol and 280 ml of water is refluxed for a total of 68 hours. The alcohol is removed under partial vacuum and the oil layer extracted with ether; the ether extracts are dried and concentrated. The residual oil is then distilled under reduced pressure. The yield of III, b.p. 149°–151° C/8mm, is 35 percent.

(IV) 4-(2,5-Dichlorophenylazo)-N-ethyl-3-methoxy-N-(β -methoxyethyl)aniline: This azo dye is prepared from III in exactly the same way as described for the preparation of the azo dye used for developing agent (3). The yield of IV, m.p. 94°–96° C (from ethanol), is approximately 73 percent.

The di-p-toluenesulfonic acid salt of 4-amino-N-ethyl-3-methoxy-N-(β -methoxyethyl)aniline Developing Agent 5): Exactly 4.86 g (0.127 mole) of the azo dye, IV, is reduced on Parr shaker, using 300 ml of absolute alcohol and Raney nickel as catalyst. When complete, the catalyst is filtered off, washed on funnel with more alcohol. A total of 4.84 g (0.0254 mole) of p-toluenesulfonic acid (hydrate) in 50 ml of ethanol is added; no precipitate occurs and the solution is concentrated to dryness under partial vacuum. The gummy residue is then dissolved in a small quantity of absolute alcohol and a large excess of ethyl ether is added; the developer salt again comes out as a gum; the solution is cooled thoroughly (refrigerator) to precipitate the suspension and then the ether-alcohol layer is decanted. This treatment is repeated twice more to remove all of the regenerated 2,5-dichloroaniline. Finally, the developer salt is slurried thoroughly with ether only, gradually becoming crystalline; it is dried in a vacuum oven. The yield of Developing Agent 5, m.p. 160°–162° C, is 62 percent.

The di-p-toluenesulfonic acid salt of Color Developing Agent 1 is made in a manner similar to the synthesis described for the corresponding acid salt of Color Developing Agent 5, excepting that an equimolar amount of N-ethyl-3-methylaniline is used in place of N-ethyl-3-methoxyaniline.

The di-p-toluenesulfonic acid salt of Color Developing Agent 2 is made in a manner similar to the synthesis described for the corresponding acid salt of Color Developing Agent 5, excepting that an equimolar amount of ω -bromobutyl methyl ether is used in place of 2-bromoethyl methyl ether.

The di-p-toluenesulfonic acid salt of Color Developing Agent 4 is advantageously made in a manner similar to that described for the corresponding acid salt of Color Developing Agent 3, excepting that an equimolar amount of N-ethyl-3-propylaniline is used in place of N-ethyl-3-methylaniline.

Still other color developing agents of Formula I are made using the syntheses illustrated herein using the appropriate intermediates.

The following examples are included for a further understanding of our invention:

Example 1

Two samples of a multilayer color film having a cellulose acetate film support coated in succession with a red-sensitive gelatino silver bromiodide emulsion layer, a green-sensitive gelatino silver bromiodide emulsion layer, a gelatin layer containing bleachable yellow colored Carey Lea silver and a blue-sensitive gelatino silver bromiodide emulsion layer are sensitometrically exposed to a step tablet and processed at 27° C through the following process sequence:

Treatment Step	Time
Prehardener	2 min.
Water wash	30 sec.
MQ developing composition	3 min. 40 sec.
Water wash	1 min.
Red light exposed through support	
Cyan developing composition	4 min. 30 sec.
Water wash	2 min.
Blue light exposed through emulsion	
Yellow developing composition	4 min.
Water wash	2 min.

Borohydride bath	1 min.
Water wash	30 sec.
Magenta developing composition	5 min. 30 sec.
Water wash	4 min.
Ferricyanide bleach	2 min.
Hypo fix bath	2 min.
Water wash	4 min.
Dry	

10 The solutions used have the compositions given below:

Prehardener	
Sodium hexametaphosphate	0.5 g.
Sulfuric acid	1.7 ml.
Sodium tetraborate $\cdot 5H_2O$	15.0 g.
Sodium bromide	2.0 g.
Sodium sulfate	200.0 g.
Formalin (37.5%)	20.0 ml.
Sodium bisulfite	1.0 g.
Water to make	1 liter

MQ Negative Developing Composition	
Sodium hexametaphosphate	0.6 g.
Sodium sulfite	79.0 g.
Monomethyl-p-aminophenol sulfate	5.0 g.
Sodium hydroxide	1.0 g.
Hydroquinone	2.0 g.
Sodium carbonate	35.0 g.
Potassium iodide (0.1%)	12.5 ml.
Sodium bromide	3.0 g.
Sodium thiocyanate	1.7 g.
Hydroquinone monosulfate	4.0 g.
Water to make	1 liter

Cyan Developing Composition	
Sodium hexametaphosphate	0.6 g.
Sodium bromide	2.5 g.
5-Nitrobenzimidazole nitrate (1% in 0.1% NaOH)	3.0 ml.
Potassium iodide (0.1%)	11.0 ml.
Sodium sulfite	10.0 g.
Sodium sulfate	60.0 g.
Sodium hydroxide	3.8 g.
Sodium thiocyanate	1.0 g.
Hydroxylamine sulfate	0.65 g.
4-Amino-N-ethyl-N- β -hydroxyethyl-3-methyl aniline sulfate	2.05 g.
1-Hydroxy-N-(2-acetamidophenethyl)-2-naphthamide	1.65 g.
Hexylene glycol	5.0 ml.
Polyoxyethylene (m.wt. 1540)	1.0 g.
N-Benzyl-p-aminophenol	0.45 g.
Methanol	2.0 ml.
p-Aminophenol	0.16 g.
Water to make	1 liter

Yellow Developing Composition	
Sodium hexametaphosphate	0.6 g.
Sodium sulfite	10.0 g.
Sodium bromide	0.55 g.
Polyoxyethylene (m.wt. 4000)	1.00 g.
Potassium iodide (0.1% soln.)	26.0 ml.
Color developing agent	
5-Nitrobenzimidazole (1% soln.)	10.0 ml.
Sodium hydroxide	2.1 g.
Sodium sulfate	64.0 g.
Hexylene glycol	10.0 ml.
An α -pivalyl-acetanilide)	
Yellow dye-forming coupler)	2.0 g.
Diethyl hydroxylamine	1.38 ml.
1-Phenyl-5-pyrazolidone	0.5 g.
Water to make	1 liter
pH at 27° C.=12.0	

65 Film Sample I is yellow developed in the yellow developing composition having 1.06 g/l of Color Developing Agent B, i.e., N-ethyl-N-(β -hydroxyethyl)-3-methyl-p-phenylenediamine and Film Sample II is yellow developed in the yellow developing composition having 2.0 g/l of Color Developing Agent 1, i.e., N-ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine.

Borohydride Bath	
Sodium hexametaphosphate	0.6 g.
Sodium hydroxide	2.16 g.
Potassium borohydride	0.10 g.
Water to make	1 liter

Magenta Developing Composition

Sodium hexametaphosphate	4.0 g.
Sulfuric acid	2.1 ml.
Sodium phosphate · 12H ₂ O	40.0 g.
Sodium sulfite	5.0 g.
Sodium thiocyanate	1.0 g.
Potassium iodide (0.1%)	7.5 ml.
Sodium bromide	0.5 g.
Sodium sulfate	60.0 g.
4-Amino-N-ethyl-N-β-hydroxyethyl-3-methylaniline sulfate	2.9 g.
Citrazinic acid	0.72 g.
Ethylenediamine	3.0 ml.
Polyoxyethylene (m. wt. 4000)	1.0 g.
Hexylene glycol	10.0 ml.
A 5-pyrazolone coupler of U.S. Pat. No. 3,152,896	1.67 g.
Sodium hydroxide	0.32 g.
Water to make	1 liter

The bleach solution is a conventional alkali metal bromide and alkali metal ferricyanide bleach, and the hypo-fix a conventional alkali metal thiosulfate fixing bath. A comparison of processed Film Sample I given the prior art process with Film Sample II given our process shows that our process produces better color reproductions of the original step tablet than the prior art process with brighter blue images.

Example 2

Example 1 is repeated, but comparing the prior art process used in Example 1 against each of five of our processes in which Color Developing Agents 2, 3, 4, 5 and 6, respectively, are substituted in equimolar amounts for Color Developing Agent 1 in the yellow developing composition. In each instance, our processes produce color reproductions that are superior to the reproduction produced by the prior art process with brighter blue images.

Example 3

Two samples, I and II, of a multilayer, multicolor photographic element which element produces an interimage effect comprising a cellulose acetate film support coated in succession with a red-sensitive gelatino silver bromoiodide emulsion layer (with 6 mole percent iodide) containing a mixture of nondiffusible cyan dye-forming couplers, i.e., a naphthamide coupler of U.S. Pat. No. 2,474,293 and a phenol coupler of U.S. Pat. No. 2,895,826, a green-sensitive gelatino silver bromoiodide emulsion layer (with 6 mole percent iodide) containing a nondiffusible 5-pyrazolone magenta dye-forming coupler of U.S. Pat. No. 2,908,573 and a blue-sensitive gelatino silver bromoiodide emulsion layer (with 6 mole percent iodide) containing a nondiffusible α-pivalyl-α-phenoxyacetanilide yellow dye-forming coupler of U.S. Pat. No. 3,408,194 are sensitometrically exposed. Sample I of the exposed film is processed at 38° C through the prior art process described in Example 2 of Henn et al. U.S. Pat. No. 2,984,567, but using in place of the reference color developing solution, a solution having the composition:

Sodium sulfite	2.9 g.
Trisodium phosphate · 12H ₂ O	36.0 g.
N-ethyl-N-(β-methanesulfonamidoethyl)-3-methyl-p-phenylenediamine	10.5 g.
Citrazinic acid	1.35 g.
Dithiooctanediol	1.00 g.
Water to pH	11.25

Sample II of the exposed film is processed through our process which is the same as the process used for Sample I, excepting that the 10.5 g/l of N-ethyl-N-(β-methylsulfonamidoethyl)-3-methyl-p-phenylenediamine is replaced by 14 g/l of N-ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine. The Dmax values determined for the processed films are summarized in the following table.

TABLE 6

Process	Cyan Dye	Yellow Dye	Magenta Dye
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	2.9	2.4	3.2
Prior art	2.9	2.4	3.2
Our process	3.3	2.7	3.6

The results show that our process produces higher Dmax than the prior art process for each of the image dyes.

Example 4

Two samples, III and IV, of the multilayer, multicolor element described in Example 3 are each given an exposure that is used to check for interimage effects. The exposure comprises a stepped exposure to red light, superimposed by a stepped exposure to blue light and a flash to green light. Exposed Sample III is given the prior art process described in Example 3 for Sample I and exposed Sample IV is given our process described in Example 3 for Sample II. A comparison of the density vs. exposure curves plotted for the processed films shows that the unwanted green light absorption in the cyan and yellow dye images is corrected in Sample IV with our process while the unwanted light absorptions are undercorrected by a considerable amount in Sample III with the prior art process.

Example 5

A multilayer, multicolor photographic element like the element described in Example 3, except that a nondiffusible phenol cyan-dye-forming coupler of U.S. Pat. No. 2,423,730 is used in the red-sensitive layer and a nondiffusible α-acetylacetamide yellow-dye-forming coupler is used in the blue-sensitive layer in place of the cyan couplers and the yellow coupler used in Example 3, is made. Samples I and II of this element are exposed as described in Example 4. Exposed Samples I and II are processed with the prior art process and with our process, each as described in Example 3. A comparison of the density vs. exposure curves plotted for the processed films shows that the unwanted green light absorption in the cyan and yellow dye images is corrected by enhancement with our process of the interimage effect while the unwanted light absorptions are undercorrected by a considerably amount with the prior art process.

Example 6

Four samples, identified as V, VI, VII and VIII, of the multilayer, multicolor photographic element described in Example 3 are sensitometrically exposed to a step tablet and processed. Samples V and VI are processed in the prior art process described in Example 3 with the color developing solution pH adjusted at 10.4 for Sample V and adjusted at 11.6 for Sample VI. Samples VII and VIII are processed in our process described in Example 3 with the color developer pH adjusted at 10.4 for Sample VII and at 11.6 for Sample VIII. The change in developed cyan dye density, caused by increasing the pH of the color developer from 10.4 to 11.6 at an exposure level that gives a cyan density between 1 and 2 at a pH of 10.4, is determined for each process. This is repeated for the developed yellow dye and the developed magenta dye. The results are summarized in the following table.

TABLE 7

Dye	Prior Art Process	Our Process
Cyan	+0.30	+0.12
Magenta	-0.25	-0.12
Yellow	+0.43	+0.14

The results show that over the pH range tested, our process produces less dye density change at a given exposure level and is, therefore, less pH-sensitive than the prior art process.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

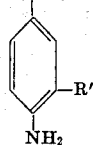
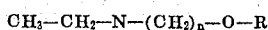
1. In a color photographic process for treating an image-wise exposed multicolor photographic element comprising a transparent film support having coated thereon silver halide emulsion layers sensitive to at least two of the red, green and blue areas of the visible spectrum and black-and-white developing said silver halide emulsion layers to silver images in areas of exposure to produce interimage effects, the improvement which comprises enhancing said interimage effects by color developing resulting undeveloped silver halide in the presence of photographic couplers to form nondiffusible dyes substantially complementary to the sensitivity of the respective silver halide emulsion layers in an aqueous alkaline color developing composition containing a color developing agent selected from the group consisting of a 3-alkyl-N-alkyl-N-alkoxyalkyl-p-phenylenediamine and a 3-alkoxy-N-alkyl-N-alkoxyalkyl-p-phenylenediamine.

2. The process of claim 1 wherein the silver halide emulsions are silver bromiodide emulsions.

3. The process of claim 1 wherein nondiffusible cyan, magenta and yellow-forming photographic couplers are incorporated in the red, green and blue-sensitive silver halide emulsion layers, respectively.

4. The process of claim 1 wherein the black-and-white developing is carried out with an aqueous alkaline developing composition containing at least one developing agent selected from the class consisting of hydroquinone, p-methylaminophenol, 1-phenyl-3-pyrazolidone and 4,4-dimethyl-1-phenyl-3-pyrazolidone.

5. In a color photographic process for treating an image-wise exposed multicolor, multilayer photographic element comprising a transparent film support having coated thereon red, green and blue-sensitive silver bromiodide emulsion layers and black-and-white developing said silver bromiodide emulsion layers to silver images in areas of exposure to produce interimage effects, the improvement which comprises (1) making residual unexposed and undeveloped silver bromiodide developable and (2) thereafter enhancing said interimage effects by color developing said undeveloped silver bromiodide in the presence of photographic couplers to form nondiffusible dyes substantially complementary to the sensitivity of the respective silver bromiodide emulsion layers in an aqueous alkaline color developing composition containing a color developing agent having the formula:



wherein n is an integer of 2 to 4; R is an alkyl group having one to four carbon atoms, and R' is an alkyl group having one to four carbon atoms or an alkoxy group having one to four carbon atoms.

6. The process of claim 1 wherein said light-sensitive layers of said black-and-white developed photographic element are sequentially treated to make residual undeveloped silver halide in one layer at a time developable and then before silver halide in another layer is made developable, color develop said layer initially made developable with an aqueous alkaline color developing composition containing a color developing agent and a diffusible color-forming coupler which reacts with oxidized color developing agent to form a nondiffusible dye, said process after the black-and-white development comprising:

1. selectively treating said red-sensitive layer to make residual undeveloped silver halide developable,

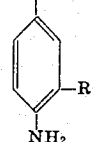
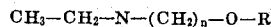
2. treating said element with an aqueous alkaline cyan color developing composition containing a diffusible cyan-dye-forming coupler and an aromatic primary amine color developing agent which develops said developable silver halide in said red-sensitive layer to a silver image and a corresponding image-wise pattern of oxidized color developing agent which reacts with said cyan-dye-forming coupler to form a corresponding nondiffusible cyan dye image,

3. selectively treating said blue-sensitive layer to make residual undeveloped silver halide developable,

4. treating said element with an aqueous alkaline yellow color developing composition containing a diffusible yellow-dye-forming coupler and an aromatic primary amine color developing agent which develops said developable silver halide in said blue-sensitive layer to a silver image and a corresponding image-wise pattern of oxidized color developing agent which reacts with said yellow-dye-forming coupler to form a corresponding nondiffusible yellow dye image,

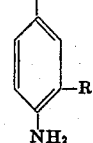
5. selectively treating said green-sensitive layer to make residual undeveloped silver halide developable,

6. treating said element with an aqueous alkaline magenta color developing composition containing a diffusible magenta-dye-forming coupler and an aromatic primary amine color developing agent which develops said developable silver halide in said green-sensitive layer to a silver image and a corresponding image-wise pattern of oxidized color developing agent which reacts with said magenta-dye-forming coupler to form a corresponding nondiffusible magenta dye image, such that at least one of said color developing compositions contains as the color developing agent a compound having the formula:



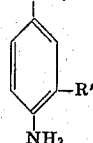
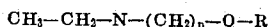
wherein n is an integer of 2 to 4; R is an alkyl group having one to four carbon atoms, and R' is an alkyl group having one to four carbon atoms or an alkoxy group having one to four carbon atoms.

7. The process of claim 6 in which said yellow color developing composition contains a diffusible acylacetanilide yellow-dye-forming coupler and a color developing agent selected from those having the formula:



wherein n is an integer of 2 to 4; R is an alkyl group having one to four carbon atoms, and R' is an alkyl group having one to four carbon atoms or an alkoxy group having one to four carbon atoms.

8. The process of claim 6 in which said yellow color developing composition contains a diffusible α -pivalyl acetanilide yellow-dye-forming coupler and a color developing agent selected from those having the formula:



9. The process of claim 6 in which said yellow color developing composition contains a diffusible acylacetanilide yellow-dye-forming coupler and a color developing agent selected from the class consisting of N-ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine, N-ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine, N-ethyl-N-ethoxyethyl-3-methyl-p-phenylenediamine, N-ethyl-N-methoxyethyl-3-propyl-p-phenylenediamine, N-ethyl-N-methoxyethyl-3-methoxy-p-phenylenediamine and N-ethyl-N-butoxyethyl-3-methyl-p-phenylenediamine.

10. The process of claim 6 in which said yellow color developing composition contains a diffusible acylacetanilide yellow-dye-forming coupler and N-ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine.

11. The process of claim 6 in which said yellow color developing composition contains a diffusible acylacetanilide yellow-dye-forming coupler and N-ethyl-N-methoxyethyl-3-methoxy-p-phenylenediamine.

12. The process of claim 6 wherein nondiffusible cyan, magenta and yellow-forming photographic couplers are incorporated in the red, green and blue-sensitive silver bromiodide emulsion layers, respectively, and said cyan coupler is selected from the class consisting of a phenol and a naphthol; said magenta coupler is a 5-pyrazolone coupler and said yellow coupler is an acylacetamide.

13. The process of claim 5 wherein at least one of said silver bromiodide emulsion layers contains at least 1 mole percent more iodide than at least one of the other silver bromiodide emulsion layers.

14. The process of claim 5 wherein said silver bromiodide emulsion layers contain in the range of from about 1 to 20 mole percent iodide and at least one of said silver bromiodide emulsion layers contains at least one mole percent more iodide than at least one of the other silver bromiodide emulsion layers.

15. The process of claim 5 wherein said silver images are formed in the black-and-white development step in the presence of a diffusible 4-thiazoline-2-thione, whereby interimage effects are obtained.

16. The process of claim 5 wherein the color developing agent is selected from the group consisting of:

- N-Ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine,
- N-Ethyl-N-methoxybutyl-3-methyl-p-phenylenediamine,
- N-Ethyl-N-ethoxyethyl-3-methyl-p-phenylenediamine,
- N-Ethyl-N-methoxyethyl-3-n-propyl-p-phenylenediamine,
- N-Ethyl-N-methoxyethyl-3-methoxy-p-phenylenediamine
- and
- N-Ethyl-N-butoxyethyl-3-methyl-p-phenylenediamine.

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Disclaimer

3,658,525.—*Richard L. Bent* and *Rowland G. Mowrey*, Rochester, N.Y.
REVERSAL COLOR PHOTOGRAPHIC PROCESSES. Patent
dated Apr. 25, 1972. Disclaimer filed Oct. 15, 1974, by the assignee,
Eastman Kodak Company.

Hereby disclaims the entire remaining term of said patent.

[*Official Gazette April 8, 1975.*]