

United States Patent

Bent et al.

[15] 3,656,950

[45] Apr. 18, 1972

[54] COLOR PHOTOGRAPHIC PROCESSES

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[22] Filed: **Dec. 3, 1970**

[21] Appl. No.: **94,993**

[52] U.S. Cl. **96/22, 96/55, 96/66 R**
260/577

[51] Int. Cl. **G03c 7/30, G03c 7/32, C07c 87/58**

[58] Field of Search..... **96/22, 55, 66 R**

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[57] ABSTRACT

Color development processes with aqueous alkaline color developing compositions 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 are advantageously used to produce good color reproductions with image dyes of superior stability to prolonged exposure to heat, humidity and/or light in multilayer, multicolor photographic elements coated on opaque supports and containing 65 mg to 375 mg of silver chlorobromide per m² in at least the red-sensitive layer and the green-sensitive layer.

9 Claims, No Drawings

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 which couples with color-producing coupler compounds present to produce a dye image-wise with respect to silver development.

Color development processes use active aromatic primary amino dye 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 also desired which produce dye, images having better stability to prolonged exposure to heat, light and high humidities.

It is, therefore, an object of our invention to provide a novel color development process which develops substantially all silver halide grains containing latent images and leaves substantially no "dead grains."

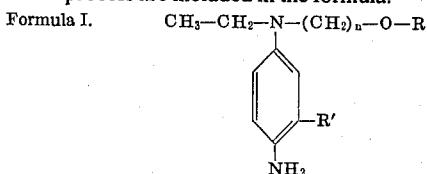
Another object of our invention is to provide a novel color development process which not only develops substantially all silver halide grains containing latent image centers, but produces a higher developed dye to silver ratio than is produced by prior art color processes.

Another object of our invention is to provide a novel color development process which gives good color reproduction with color photographic elements containing in the range of from about 65 to about 375 mg/m² of red-sensitized silver halide, in the range of from about 65 to about 375 mg/m² of green-sensitized silver halide and in the range of from about 120 to about 375 mg/m² of blue-sensitive silver halide.

Another object of our invention is to provide a novel color development process which produces dye images having improved stability to prolonged exposure to heat, elevated humidities and/or light.

Still other objects of our invention will be apparent from the following specification and claims.

The above and still other objects are accomplished by use of our color photographic processes for treating an image-wise exposed multicolor reflection photographic element comprising an opaque support having coated thereon red, green and blue-sensitive silver halide emulsion layers containing nondiffusible cyan, magenta and yellow-forming photographic couplers which react with oxidized aromatic primary amine color developing agents to form nondiffusible dyes with at least the red-sensitive layer and the green-sensitive layer being coated at silver halide coverages in the range of from about 65 mg/m² to about 375 mg/m², and particularly in the range from about 89 mg/m² to about 320 mg/m², which process comprises image-wise color developing the exposed element by contacting it with an aqueous alkaline color developing composition containing either a 3-alkyl-N-alkoxyalkyl-p-phenylenediamine or a 3-alkoxy-N-alkoxyalkyl-p-phenylenediamine color developing agent. These color developing agents used to advantage in our process are included in 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.

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

COLOR DEVELOPING AGENT

No.

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 inorganic or organic acids. For example, the hydrochloric acid salts, the sulfuric acid salts, the phosphoric acid salts, the oxalic acid salts, the p-toluenesulfonic acid salts, the benzene disulfonic acid salts and the naphthalene disulfonic acid salts are used to advantage in our process.

The color developing agents of Formula I are used advantageously in aqueous alkaline color developing composition 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 10.0 g/l. Other addenda used to advantage in these developing compositions include benzyl alcohol, alkali metal chlorides, alkali metal bromides, alkali metal sulfites, alkali metal salts of weak acids (e.g., carbonates, borates, phosphates, etc.) and any other salts capable of buffering in the range of from about 9 to about 13, stabilizers for color developing agents (e.g., hydroxylamine sulfate, dihydroxyacetone, glycolaldehyde, glyceraldehyde, dihydroxymaleic acid, etc.), water softeners (e.g., sodium hexametaphosphate, etc.), etc. A typical color developing composition used in our process is as follows:

Benzyl alcohol	0-15.0 ml/l
Alkali metal chloride (e.g., KCl & NaCl)	0-15.0 g/l
Alkali metal bromide (e.g., KBr & NaBr)	0.1-1.0 g/l
Stabilizing agent for color developer (e.g., hydroxylamine sulfate & dihydroxyacetone)	
Alkali metal sulfite (e.g., Na ₂ SO ₃ & K ₂ SO ₃)	0.1-5.0 g/l
Color developing agent of Formula I	0.1-5.0 g/l
Alkali metal salt of a weak acid or any other salt capable of buffering in the range of from about 9. to about 13.	1.0-10.0 g/l
pH	10.0-50.0 g/l 9.0-13.0

The process of our invention comprises treating latent image exposed multicolor reflection photographic elements with an aqueous alkaline color developing composition, as described herein previously, and containing either a 3-alkyl-N-alkoxyalkyl-p-phenylenediamine or a 3-alkoxy-N-alkoxyalkyl-p-phenylenediamine color developing agent, especially as defined by Formula I until substantially all of the silver halide grains containing latent image sites are developed to silver and the oxidized developing agent has reacted with the color-forming coupler in the layer containing the developed silver to form the corresponding nondiffusible dye image. In this treatment step, the photographic element is contacted with the developer solution which is advantageously at a temperature in the range of from about 15° C to about 40° C. The optimum development time depends upon the particular element, the particular developer solution, temperature

and other factors and is easily determined by methods well-known in the art. Treatment with the aqueous developing composition is advantageously accomplished by any of the methods conventionally used including immersion of the element in a tank of the developer, contacting and coating the element with a film of developer transferred to the element with any appropriate means, such as, roller applicator, coating hopper, etc.

Following the color development step, the color developed element is treated to convert silver to a silver salt with a bleach and then remove the silver salts from the element with a fixing bath or, alternatively, combining these steps into a single bleach-fix step. The element is advantageously given a stabilizing step at the end of the process just prior to drying. In one process sequence for doing this, the color developed element is treated with the following steps: a stop-fix, wash, bleach, wash, harden-fix, wash and stabilize. In another process sequence, the color developed element is bleach-fixed, bleached, washed and stabilized as described in Bard et al., U.S. Pat. No. 3,189,452, or using the same sequence but leaving out the bleach step, provided that the element does not contain any aldehyde hardeners and uses a yellow coupler which does not form a leuco dye. In these processes, the stop-fix, bleach, hardener-fix and stabilizer compositions described by Van Campen, U.S. Pat. No. 2,596,879 in columns 5 and 6, are used to advantage. Any of the well-known bleach-fix baths, including those described by Bard et al., U.S. Pat. No. 3,189,452 in columns 2, 3, 7 and 9, are used to advantage.

Any multicolor reflection photographic elements are used to advantage in our process. These elements are usually coated on an opaque support, such as, paper, pigmented film supports, including pigmented cellulose nitrate film, pigmented cellulose ester film, pigmented poly(vinyl acetal) film pigmented polystyrene film, pigmented poly(ethylene terephthalate) film, pigmented polycarbonated film, etc., metal, etc. A particularly advantageous support is paper, paper that is partially acetylated or coated with baryta or titanium dioxide and/or coated with a hydrophobic resin, such as, a poly- α -olefin containing two to 10 carbon atoms, e.g., polyethylene, polypropylene, polybutylene, poly(ethylene terephthalate), etc., polyamides, polyacetals, polycarbonates, cellulose esters, cellulose ethers, etc. The hydrophobic resin coatings described herein are advantageously electron-bombed to improve the adhesion of hydrophilic colloid layers coated on them as has been described in the prior art, such as, by Carroll et al., U.S. Pat. No. 3,220,842; Crawford et al., U.S. Pat. No. 3,117,865, etc.

The light-sensitive silver halide emulsion layers are arranged on one side of the support in any order. Especially advantageous arrangements are red-sensitive layer nearest the support, green-sensitive next, and the blue-sensitive layer outermost, or blue-sensitive layer nearest the support green-sensitive next, and red-sensitive outermost. Hydrophobic colloid interlayers between the light-sensitive layers, light-filtering layers, etc. are also used to advantage.

Any of the hydrophilic colloids used in photographic elements are advantageously used in 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(vinyl-pyrrolidone), acrylamide polymers and the like.

Any of the ordinarily employed silver halide developing-out emulsions, e.g., silver-chloride, silver chlorobromide, silver chlorobromoiodide, silver bromide, silver bromoiodide developing-out emulsions are used to advantage in elements processed according to our invention. Particularly useful results are obtained for the gelatino silver chlorobromide emulsions. Emulsions which form the latent image mostly inside the silver halide grains, such as, the emulsions described

in Knott et al., U.S. Pat. No. 2,456,956, are also used to advantage. As indicated above, any of the hydrophilic colloids discussed earlier are used to advantage in the emulsion layers.

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, benzosenazole, naphthoselenazole, quinoline, etc., or in the case of merocyanine dyes, in 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. Pat. No. 2,526,632; Sprague, U.S. Pat. No. 2,503,776; Brooker et al., U.S. Pat. No. 2,493,748 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, allylisothiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.) (see Baldsiefen, U.S. Pat. No. 2,540,085; 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. 2,540,086), potassium chloropalladate (Stauffer et al. U.S. Pat. No. 2,598,079), etc., or mixtures of such sensitizers; anti-foggants, such as, ammonium chloroplatinate (Trivelli and Smith, U.S. Pat. No. 2,566,245), ammonium chloroplatinite (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," Macmillian 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 our photographic materials. Included among the phenol and naphthol cyan dye-forming couplers used in 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-methyl-aniline, 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, 1100 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 hydrochloride 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-methyl-aniline, 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-toluene sulfonic 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 (0.665 mole) of sodium bicarbonate, 1,000 ml of ethanol and 280 ml of water is refluxed for a total of 68 hours. The ethanol is removed under partial vacuum and the oil layer extracted with diethyl 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 developer (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 absolutely ethyl

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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 ethyl alcohol and a large excess of diethyl 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 Developer 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

A solution is prepared having the following composition:

Benzyl alcohol	12.0 ml
Sodium hexametaphosphate	3.0 g
Sodium sulfite	2.0 g
Hydroxylamine sulfate	2.0 g
Sodium chloride	0.7 g
Sodium bromide	0.4 g
Sodium metaborate	45.5 g
Water to	1.0 l
pH	10.1 at 25° C.

This solution is divided into 5 equal portions which are made into Developer Solutions (or Developers) 1, 2, 3, 4 and 5 by adding Color Developing Agents 1, 2, 3, 4 and 5, respectively, to give a concentration of 0.00918 mole of developing agent per liter of the developer solutions. Five pieces of a multilayer color reflection print element comprising a TiO₂ pigmented polyethylene-coated paper support coated on one side in succession with a gelatin layer containing about 350 mg of a blue-sensitive silver chlorobromide per m² and a nondiffusible α -pivalylacetanilide nondiffusible yellow-dye-forming coupler described in Weissberger et al., U.S. Pat. No. 3,265,506, a gelatin layer containing about 260 mg of green-sensitized silver chlorobromide per m² and a nondiffusible 5-pyrazolone nondiffusible magenta-dye-forming coupler described in Weissberger et al., U.S. Pat. No. 3,062,653 and a gelatin layer containing about 190 mg of red-sensitized silver chlorobromide per m² and a nondiffusible phenol nondiffusible cyan-dye-forming coupler described in Salminen et al., U.S. Pat. No. 2,423,730, are each sensitometrically exposed to an original light image. The light-exposed Strips 1, 2, 3, 4 and 5 are color developed in Color Developer Solutions 1, 2, 3, 4 and 5, respectively, using the following process at 30° C:

Color developer
Stop-fix

6'
2'

Wash	2'
Bleach	2'
Wash	2'
Hardener-fix	2'
Wash	4'
Stabilizer	2'

5 1.0 or of 2.0.

A conventional acetic acid, sodium sulfite stop-fix bath, a conventional potassium ferricyanide bleach, a conventional hardener-fix and a conventional citric acid and borax stabilizer bath, all as described by Van Campen, U.S. Pat. No. 2,956,879 in Columns 5 and 6, are used in this process. Good color reproductions of the original light image are obtained in each of the original light image are processed strips of reflection print element.

EXAMPLE 2

Developer Solutions (or Developers) 1, 4, B and C are prepared. Developer Solutions 1 and 4 are the same as Developer Solutions 1 and 4 in Example 1. Developer Solutions B and C are not developing solutions used according to our invention, since they differ from Color Developer Solution 1 by containing equimolar concentrations of prior art Color Developing Agent B, i.e., N-ethyl-N-β-hydroxyethyl-3-methyl-p-phenylenediamine and prior art Color Developing Agent C, i.e., N-ethyl-N-β-methanesulfonamido-ethyl-3-methyl-p-phenylenediamine. Color Developing Agents B and C are outside of Formula I Developing Agents used in the processes of our invention. Four pieces of a reflection print element similar to that described in Example 1, excepting that the red-sensitive, green-sensitive and blue-sensitive layers contained 538,538 and 500 mg of silver chlorobromide per m², respectively, (outside the invention) instead of about 190,260 and 350 mg of silver chlorobromide per m², respectively, (of the invention) are sensitometrically exposed to a step tablet through narrow band red, green and blue filters. One-half of each of the exposed pieces of the elements is developed for 6 minutes in the developer solution indicated in Table 1, then stop-fixed, washed, bleached, washed, harden-fixed, washed and stabilized as described in Example 1. The steps of the step tablet reproduction which produce a cyan dye density of 1 and 2 are determined and marked. This is repeated for the magenta and yellow dyes. The other half of each piece of exposed elements is developed for 6 minutes with one element being treated in Developer 1, one in Developer 4, one in Developer B and one in Developer C. Each of these developed elements are then stop-fixed for 4 minutes, washed for four minutes and stabilized for 2 minutes, and then the developed silver content is measured in the same steps of the step tablet reproduction which produced in the other half a cyan dye density of 1.0 and a cyan dye density of 2.0, respectively. In this way, the mg of silver/m² that is developed to produce a cyan dye density of 1.0 and to produce a cyan dye density of 2.0 are obtained. This procedure is followed for each developed element for the cyan, magenta and yellow dyes. The results are summarized in the following table:

TABLE 1 (a)

Silver (mg/m²) Required to Reach Density of 1.0

	Cyan	Magenta	Yellow	Total
Developer C	48.4	156.0	172.1	376.6
Developer B	64.6	145.3	145.3	355.1
Developer 1	43.0	96.8	118.4	258.2
Developer 4	43.0	86.0	113.0	242.1

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TABLE 1 (b)

Silver (mg/m²) Required to Reach Density of 2.0

	Cyan	Magenta	Yellow	Total
Developer C	118.4	387.4	516.4	1022.2
Developer B	129.0	322.8	473.4	925.4
Developer 1	123.7	242.1	312.0	677.9
Developer 4	102.2	236.7	247.4	586.4

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The data in Table 1 (a) and Table 1 (b) show that our processes using Developers 1 and 4 are superior to processes outside our invention which use Developers B and C in their efficiency of utilizing silver halide to produce a dye density of 1.0 or of 2.0.

EXAMPLE 3

Developer Solutions 1 and 5 containing Color Developing Agents 1 and 5, respectively, are prepared as described in Example 1. Developer Solution (or Developer) D is prepared like Developer Solution 1, but substituting 0.00918 mole of Developing Agent D, i.e., N-ethyl-N-β-hydroxyethyl-3-methoxy-p-phenylenediamine per liter of solution in place of Developing Agent 1. Three pieces of the multicolor, multi-layer color reflection print element described in Example 1 are sensitometrically exposed to a step tablet through narrow band red, green and blue filters. The exposed elements are developed for six minutes at 30° C, one being developed in Developer Solution 1, one being developed in Developer Solution 5 and one being developed in Developer Solution D. Following development, the elements are stop-fixed, washed, bleached, washed, hardened-fixed, washed and stabilized as described in Example 1. The processed and dried elements are then subjected to a 1,500-hour SANS test exposure (Simulated Average North Skylight) at 500 ft. Candle intensity, using an area of each element which has an original cyan dye density of 1.0 density units, an area of each element which has an original magenta dye density of 1.0 density units. The percentage loss in each of these dyes which has the selected areas, due to the 1,500-hour exposure is determined and listed in Table 2.

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TABLE 2

Percentage Dye Loss After 1500 Hours
SANS in Print Processed with

Dye Color	Developer 1	Developer 5	Developer D
Cyan	13	20	35
Magenta	24	31	64

The results show very substantially lower cyan and magenta losses from color prints processed with our process using Developer 1 or Developer 5 compared to dye losses in color prints processed in a process outside our invention using Developer D.

Example 4

50 A multilayer, multicolor reflection print element is prepared like the element of Example 1, excepting that a non-diffusible 5-pyrazolone coupler described in Lestina, U.S. Pat. No. 3,519,429 and a nondiffusible α- phenoxyacetanilide yellow dye-forming coupler, described in Loria, U.S. Pat. No. 3,408,194, are used in place of the magenta and yellow dye-forming couplers used in the element of Example 1. Two pieces of this element are given sensitometric exposures to produce neutral step tablet image reproductions when developed for 6 minutes in Color Developers 1 and B at 30° C. (Color Developers 1 and B are described in Example 2). The color-developed elements are bleach-fixed 2 minutes, washed 4 minutes, stabilized for 2 minutes and dried. The bleach-fix bath has the composition:

Sodium ferric ethylenediamine tetracetate	45 g
Ammonium thiocyanate	10 g
Sodium sulfite	10 g
Ammonium thiosulfate (60% aqueous solution)	100 ml
Ethylenediamine tetracetate	
tetrasodium salt	5 g
Water to	5 g
pH adjusted to 6.7 to 7.0	1 l

The stabilizer solution is a conventional aqueous citric acid stabilizer having a pH of 3.5. Areas of the processed elements having a cyan dye density of 1.0 and a magenta dye density of

1.0 are identified and these areas are subjected to 4,000 hours of SANS test with exposure to Average Simulated North Skylight at 500 ft. candles intensity. The percentage dye losses due to the SANS test are listed in the following table:

TABLE 3

Dye color	Percentage Dye Loss After 4000 Hours SANS in Print Processed with	
	Developer 1	Developer B
Cyan	36	47
Magenta	34	42

The results show that cyan and magenta dyes produced by our process in color prints are substantially more stable to prolonged exposures to light than the dyes produced by a process outside our invention.

EXAMPLE 5

Example 4 is repeated, but using a color print material containing a nondiffusible 5-pyrazolone coupler described in U.S. Pat. No. 3,062,653, instead of the 5-pyrazolone used in Example 4. The results of the 4,000-hour SANS test are listed in the following Table:

TABLE 4

Dye Color	Percentage Dye Loss After 4000 Hours SANS in Print Processed with	
	Developer 1	Developer B
Cyan	29	50
Magenta	47	54

Again the results show that cyan and magenta dyes produced by our process are more stable to light than the dyes produced by a process outside our invention.

EXAMPLE 6

Four pieces of a multilayer, multicolor reflection print element described in Example 3 are exposed as described in Example 3. Two of these exposed elements are given a 5-solution process as described in Example 3 and the other two exposed elements are given a three-solution process as described in Example 4. The percentage dye losses caused by subjecting the processed color prints to heat fading test for four weeks at 60° C/70 percent RH in an oven are listed in the following tables:

TABLE 5

Dye color	Percentage Dye Loss from Oven in Color Prints Processed in 5-solution Process	
	Developer 1	Developer B
Cyan	6	18
Magenta	3	11
Yellow	1	3

TABLE 6

Dye Color	Percentage Dye Loss from Oven in Color Prints Processed in 3-solution Process	
	Developer 1	Developer B
Cyan	7	11
Magenta	3	9
Yellow	6	10

Our color development step with Developer 1 produces cyan, magenta and yellow dyes that are substantially more stable to exposure to heat than the cyan, magenta and yellow dyes produced by color development outside our invention with Developer B, either in the five-solution process or in the three-solution process.

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Example 7

Two samples of a multilayer, multicolor reflection photographic element on a paper support are made, Sample I like the element described in Example 1 and Sample II like the element described in Example 2. These samples are given sensitometric exposures to an original light image. When exposed Sample I is given our color development process using Developer Solution 1, it is found that in only 4 minutes, photographic quality is obtained that is equivalent to the photographic quality in Sample II after 6 minutes color development outside our invention using Developer Solution C. Our color development step gives a valuable savings in time.

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EXAMPLE 8

A multilayer, multicolor reflection print element is prepared like the element in Example 1, but having only about 120 mg of silver chlorobromide per m² in the red-sensitive layer and only about 240 mg of silver chlorobromide per m² in the green-sensitive layer of the element of Example 1. Samples of this element are sensitometrically exposed to a step table as described in Example 2. A sample of the exposed print material is color developed for 6 minutes according to our invention in Developer Solution 1, then stop-fixed, washed, bleached, washed, harden-fixed, washed and stabilized as described in Example 1. A good color reproduction is obtained of the step tablet original with the required cyan, magenta and yellow dye densities in each step of the step tablet from D_{min} to D_{max} even though the red-sensitive layer and the green-sensitive layer each has a very low silver chlorobromide content. Another sample of the exposed print element is treated outside the process of our invention with Color Developer Solution C (described in Example 2 for 6 minutes, then the process is completed as described previously in this example. The color reproduction of the original step tablet produced by color development outside our invention is unsatisfactory having only about 50 percent of the cyan and magenta dye image contrast needed. Another sample of the exposed print element is treated in Developer Solution C for 12 minutes and the process completed as described previously in this example. Not only is the cyan and magenta dye image contrast still unacceptably low, but the cyan, magenta and yellow fog densities are very high and unacceptable.

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EXAMPLE 9

Example 8 is repeated, but using a multilayer color photographic element element coated over a TiO₂-pigmented electron-bombarded polyethylene-coated paper support. The support is stored about two hours after electron bombardment before the light-sensitive layers are coated on it. Good color reproductions are obtained when the exposed element containing the very low silver chlorobromide content in the red-sensitive and in the green-sensitive layers is color developed according to our invention and then either stop-fixed, bleached, harden-fixed and stabilized as described in Example 1 or bleach-fixed and stabilized as described in Example 4. However, the process outside our invention gives unsatisfactory results.

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EXAMPLE 10

Four samples of a multilayer color photographic element prepared as described in Example 9 are sensitometrically exposed as described in Example 2 and processed as described in Example 1 so that different samples are developed in Color Developer Solutions 2, 3, 4 and 5. Good color reproduction is obtained of the step tablet in each sample using our process, even though the very low amount of silver halide is used in the red-sensitive layer and the green-sensitive layer.

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EXAMPLE 11

Five samples of multilayer color photographic element, prepared as described in Example 9, but containing a nondiffusible 5-pyrazolone magenta-forming coupler of Lestina,

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U.S. Pat. No. 3,519,429, and a nondiffusible α -phenoxacetanilide yellow-dye-forming coupler, described in Loria, U.S. Pat. No. 3,408,194, are used in place of yellow-dye-forming couplers used in the element of Example 9. These elements are sensitometrically exposed as described in Example 2 and processed as described in Example 1 so that different samples are developed in Color Developer Solutions 1, 2, 3, 4 and 5. Good color reproduction is obtained of the step tablet in each sample using our processes, even though the silver halide content of the red-sensitive layer and the green-sensitive layer is very low.

EXAMPLE 12

Example 9 is repeated, but a multilayer color photographic element is used having only about 312 mg of silver chlorobromide per m^2 in the blue-sensitive layer of the element in Example 9. Good color reproductions are obtained when our process is used to color develop the exposed element, but unacceptable reproductions result when a process outside our invention is used.

EXAMPLE 13

A multilayer reflection photographic element is made like the element described in Example 9, except that the red-sensitive layer contains only about 102 mg of silver chlorobromide per m^2 ; the green-sensitive layer contains only about 236 mg of silver chlorobromide per m^2 and the blue-sensitive layer contains only about 247 mg of silver chlorobromide per m^2 . A sample of this element is sensitometrically exposed and developed with our process using Color Developer Solution 4 as described in Example 1. A good color reproduction is produced in this element with our process.

EXAMPLE 14

Example 13 is repeated, but using only about 90 mg of silver chlorobromide per m^2 , instead of 102 mg/ m^2 in the red-sensitive layer, about 200 mg of silver chlorobromide per m^2 in the green-sensitive layer, instead of 236 mg/ m^2 and about 215 mg of silver chlorobromide per m^2 , instead of 247 mg/ m^2 in the blue-sensitive layer. Our process produces a good color reproduction in this element.

EXAMPLE 15

Example 13 is repeated, but using a multilayer color reflection photographic element having about 69 mg of silver chlorobromide per m^2 in the red-sensitive layer, about 166 mg of silver chlorobromide per m^2 in the green-sensitive layer and about 178 mg of silver chlorobromide in the blue-sensitive layer. Our process, using Color Developer Solution 4 (described in Example 1) at 6 minutes and 30° C, produces useful color reproductions in this element. By extending the development time and/or raising the development temperature, the color reproduction is improved.

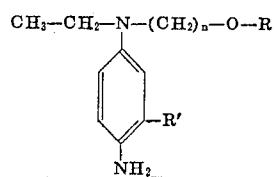
Similarly, it can be shown that our color development process, using a color developing agent of Formula I, is used to advantage to develop useful color reproductions in exposed color reflection photographic elements containing as low as 65 mg of silver chlorobromide per m^2 in at least the red-sensitive and green-sensitive emulsion layers by increasing the development time and/or developer temperature.

Our novel color development process provides a very valuable technical advance because it gives dyes having superior stability to prolonged exposure to heat and light, and advantageously produces good color reproduction in emulsions containing very low silver halide levels.

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. A color photographic process for treating an image-wise exposed multicolor reflection photographic element comprising an opaque white-pigmented support having coated thereon red, green and blue-sensitive silver halide emulsion layers containing nondiffusible cyan, magenta and yellow-forming photographic couplers, respectively, which form non-diffusible dyes, at least said red and green-sensitive silver halide emulsions being each coated at silver coverages in the range of from about 65 mg/ m^2 to about 375 mg/ m^2 , which process comprises image-wise color developing said silver halide emulsions 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.

2. The process of claim 1 wherein the silver halide emulsion layers are each gelatin silver chlorobromide emulsions.

3. The process of claim 1 wherein the support is white-pigmented polyethylene coated on paper.

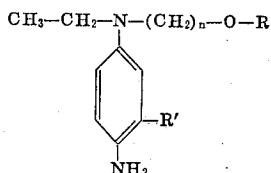
4. The process of claim 1 wherein the silver halide layers are coated with the blue-sensitive layer nearest the support and the red-sensitive layer furthest from the support.

5. A color photographic process for treating an image-wise exposed multicolor reflection photographic element comprising an opaque white-pigmented support having coated thereon red, green and blue-sensitive silver halide emulsion layers containing nondiffusible cyan, magenta and yellow-forming photographic couplers, respectively, which form non-diffusible dyes, at least said red and green-sensitive silver halide emulsions being each coated at silver coverages in the range of from about 65 mg/ m^2 to about 375 mg/ m^2 which process comprises image-wise color developing said silver halide emulsions in an aqueous alkaline color developing composition containing a color developing agent selected from the class 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.

6. A color photographic process for treating an image-wise exposed multicolor reflection photographic element comprising an opaque white-pigmented support having coated thereon red, green and blue-sensitive silver halide emulsion layers containing nondiffusible cyan, magenta and yellow-forming photographic couplers, respectively, which form non-diffusible dyes, at least said red and green-sensitive silver halide emulsions being each coated at silver coverages in the range of from about 65 mg/ m^2 to about 375 mg/ m^2 , which process comprises image-wise color developing said silver halide emulsions in an aqueous alkaline color developing composition containing

Benzyl alcohol	0-15.0 ml/l
Alkali metal chloride	0-15.0 g/l
Alkali metal bromide	0.1-1.0 g/l
Stabilizing agent for color developing agent	0.1-5.0 g/l
Alkali metal sulfite	0.1-5.0 g/l
Alkali metal salt of a weak acid	10.0-50.0 g/l
Color developing agent	1.0-10.0 g/l

in which said stabilizing agent for color developing agent is hydroxylamine sulfate or dihydroxyacetone and in which said color developing agent has 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. A color photographic process for treating an image-wise exposed multicolor reflection photographic element comprising an opaque white-pigmented support having coated thereon red, green and blue-sensitive silver halide emulsion layers containing nondiffusible cyan, magenta and yellow-forming photographic couplers, respectively, which form non-diffusible dyes, at least said red and green-sensitive silver halide emulsions being each coated at silver coverages in the range of from about 65 mg/m² to about 375 mg/m², which process comprises image-wise color developing said silver halide emulsions in an aqueous alkaline color developing composition containing N-ethyl-N-methoxyethyl-3-methyl-p-phenylenediamine.

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8. A color photographic process for treating an image-wise exposed multicolor reflection photographic element comprising an opaque white-pigmented support having coated thereon red, green and blue-sensitive silver halide emulsion layers containing nondiffusible cyan, magenta and yellow-forming photographic couplers, respectively, which form non-diffusible dyes, at least said red and green-sensitive silver halide emulsions being each coated at silver coverages in the range of from about 65 mg/m² to about 375 mg/m², which process comprises image-wise color developing said silver halide emulsions in an aqueous alkaline color developing composition containing N-ethyl-N-methoxyethyl-3-n-propyl-p-phenylenediamine.

9. A color photographic process for treating an image-wise exposed multicolor reflection photographic element comprising an opaque white-pigmented support having coated thereon red, green and blue-sensitive silver halide emulsion layers containing nondiffusible cyan, magenta and yellow-forming photographic couplers, respectively, which form non-diffusible dyes, at least said red and green-sensitive silver halide emulsions being each coated at silver coverages in the range of from about 65 mg/m² to about 375 mg/m², which process comprises image-wise color developing said silver halide emulsions in an aqueous alkaline color developing composition containing N-ethyl-N-methoxyethyl-3-methoxy-p-phenylenediamine.

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