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[54] **COBALT (III) COMPLEX AMPLIFIER BATHS IN COLOR PHOTOGRAPHIC PROCESSES**

[75] Inventors: **Rowland George Mowrey; Glenn Richard Wilkes,** both of Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company,** Rochester, N.Y.

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[58] **Field of Search** ..... 96/3, 29 D, 22, 55, 60 R, 96/66.3

[56] **References Cited**

UNITED STATES PATENTS

3,615,508	10/1971	Stephen et al.	96/60 BF
3,674,490	7/1972	Matejec et al.	96/3
3,748,138	7/1973	Bissonette	96/66.3
3,762,922	10/1973	Lugosy et al.	96/60 R
3,765,891	10/1973	Travis	96/66.3
3,772,020	11/1973	Smith	96/60 BF

Primary Examiner—Ronald H. Smith
Assistant Examiner—Richard L. Schilling
Attorney, Agent, or Firm—Gerald E. Battist

[57] **ABSTRACT**

Improved processes are disclosed for providing an image record in a photographic element which comprises a support and at least one layer thereon containing a silver halide emulsion which has associated therewith an image dye-providing color coupler. Generally, the process comprises contacting a photographic element containing a silver halide and an imagewise distribution of metallic silver with a color-developing agent, and then contacting the developed photographic element with an amplifier composition which contains a cobalt(III) complex and an oxidant such as an alkali metal peracid or an alkali metal ferricyanide.

17 Claims, No Drawings

COBALT (III) COMPLEX AMPLIFIER BATHS IN COLOR PHOTOGRAPHIC PROCESSES

This invention relates to a process for developing photographic elements which comprise layer units containing imagewise-exposed silver halide having associated therewith a photographic color coupler. In one aspect, this invention relates to a process for developing a visible image record in photographic elements which comprise color-providing layer units containing a low silver coverage. In another aspect, this invention relates to a continuous process for developing imagewise-exposed photographic elements which comprise at least two color-providing layer units.

It is known in the art to process photographic elements comprising silver halide emulsions and photographic color couplers wherein said element is contacted with an aromatic primary amino silver halide developing agent to form silver and dye. References such as U.S. Pat. No. 2,750,292 by Dippel et al, issued June 12, 1956, and 2,173,739 by Weber issued Sept. 19, 1939, disclose processes for intensifying an image formed by a light-sensitive metal salt by treating the imagewise-exposed element with a color-developing agent and a photographic color coupler in the presence of developable silver halide or with a physical developing agent to form an image dye in the area of development. More recently, British Pat. No. 1,268,126 also discloses a process of intensifying a silver image by treating a developed silver image with solutions containing peroxy compounds and color developers.

However, several of the methods available in the art do not appear to be practical on a commercial basis due to several problems inherent in the system, including instability of the solutions used to intensify the image record recorded by the light-sensitive metal salt. Where the silver is bleached and redevelopment takes place with a color developer and a coupler, the bleaching step is quite critical as the developable silver centers can be lost where bleaching has completely converted a silver grain to silver halide. Moreover, solutions containing both color-developing agent and color coupler are prone to formation of dye in the bath through aerial oxidation of the developer, etc., causing dye contamination, and also these systems are generally limited to one-color systems. Where a physical developing agent is used in combination with a color coupler and a color-developing agent, the processing baths are often autocatalytic since the reaction products of the redox reaction with the physical developer provide a catalyst for more redox reactions.

Improved processes for developing and amplifying an image record recorded in a light-sensitive metal salt are disclosed in Belgian Pat. Nos. 784,471, 784,472 and 784,473, incorporated herein by reference. In one embodiment, the process disclosed in these patents relates to image formation in photographic elements comprising color-providing layer units containing a silver halide emulsion having associated therewith a color coupler. In the process, the photographic element is contacted with a photographic color-developing agent and a metal complex, such as a cobalt(III) complex having a coordination number of 6, until the desired dye density is obtained. the cobalt complex is apparently reduced to cobalt(II), which is not a catalyst for further redox reaction, in the presence of silver, and the color developer is oxidized whereby it can react with the color coupler in each respective layer unit to form the desired image dye. Certain preferred photographic elements which can be processed by this procedure are described in Bissonette, U.S. Ser. No. 256,072 filed May 23, 1972, incorporated herein by reference.

These patents also disclose a process of producing image dye in an imagewise-exposed photographic element having a support and at least one layer thereon containing a silver halide emulsion having associated therewith an image dye-providing color coupler wherein said process comprises 1) development of said imagewise-exposed photographic element with a silver halide developing agent to produce an imagewise distribution of metallic silver and imbibition of a color-developing agent in said photographic element, and then 2) contacting said photographic element which contains silver halide and said imagewise distribution of metallic silver with an amplifier composition which represses substantially additional net silver development, wherein said amplifier composition contains a cobalt-(III) metal complex having a coordination number of 6 and said amplifier composition is maintained in said photographic element under conditions which reduce cobalt(III) to cobalt(II), which in turn oxidizes said color-developing agent whereby additional image dye is provided from said image dye-providing color coupler and said oxidized color-developing agent.

The amplifier composition acts essentially as a stop bath so far as further production of catalytic silver surface is concerned. Further H and D curve shape changes due to continued development are therefore minimized. However, in some continuous deep-tank machine developing processes, it has been observed that carry-over of color-developing agent from the developer bath to the amplifier bath has caused some sensitometric fluctuations and changes in the H and D curve shape. These fluctuations are presumably caused by excess color-developing agent in the amplifier bath which reduces the diffusion rate of color developer from the photographic element. This causes a gradual contrast increase, thereby creating a problem of precise sensitometric control.

This invention relates to an improved process of producing image dye in an imagewise-exposed photographic element having a support and at least one layer thereon containing a silver halide emulsion having associated therewith an image dye-producing color coupler wherein said process comprises 1) development of said imagewise-exposed photographic element with a silver halide developing agent to produce an imagewise distribution of metallic silver and imbibition of a color-developing agent in said photographic element, and then 2) contacting said photographic element with an amplifier composition which represses substantially additional net silver development, wherein said amplifier composition contains a strong oxidizing agent, such as a peracid or a ferricyanide, and a cobalt(III) metal complex having a coordination number of 6.

In one highly preferred embodiment, an image dye is produced in an imagewise-exposed photographic element having a support and at least one layer thereon containing a silver halide emulsion having associated therewith an image dye-providing color coupler. The imagewise-exposed photographic element is developed in the presence of a silver halide color-developing agent. This produces an imagewise distribution of metallic silver and imbibition of a color-developing agent

in the photographic element. The developed photographic element which contains silver halide and the imagewise distribution of metallic silver is then contacted with an amplifier composition which represses substantially additional net silver development. A strong oxidant is added to the amplifier during processing to oxidize selectively any excess developing agent which may have been carried into the amplifier bath.

Generally, good results have been obtained when the strong oxidant used in the amplifier bath is an alkali metal salt of a peracid or of a ferricyanide, and preferably when it is an alkali metal salt of a peracid. Typical useful ferricyanides include potassium ferricyanide and the like. Typical useful peracids include potassium persulfate, potassium perbromate, potassium permanganate, potassium perchlorate, sodium persulfate, sodium perbromate, sodium permanganate and the like. While the oxidizing agent can comprise any of the alkali metal ions such as sodium, potassium, lithium and the like, it preferably comprises a potassium ion, i.e., the potassium salt of the peracid or of ferracyanide.

the photographic elements processed as above can, of course, be bleached, fixed, and washed, etc., in the normal manner after contact with the amplifier. Generally, this process also provides highly improved stability of development compositions and amplifying compositions and is especially suited to continuous processing of color photographic elements. The process is especially advantageous in processing multicolor photographic elements since stability in processing solutions is highly improved, allowing reproducible results over long periods of operating time.

In one preferred embodiment, the amplifier solution contains a sufficient quantity of a development restrainer or combination of development restrainers to repress substantially any further net silver development. The development restrainers may be water-soluble bromide compounds such as KBr, etc., or heterocyclic compounds such as tetrazoles, azaindines and triazoles which are free from mercapto or ionic iodide groups. Development restrainers as a class of compounds are known in the art, as mentioned in U.S. Pat. No. 3,458,317. Development restrainers which have ionic iodide groups or mercapto groups appear to retard the catalytic effect of silver. Typical preferred development restrainers include high levels of KBr such as 2 to 40 g./l., methyl benzotriazole, benzotriazole, 3-methyl-1,3-benzothiazolium bromide, 5-nitrobenzimidazole, decamethylene bis(benzothiazolium bromide) and the like. Other useful organic development restrainers include the sodium salt of 4-hydroxy-6-methyl-1,3,3*a*,7-tetrazaindene, the sodium salt of 4-hydroxy-6-methyl-2-methylmercapto-1,3,3*a*,7-tetrazaindene, 4,5-dihydro-1,4-diphenyl-3,5-phenylamino-1,2,4-triazole and the like. The heterocyclic development restrainers are generally incorporated in the amplifier at concentrations of 0.01 to 2.0 g./l. In certain embodiments, the heterocyclic groups containing sulfur substitution can be used as development restrainers where the compound as used in the amplifier remains in its thione form rather than in the thiol or mercapto forms. In highly preferred embodiments, a combination of an alkali metal bromide and an organic development restrainer are present in the amplifier composition.

The amplifying baths of this invention preferably contain only low amounts or are substantially free from silver halide solvents. If high amounts of solvents are present, there is very little noticeable amplification effect in the bath. Therefore, the amplifying baths generally comprise less than 30 percent by weight of the amount of a silver halide solvent which would be necessary to fix a silver halide emulsion. The fixing processes are well-known in the art, for example, as disclosed in U.S. Pat. No. 3,615,508.

As used herein, the terms "photographic color coupler" and "image dye-providing color coupler" include any compound which reacts (or couples) with the oxidation products of primary aromatic amino developing agent on photographic development to form an image dye, and are preferably nondiffusible in a hydrophilic colloid binder, useful for photographic silver halide, and also those couplers which provide useful image dyes when reacted with oxidized primary aromatic amino developing agents such as by a coupler-release mechanism. The couplers can form diffusible or nondiffusible dyes. Typical useful color couplers include phenolic 5-pyrazolone and open-chain ketomethylene couplers. Specific cyan, magenta and yellow dye-forming couplers which can be employed in the practice of this invention are described in U.S. Pat. No. 3,046,129, column 15, line 45, through column 18, line 51, which disclosure is incorporated herein by reference. Such color couplers can be dispersed in any convenient manner, such as by using the solvents and techniques described by U.S. Pat. Nos. 2,322,027 or 1,801,171. When coupler solvents are employed, the most useful weight ratios of color coupler to coupler solvent range from about 1:3 to 1:0.1. Useful couplers include Fischer-type incorporated couplers such as those described in U.S. Pat. No. 1,055,155 and particularly nondiffusible Fischer-type couplers containing branch carbon chains, e.g., those referred to in the references cited in U.S. Pat. No. 2,376,679, column 2, lines 50–60. Particularly useful in the practice of this invention are the nondiffusible color couplers which form nondiffusible dyes.

In certain preferred embodiments, the incorporated couplers in the layer units of this invention are water-insoluble color couplers which are incorporated in a coupler solvent which is preferably a moderately polar solvent. Typical useful solvents include tri-o-cresyl phosphate, di-n-butyl phthalate, diethyl lauramide, 2,4-diaryphenol, liquid dye stabilizers as described in an article entitled "Improved Photographic Dye Image Stabilizer-Solvent," *Product Licensing Index*, Vol. 83, March, 1971, and the like. The coupler solvents in the elements appear to aid the imbibition of color developer where it is carried into an amplifier bath via the element.

The photographic elements processed in accordance with this invention generally comprise a light-sensitive silver halide emulsion wherein the halide is generally less than 6 mole percent iodide and preferably less than 3 percent iodide and, in some highly preferred embodiments, is less than 0.25 percent iodide. If iodide is near the surface of the emulsion grains, it can build up in the solutions at a high level during development and amplification and affect dye production in the amplification step. Therefore, high amounts of iodide in the emulsion are generally avoided, especially when the element is to

be processed in a continuous-process deep-tank apparatus where seasoning can occur.

The term "nondiffusible" used herein as applied to couplers and products derived from couplers has the meaning commonly applied to the term in color photography and denotes materails which for all practical purposes do not migrate or wander through photographic hydrophilic colloid layers, such as gelatin, particularly during processing in aqueous alkaline solutions. The same meaning is attached to the term "immobile." The terms "diffusible" and "mobile" have the converse meaning.

In certain embodiments, the photographic elements processed in accordance with this invention comprise a support having thereon image dye-providing layers units. A multicolor photographic element comprises at least two of said image dye-providing layer units, each of which records light primarily in different regions of the light spectrum. The layer unit comprises a light-sensitive silver salt, which is generally spectrally sensitized to a specific region of the light spectrum, and has associated therewith a photographic color coupler. In certain embodiments, the color-providing layer units are effectively isolated from other layer units by barrier layers, spacer layers, layers containing scavengers for oxidized developer and the like to prevent any substantial color contamination between the image dye-providing layer units. The effective isolation of the layer units is known in the art and is utilized to prevent color contamination in many commercial color products.

the photographic elements prepared in accordance with this invention preferably comprise a support having thereon at least one image dye-providing layer unit, and preferably at least two image dye-providing layer units, containing a light-sensitive silver salt, preferably silver halide, having associated therewith a stoichiometric excess of coupler of at least 40 percent and preferably at least 70 percent. The equivalency of color couplers is known in the art; for example, the 4-equivalent couplers require 4 moles of oxidized color developer, which in turn require development of 4 moles of silver, to produce 1 mole of dye. Thus, for a stoichiometric reaction with silver halide, 1-equivalent weight of this coupler will be 0.25 mole. In accordance with this embodiment, the color image-providing unit comprises at least a 40 percent excess of the equivalent weight of image dye-providing color coupler required to react with the silver and preferably a 70 percent excess of said coupler based on effective silver. In certain highly preferred embodiments, the photographic color couplers are employed in the image dye-providing layer units at a concentration of at least 3 times, such as from 3 to 20 times, the weight of the silver in the silver halide emulsion, or at a stoichiometric excess of at least 110 percent based on effective silver in said layer unit. Advantageously, the coupler is present in an amount sufficient to give a density of at least 1.7 and preferably at least 2.0 when coated on a paper support, and preferably at least 3.0 when coated on a transparent film support. Generally, the coupler is present in said layer units in at least 1×10^{-5} moles/ft.^{2}. Preferably, the difference between the maximum density and the minimum density (which can comprise unbleached silver) is at least 0.6 and preferably at least 1.0. Preferably, the photographic elements prepared in accordance with this invention are those described in the above Bissonette application U.S. Ser. No. 256,072.

Advantageously, the photographic color couplers utilized are selected so that they will give a good neutral. Preferably, the cyan dye formed has its major absorption between about 600 and 700 nm., the magenta dye has its major absorption between about 500 and 600 nm., and the yellow dye has its major absorption between about 400 and 500 nm.

Generally, each of the color-providing layer units of the photographic elements contains a light-sensitive silver halide. In one preferred embodiment, the color-providing layer units comprise a silver salt at a concentration of up to 30 mg. silver/ft.^{2}. However, while the silver halide is preferably present at concentrations based on silver of less than 30 mg./ft.^{2}, it is possible to coat emulsions at higher silver coverages within this embodiment, as long as no more than 30 mg./ft.^{2} of silver develops; for example, such emulsions may contain silver halide grains which are relatively light-insensitive, or may contain developer restrainers such as development inhibitor-releasing couplers, and still provide a photographic element which is advantageously used in the various processes as described herein to produce improved image records. In some instances, relatively light-insensitive silver halide grains or development restrainers are desirable to enable one to obtain more uniform coating coverage with less precise coating equipment, as well as for other reasons. Thus, highly preferred photographic elements processed according to this invention contain at least two color-providing layer units, each containing a silver halide emulsion, defined in terms of "effective coverage" and developability as one which, when it is fully exposed and processed for about 1 min. at 100° F. in the color developer as described in Example 1, will provide less than 30 mg. of metallic silver/ft.^{2} and preferably less than 15 mg./ft.^{2}. It is understood that the term "effective silver" refers to that amount of silver which is produced in this test and that ratios of coupler to silver are based on "effective silver" which is produced by this type of development when so specified herein. In most instances, the quantity of effective silver as silver halide in the undeveloped, unexposed photographic element will be quite similar to quantity of total silver present as silver halide. The fully exposed layer containing silver halide emulsion is one which is exposed to Dmax, as is well-known in the art, for example, by exposure to a 500-watt, 3,000° K. lamp for about 10 sec. (total exposure at the film plane = 11.3×10^4 ergs/cm.^{2}.

The photographic elements processed in accordance with this invention generally can contain negative silver halide emulsions, direct-positive silver halide emulsions, silver halide emulsions designed for processing in reversal processes and the like. It is understood, of course, that with negative emulsions the catalytic metallic silver development will be in the exposed areas, whereas with direct-positive emulsions the catalytic metallic silver will be formed in the unexposed areas.

The amplifier compositions of this invention include a cobalt(III) metal complex. Such complexes feature a molecule having a cobalt atom or ion. This cobalt atom or ion is surrounded by groups of atoms, ions or other molecules, which are generically referred to as ligands. The cobalt atoms or ion in the center of these com-

plexes is a Lewis acid; the ligands are Lewis bases. Werner complexes are well-known examples of such complexes. The useful cobalt salts are typically capable of existing in at least two valent states. In a preferred aspect of the invention, the cobalt complexes are those referred to by American chemists as "inert" and by European chemists as "robust." Particularly useful are complexes of a cobalt ion with a ligand which, when a test sample thereof is dissolved at 0.1 molar concentration at 20° C. in an inert solvent solution also containing 0.1 molar concentration of a tagged ligand of the same species which is uncoordinated, exhibits essentially no exchange of uncoordinated and coordinated ligands for at least 1 min., and preferably for at least several hours such as up to 5 hr. or more. This test is advantageously conducted under the pH conditions which will be utilized in the practice of the invention. In silver halide photography, this generally will be a pH of over about 8. Many cobalt metal complexes useful in this invention show essentially no exchange of uncoordinated and coordinated ligands for several days. The definition of "inert" metal complexes and the method of measuring ligand exchange using metal radioactive isotopes to tag ligands is well-known in the art: see, for example, Taube, *Chem. Rev.*, Vol. 50, p. 69 (1952), and Basolo and Pearson, *Mechanisms of Inorganic Reaction, A Study of Metal Complexes and Solutions*, 2nd Edition, 1967, published by John Wiley and Sons, p. 141. Further details on measurement of ligand exchange appear in articles by Adamson et al, *J. Am. Chem. Soc.*, Vol. 73, p. 4,789 (1952). The inert metal complexes should be contrasted with labile complexes which, when tested by the method described above, have a reaction half-life generally less than 1 min. Metal chelates are a special type of metal complex in which the same ligand (or molecule) is attached to the central metal ion at two or more different points. The metal chelates generally exhibit somewhat slower ligand exchange than nonchelated complexes. Labile-type chelates may have a half-life of several seconds or perhaps slightly longer. Generally, the oxidizing agents employed are not reduced to a zero valent metal during the redox reaction of the invention.

A wide variety of ligands can be used with a metal ion to form suitable cobalt complexes. Nearly all Lewis bases (i.e., substances having an unshared pair of electrons) can be ligands in cobalt complexes. Some typical useful ligands include the halides, e.g., chloride, bromide, fluoride, nitrite, water, amino, etc., as well as such common ligands as those referred to on p. 44 of Basolo et al, supra. The lability of a complex is influenced by the nature of the ligands selected in forming said complex.

Particularly useful cobalt complexes have a coordination number of 6 and have a ligand selected from the group consisting of ethylenediamine(en), propylenediamine(tn), diethylenetriamine(dien), triethylenetetraamine(trien), ammine(NH_3), nitrate, nitrite, azide, chloride, thiocyanate, isothiocyanate, water and carbonate. the preferred cobalt complexes comprise 1) at least 2 ethylenediamine ligands or 2) at least 5 amine ligands or 3) 1 triethylenetetraamine ligand. Especially useful are the cobalt hexammine salts (e.g., the chloride, bromide, sulfite, sulfate, perchlorate, nitrite and acetate salts). Some other specific highly useful cobalt complexes include those having one of the following formulas: $[Co(NH_3)_5H_2O]X$, $[Co(NH_3)_5CO_3]X$, $[Co(NH_3)_5Cl]X$, $[Co(NH_3)_4CO_3]X$, $[Co(en)_3]X$, cis-$[Co(en)_2(N_3)_2]X$, trans-$[Co(en)_2Cl(NCS)]X$, trans-$[Co(en)_2(N_3)_2]X$, cis-$[Co(en)_2(NH_3)N_3]X$, cis-$[Co(en)_2Cl_2]X$, trans-$[Co(en)_2Cl_2]X$, $[Co(en)_2(SCN)_2]X$, $[Co(en)_2(NCS)_2]X$, $[Co(tn)_3]X$, $[Co(tn)_2(en)]X$ and $[Co(tn)(en)_2]X$, wherein X represents one or more anions determined by the charge neutralization on rule.

With many complexes, such as cobalt hexammine, the anions selected can substantially affect the reducibility of the complex. The following ions are listed in the order of those which give increasing stability to cobalt hexammine complexes: bromide, chloride, nitrite, perchlorate, acetate, carbonate, sulfite and sulfate. Other ions will also affect the reducibility of the complex. These ions should therefore be chosen to provide complexes exhibiting the desired degree of reducibility. Some other useful anions include chloride, nitrate, thiocyanate, dithionate and hydroxide. Neutral complexes such as $[Co(dien)(SCN)_2OH]$ are useful, but positively charged complexes are generally preferred.

Where highly active complexes are selected for use in the amplifier bath, such as $[Co(NH_3)_5H_2O]X_3$ or $[Co(NH_3)_5Cl]X_2$, either as the sole cobalt complex or as one to be used in combination with another cobalt complex, the effects of the buildup of color developer appear to be minimized. However, the use of alkali metal peracids or ferricyanide which are very effective for controlling buildup of color developer in amplifier baths containing the less active cobalt complexes also show some improvements even when the highly active cobalt complexes are used.

Numerous color-developing agents can be imbibed in the photographic element in accordance with the present invention. The color-developing agents utilized herein undergo redox reaction with the oxidizing agent at a catalytic surface. Especially preferred color-developing agents are those which reduce silver halide to metallic silver, such as those which are capable of developing imagewise-exposed light-sensitive photographic silver halide. Typical preferred color-developing agents are aromatic primary amino color-developing agents such as p-aminophenols, which form particularly stable redox combinations with certain complexes, e.g., $[Co(en)_3Cl_3]$ or p-phenylenediamines. Useful color-developing agents include 3-acetamido-4-amino-N,N-diethylaniline, p-amino-N-ethyl-N-β-hydroxyethylaniline sulfate, N,N-diethyl-p-phenylenediamine, 2-amino-5-diethylaminotoluene, N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline, 4-amino-N-ethyl-3-methyl-N-(β-sulfoethyl)aniline, 4-amino-N-butyl-N-α-sulfobutylaniline, 4-amino-N,N-diethyl-3-n-propylaniline hydrochloride and the like. See Bent et al, *JACS*, Vol. 73, pp. 3,100–3,125 (1951), and Mees and James, *The Theory of the Photographic Process*, 3rd Edition, 1966, published by MacMillan Co., New York, pp. 278–311, for further typical, useful developing agents. It will be appreciated that many of the subject color-developing agents are most effective at high pH, such as a pH from about 8 to 13.

In one highly preferred embodiment, aromatic primary amino color-developing agents which provide good results in the process of this invention are 4-amino-N,N-diethylaniline hydrochloride, 4-amino-3-methyl-N,N-diethylaniline hydrochloride, 4-amino-3-

methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sulfate hydrate, 4-amino-3-methyl-N-ethyl-N-β-hydroxyethylaniline sulfate, 4-amino-3-dimethylamino-N,N-diethylaniline sulfate hydrate, 4-amino-3-methoxy-N-ethyl-N-β-hydroxyethylaniline hydrochloride, 4-amino-N-ethyl-N-(2-methoxyethyl)-*m*-toluidine di-paratoluene sulfonate and 4-amino-3-β-(methanesulfonamido)- ethyl-N,N-diethylaniline dihydrochloride.

The term "color developer" as used herein generally refers to those silver halide developing agents which after oxidation couple with a photographic color coupler to form an addition compound such as an image dye. Generally, these compounds contain a primary amino group ($-NH_2$) and they are perferably aromatic primary amino compounds where the primary amino group is a substituent on the aromatic ring.

The term "black-and-white silver halide developers" as referred to herein generally refers to those developers which do not couple with photographic color couplers to form useful image dyes. The black-and-white silver halide developers can be effectively used in some instances in the formation or development of the metallic silver in the photographic element. Typical useful developers of this type include hydroquinones, catechols, 3-pyrazolidones such as 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidone and the like, l-, d- or isoascorbic acid, reductones, N-methyl-p-aminophenols, and the like.

The amplifier bath can generally comprise any liquid as a carrier medium, but the liquid is preferably predominantly water. The bath generally comprises from about 0.2 to about 20 g./l. of the transition metal-ion complex which preferably is maintained at between about 1 to about 15 g./l. However, generally higher concentrations of cobalt complexes can be used in preferred amplifier baths of this invention without adverse sensitometric effects, compared with color-developing solutions which contain the cobalt complexes which contain sufficient color-developing agent to develop substantial amounts of silver halide rapidly.

The alkali metal peracid or alkali metal ferricyanide are generally added to the amplifier during processing in a concentration sufficient to maintain the color-developer concentration at a level of below 0.5 g./l., and preferably at a level of below 0.05 g./l. Since the rate of color-developer buildup will depend on the type of element being processed, the size of the equipment, etc., the rate of addition of the strong oxidant is determined for each particular situation. While excess strong oxidant can be used, it is generally not preferred to use excess strong oxidant since the efficiency of color formation in the processed element could be lowered, adverse interaction could occur, etc.

The amplifier bath also generally contains a solubilizer for the oxidized color developer or soluble competing couplers which form colorless dyes with the oxidized color developer. Suitable soluble couplers include those described by Puschel, U.S. pat. No. 3,028,238, and the like. Suitable solubilizers include sodium sulfite and the like. Generally, when solubilizers such as sulfites are used in the amplifier bath, they are added to maintain the sulfite level at at least 0.5 g./l. and preferably at least 2.0 g./l. When either the solubilizers or the competing couplers are used, it is desirable to have at least a stoichiometric amount present based on the oxidized color developer or the strong oxidant, and preferably at least a 20 percent excess, especially when excess oxidant is present in the amplifier.

The amplifier bath generally contains a development restrainer and preferably contains enough development restrainer to repress any further silver formation. Thus, the sensitometric changes associated with the development of silver are avoided. Moreover, this feature enables one to use various grain sizes in various layers of a multicolor element to obtain a balanced photographic element and simultaneously to provide substantially uniform color formation in each layer, whereby balanced color can be obtained at several densities by inspection.

The organic development restrainers (i.e., other than the inorganic development restrainers such as the alkali metal bromides) mentioned previously can be used in the bath in combination with the inorganic development restrainers or alone, but are preferably used in combination with alkali metal bromides. Generally, the organic development restrainers are used in concentrations of from 0 to 2 g. and preferably from 0.01 to 1 g./l.

The amplifier bath is generally operated in a pH range of from 6 to 14 and preferably at pH ranges of 8 to 12.

The amplifying baths contain only small amounts of or are substantially free from silver halide solvents such as sodium thiosulfate, thiocyanates, thioethers and the like. While bromide ions are often desirable in small amounts of about 2 to 40 g./l. of amplifying solution to repress development, high concentrations such as above 200 g./l. could function to bleach silver halide layers and, likewise, defeat the primary amplification step. In certain embodiments, it is also desirable to maintain the ammonia in the amplifier at less than 10 g./l. since high ammonia concentrations can act as a silver halide solvent, thus allowing bleaching of the silver image.

The term "silver halide solvents" generally refers to compounds and concentration levels of those compounds which, when employed in an aqueous solution (60°C.), are capable of dissolving more than 10 times the amount (by weight) of silver chloride than that which can be dissolved by water at 60° C.

The concentration of a solvent necessary to fix a silver halide layer is understood to mean that concentration of solvent in a liquid bath which will remove substantially all silver bromide from a photographic element containing a single silver bromide gelatin emulsion layer coated at 30 mg. silver/ft.^{2} in 1½ min. at 105° F. maintained at a pH range within 4.0–12.0.

The amplifier bath can be operated over a wide range of temperatures depending on the effect desired. Generally, the amplifier bath is much more stable than amplifier baths previously used and, therefore, is preferably used in processes where it is operated at temperatures above 90° F. and more preferably above 100° F. to decrease the residence time of a photographic element in the bath, thus speeding up the process. The amplifier baths of this invention which are used continuously for 1 week at 105° F. provide substantially the same development properties as a fresh amplifier bath.

The developing baths and amplifier solutions of this invention preferably contain a coupling accelerator

which can be an alcohol, including aromatic alcohols such as benzyl alcohol, which appears to increase dye yields. Preferably, the alcohol is used in the respective baths at a concentration of up to 40 g./l. and preferably from about 2 g. to 20 g./l. Coupling accelerators are known in the art, for example, the alcohols disclosed in U.S. Pat. Nos. 2,304,925, 2,950,920 and the like.

In certain instances, alcohols such as benzyloxyethanol, cyclohexanol, pentyl alcohol, phenoxyethyl alcohol, phenylethyl alcohol and the like provide better thermal stability in the amplifier than benzyl alcohol and still aid in increasing dye yields.

Preferably, the process is carried out in a unidirectional processing equipment where the element leaves a bath in the same relative direction with respect to the plane of the element as it eneters the bath. In certain preferred embodiments, a continuous web of the photographic material is processed in unidirectional continuous-processing equipment.

The invention can be further illustrated by the following examples.

EXAMPLE 1–A

To serve as one control, a photographic element is prepared by coating the following layers in order on a paper support:

1. layer containing a blue-sensitive silver halide emulsion (1.2 microns mean grain size) at 16 mg./ft.^{2} based on silver, gelatin at 122 mg./ft.^{2}, and the yellow image dye-providing coupler α-pivalyl-4-(4-benzyloxyphenylsulfonyl)-phenoxy-2-chloro-5-[α-(2,4-di-tert-amylphenoxy)butyramido] acetanilide at 60 mg./ft.^{2} dissolved in di-*n*-butyl phthalate coupler solvent at 15 mg./ft.^{2};
2. gelatin interlayer at 100 mg./ft.^{2} and the scavenger for oxidized developer di-tert-octyl hydroquinone at 5 mg./ft.^{2}.
3. layer containing a green-sensitive silver halide emulsion (0.3 micron mean grain size) at 10 mg./ft.^{2} based on silver gelatin at 132 mg./ft.^{2} and the magenta dye-providing color coupler 1-(2,4,6-trichlorophenyl)-3-{5-[α-(3-tert-butyl-4-hydroxyphenoxy)tetradecaneamido]-2-chloroanilino} -5-pyrazolone at 25 mg./ft.^{2} dissolved in tri-cresyl phosphate coupler solvent at 12.5 mg./ft.^{2};
4. gelatin interlayer at 160 mg./ft.^{2} and di-tert-octyl hydroquinone at 4.5 mg./ft.^{2};
5. layer containing a red-sensitive silver halide emulsion (0.3 micron mean grain size) at 6 mg./ft.^{2} based on silver gelatin at 90 mg./ft.^{2} and the cyan dye image-providing coupler 2-[α-(2,4-di-tert-amylphenoxy)butyramido]-4,6-dichloro-5-methylphenol at 35 mg./ft.^{2} dissolved in di-*n*-butyl phthalate coupler solvent at 17.5 mg./ft.^{2};
6. gelatin overlayer at 100 mg./ft.^{2} of gelatin.

Samples of the coating are sensitometrocally exposed to a multicolor graduated-density test object and then processed in the following sequence:

color-develop	1.0 min. (40° C.)
amplify	1.5 min. (40° C.)
bleach-fix	1.0 min. (40° C.)
wash	1.5 min. (26° C.)
dry	

The respective baths have the following compositions:

Color Developer A

benzyl alcohol	15	ml.
K_2SO_3	4	g.
KBr	0.4	g.
hydroxylamine sulfate	2	g.
4-amino-N-ethyl-N-(2-methoxyethyl-m-toluidine di-paratoluene sulfonate	7.5	g.
K_2CO_3	30	g.
diaminopropanol tetraacetic acid	5	g.
water to 1 liter		
pH 10.1		

Amplifier A

$[Co(NH_3)6]Cl_3$	10	g.
KBr	2	g.
benzyl alcohol	15	ml.
K_2CO_3	7.5	g.
K_2SO_3	2.0	g.
diaminopropanol tetraacetic acid	10.0	g.
water to 1 liter; pH 10.1		

Bleach-Fix

diaminopropanol tetraacetic acid	3	g.
acetic acid	20	ml.
60% $(NH_4)_2S_2O_3$	150	ml.
Na_2SO_3	15	g.
$[Co(NH_3)6]Cl_3$	3	g.
water to 1 liter		
pH 4.5		

EXAMPLE 1–B

A sample (Element 1) of the photographic element of Example 1–A is processed as in Example 1–A wherein Amplifier A is replaced with Amplifier B which contains 700 ml. of Amplifier A and 300 ml. of Color Developer A which simulates the carry-over of color-developer solution carried over during a continuous deep tank-processing step.

EXAMPLE 1–C

Additional samples of the photographic element of Example 1–A are processed as in Example 1–A using Amplifier B with the addition of the ingredients as specified as follows:

Element 2	Amplifier B + 5 ml. ammonium hydroxide
Element 3	Amplifier B + 0.2 g./l. of potassium persulfate
Element 4	Amplifier B + 0.4 g./l. of potassium persulfate
Element 5	Amplifier B + 0.8 g./l. of potassium persulfate
Element 6	Amplifier B + 1.6 g./l. of potassium persulfate
Element 7	Amplifier B + 3.2 g./l. of potassium persulfate

The photographic elements so processed are examined visually and compared with the element processed according to Examples 1–A and 1–B. Elements 1–3 exhibit a contrast and Dmin increase over the control element of Example 1. The contrast and Dmin decrease progressively in Elements 3–6. An increase in fog is observed in Element 7. The fog is apparently due to the presence of an excess of persulfate and an amount of sulfite insufficient to scavenge the excess persulfate.

EXAMPLE 2

A multilayer photographic element is prepared by coating the following layers in order, with the ingredients being listed in mg./ft.^{2}:

1. paper support;
2. layer containing blue-sensitive silver halide emulsion at 16 mg./ft.^{2} based on silver, gelatin at 150, and the yellow image dye-forming coupler α-pivalyl-4-(4-benzyloxyphenylsulfonyl)phenoxy-2-

chloro-5-[α-(2,4-di-tert-amylphenoxy)-butyramido]acetanilide at 75;

3. layer containing gelatin at 80;

4. layer containing a green-sensitive silver halide emulsion at at 10 mg./ft.² based on silver, gelatin at 60, and the magenta image dye-forming color coupler 1-(2,4,6-trichlorophenyl)-3-{5-[-(3-tert-4-hydroxyphenoxy)tetradecaneamido]-2-chloroanilino}-5-pyrazolone at 30;

5. layer containing gelatin at 231;

6. layer containing a red-sensitive silver halide emulsion at 6 mg./ft.² based on silver, gelatin at 65, and the cyan dye image-forming coupler 2-[α-(2,4,-di-tert-amylphenoxy)butyramido]-4,6-dichloro-5-methylphenol at 35;

7. layer containing gelatin at 100.

The photographic element is exposed through a graduated-density test object and processed in the following sequence at 40° C.:

color-develop	1.0 min.
amplify	1.5 min.
bleach-fix	1.0 min.
wash	1.5 min.
dry	

The processing baths have the following composition:

Color Developer		
benzyl alcohol	15	ml.
K_2SO_3	4	g.
KBr	0.4	g.
hydroxylamine sulfate	2	g.
4-amino-N-ethyl-N-(2-methoxyethyl-m-toluidine di-paratoluene sulfonate	7.5	g.
K_2CO_3	30	g.
diaminopropanol tetraacetic acid	5	g.
water to 1 liter		
pH 10.1		
Amplifier C		
benzyl alcohol	15	ml.
$[Co(NH_3)6]Cl_3$	10	g.
KBr	2	g.
K_2CO_3	7.5	g.
K_2SO_3	2.0	g.
diaminopropanol tetraacetic acid	10.0	g.
5-methylbenzotriazole	300	mg.
water to 1 liter		
pH 10.1		
Bleach-Fix		
diaminopropanol tetraacetic acid	3	g.
acetic acid	20	ml.
60% $(NH_4)_2S_2O_3$	150	ml.
Na_2SO_3	15	g.
$[Co(NH_3)6]Cl_3$	3	g.
water to 1 liter		
pH 4.5		

The processed sample (control) is sensitometrically evaluated by recording the H and D curves of the developed yellow, magenta and cyan dye images. the results are shown in Table 1.

Additional samples of the above photographic element are processed by the above procedure wherein Amplifier C additionally contains 5 g./l. of the developing agent 4-amino-N-ethyl-N-(2-methoxyethyl-*m*-toluidine di-paratoluene sulfonate and also $K_2S_2O_8$ and Na_2SO_3 as indicated in the following table.

Similar improvements are also obtained when potassium ferricyanide, potassium perbromate, potassium permanganate or potassium perchlorate are used in Amplifier C in place of the potassium persulfate.

Table 1

Element	$K_2S_2O_8$ g./l.	Na_2SO_3 g./l.	Dmin R	Dmin G	Dmin B	Contrast (γ) R	Contrast (γ) G	Contrast (γ) B
8 (control-Amplifier C)	—	—	0.15	0.14	0.22	2.5	2.9	2.6
9	—	—	0.21	0.22	0.30	3.6	3.8	3.3
10	2.43	—	0.23	0.19	0.27	2.4	3.0	2.8
11	2.43	2.0	0.14	0.16	0.24	2.5	2.9	2.6
12	2.43	4.0	0.20	0.17	0.27	2.6	2.8	2.4
13	2.43	6.0	0.15	0.17	0.24	2.3	2.7	2.3
14	2.43	8.0	0.16	0.16	0.25	2.4	2.6	2.3
15	2.43	10.0	0.18	0.18	0.26	2.6	2.8	2.2

EXAMPLE 3

Additional samples of the photographic element of Example 2 are processed as in that example, except the following amplifier baths are used.

Element	Amplifier
16	Amplifier C of Example 2
17	Amplifier C + 5 g./l. color developer of Example 2
18	Amplifier C + 1.0 ml./l. H_2O_2 (30% solution) and 5 g./l. Na_2SO_3

The processed samples are sensitometrically evaluated. Element 18 has substantially the same H and D curve shape as Element 17, except that Element 18 has a higher Dmin than either Elements 17 or 16.

As can be observed from the foregoing examples, the changes in Dmin, Dmax and Contrast of continuously processed photographic elements are minimized by the addition to the bath of certain alkali metal peracids or alkali metal ferricyanides. These examples also show that other strong oxidants such as hydrogen peroxide do not minimize the changes brought about by excess color developer's presence in the amplifier bath.

The invention has been described in detail with particular reference to 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 process of developing an imagewise-exposed photographic element comprising a support and at least one image dye-providing layer unit thereon which contains a light-sensitive silver halide emulsion having associated therewith a color coupler, which process includes development of the imagewise-exposed silver halide emulsion to provide an imagewise distribution of metallic silver and imbibition of a color-developing agent in said photographic element, and then contacting said photographic element with an amplifier composition which represses substantially additional net silver development, wherein said amplifier solution contains a cobalt(III) metal complex having a coordination number of 6 and said amplifier solution is maintained in contact with said photographic element under condi-

tions which reduce said cobalt(III) to cobalt(II) and in turn oxidize said color-developing agent to provide an increase in dye density with dye produced from said coupler in the areas corresponding to the imagewise distribution of said metallic silver, the improvement comprising including in said amplifier composition a compound which is an alkali metal salt of a peracid or of ferricyanide.

2. A process according to claim **1** wherein said amplifier bath contains a sufficient quantity of development restrainer to repress substantially any further net silver development.

3. A process according to claim **1** wherein said color-developing agent imbibed in said photographic element is an aromatic primary amino compound.

4. A process according to claim **1** wherein said development of the imagewise-exposed silver halide emulsion is carried out in a liquid which is substantially free from cobalt (III) metal complex salts.

5. A process according to claim **1** wherein said amplifier bath is substantially free from silver halide solvents or contains less than 30 percent by weight of the silver halide solvent which would be necessary to fix a silver halide emulsion.

6. A process according to claim **1** wherein the compound is potassium persulfate.

7. A process according to claim **1** wherein said compound is added to said amplifier to maintain the concentration of color-developing agent below 0.5 g./l.

8. A process according to claim **1** wherein said photographic element is a multicolor photographic element comprising at least two color-providing layer units, each of which contains a silver halide emulsion having associated therewith a photographic color coupler in at least a 40 percent stoichiometric excess based on silver.

9. A process according to claim **1** wherein said photographic element is a photographic element comprising at least one image dye-providing layer unit which contains a silver halide emulsion having associated therewith a water-insoluble image dye-providing coupler dissolved in a coupler solvent wherein said coupler is present in at least a 40 percent stoichiometric excess based on effective silver.

10. A process according to claim **8** wherein each of said color-providing layer units contains a silver halide emulsion at a concentration of less than 30 mg. silver/ft.^{2}.

11. A process according to claim **1** wherein the halide concentration of all silver halide emulsions in said element is less than 3 mole percent iodide.

12. A process according to claim **2** wherein said development restrainer is substantially free from ionic iodide groups and free mercapto groups.

13. A process according to claim **2** wherein said development restrainer is the combination of from about 0.01 to about 2 g./l. of a benzotriazole and from 2 g. to about 40 g./l. of an alkali metal bromide.

14. A process according to claim **1** wherein said amplifier bath contains from about 2 g. to about 40 g./l. of an alkali metal bromide.

15. A process according to claim **1** wherein said cobalt(III) metal complex is a cobalt hexammine salt.

16. A process according to claim **1** wherein said amplifier contains at least 0.5 g./l. of a sulfite compound.

17. A process according to claim **1** wherein said compound is a peracid.

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