

1

3,822,129

PHOTOGRAPHIC MATERIALS AND PROCESSES
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ter, N.Y.

No Drawing. Continuation-in-part of abandoned applica-
tion Ser. No. 189,330, Oct. 14, 1971. This application
Aug. 31, 1972, Ser. No. 285,399

Int. Cl. G03c 1/40

U.S. Cl. 96—60 R

26 Claims

ABSTRACT OF THE DISCLOSURE

Photographic materials are provided which comprise a support having coated thereon an image dye-providing layer unit containing a light-sensitive photographic silver halide emulsion layer comprising up to about 320 mg. silver per square meter, a photographic color coupler coated at a concentration of at least two times the weight of the silver and a hydrophilic colloid binder for the silver halide and coupler coated at a coverage of from about 215 to 970 mg. per square meter, the weight ratio of silver to hydrophilic colloid being from 1:2 to 1:20 and the weight ratio of coupler to hydrophilic colloid binder being from 1:½ to 1:2. The photographic elements of the invention are preferably processed in a developer solution comprising a photographic color-developing agent and an oxidizing agent such as a cobalt complex which undergoes redox reaction with the color-developing agent in the presence of metallic silver.

This application is a continuation-in-part of U.S. Ser. No. 189,330 filed Oct. 14, 1971, now abandoned.

This invention relates to photographic materials and processes. In one aspect, this invention relates to improved photographic elements which contain light-sensitive silver halide layers having low coverages of silver halides. In another aspect, this invention relates to photographic elements comprising at least one image dye-providing layer unit which contains a light-sensitive silver halide, a color coupler and a hydrophilic colloid in a ratio to coupler of less than 2:1 (colloid:coupler).

Photographic elements containing a light-sensitive silver halide layer with relatively low coverages of silver have been described in the literature. U.S. Pat. 2,614,808 by Dimsdale and 2,173,737 by Weber disclose methods for intensifying the silver image in a photographic element. More recently disclosures have appeared in Belgian Pat. 742,768 of June 8, 1970, and British Pat. 1,268,126 of photographic elements containing a layer of a silver halide emulsion at a coverage of 50 to 200 mg. of silver per square meter.

Bissonette in U.S. Patent Application Ser. No. 189,289 filed Oct. 14, 1971, entitled "Image-Forming Photographic Processes and Compositions" describes *inter alia* processes for amplifying silver images in light-sensitive silver halide emulsions layers containing photographic color coupler which features the use of developer solutions containing photographic aromatic primary amine color-developing agent together with certain oxidizing agents, for example, cobalt hexammine (III) chloride or other metal complexes having similar reactivity. The procedures described in the Bissonette application are suitable for use in the amplification of photographic elements comprising light-sensitive silver halide emulsion layers coated at low silver coverages and containing color coupler.

While the photographic elements referred to above which contain low silver coverages can produce good results, it would be desirable if further modifications could be made in such elements, and the processing

2

thereof, to increase speed, decrease fog, improve incubation stability before exposure and processing, provide more stable dye images and improve image structure, particularly with regard to sharpness and reduced granularity.

One object of this invention is to provide photographic elements which have silver halide coated at low silver coverages which exhibit increased speed.

Another object of this invention is to provide photographic elements which have low silver coverages which exhibit reduced fog.

A further object of this invention is to provide photographic elements which have low coverages of silver halide and which produce sharp dye images which have relatively low granularity.

A further object of this invention is to provide a process for obtaining dye images which are sharp and which have low granularity, from photographic elements which contain silver halide emulsion layers coated at low silver coverages.

Another object of this invention is to increase the rate at which multicolor photographic elements can be developed.

Still another object of this invention is to provide a process for obtaining reduced fog and increased speed in photographic silver halide emulsions coated at low coverages of silver halide.

Another object of this invention is to provide photographic elements and processes which produce dye images having good stability.

Still other objects of this invention will be apparent from this disclosure and the appended claims.

In accordance with this invention an improvement is provided in photographic elements comprising a support having coated thereon at least one image dye-providing layer unit containing a light-sensitive photographic silver halide emulsion coated at a coverage of up to 320 mg. silver per square meter and a photographic color coupler at a concentration of at least two times the weight of the silver. The improvement in accordance with this invention is achieved by employing a hydrophilic colloid binder for the silver halide and coupler at a concentration of from about 215 to 970 mg. per square meter and maintaining a weight ratio of coupler to hydrophilic colloid in said image dye-providing layer unit of from about 1:½ to 1:2, and a weight ratio of silver to hydrophilic colloid of from 1:2 to 1:20. The reduction in the amount of hydrophilic colloid employed over the levels heretofore suggested in the prior art results in substantial improvement in image structure, particularly with respect to improved sharpness, reduced granularity and better heat stability. In addition, photographic elements in accordance with the invention typically exhibit reduced low fog, improved aging properties, increased speed and developability compared with corresponding elements containing conventional binder coverages of over 1080 mg. per square meter. These results are particularly surprising since photographic elements containing conventional concentrations of silver halide (typically in excess of about 1080 mg. silver per square meter), together with color coupler at levels of from about two to ten times the amount of silver, fail to show significant increases in speed, developability, reduced fog or better image structure when the concentration of hydrophilic colloid is lowered and the elements are processed in conventional color processes.

The photographic elements of this invention can be processed to provide image records by several procedures.

In a highly preferred embodiment, the photographic elements can be processed to provide an image record by the procedures described in aforementioned copend-

ing application U.S. Ser. No. 189,289, entitled "Image-Forming Process and Compositions" filed Oct. 14, 1971, and incorporated herein by reference. In one embodiment of this process, the imagewise-exposed element is contacted with a photographic color-developing agent and an oxidizing agent, such as a cobalt(III) metal complex having a coordination number of 6, until the desired dye density is obtained. The cobalt metal complex is apparently reduced to cobalt(II) in the presence of silver, which appears to act as a catalyst, 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. The formation of oxidized developer can continue as long as there is a sufficient supply of the metal complex and color developer in the presence of the silver catalyst.

In another highly preferred process, a photographic element in accordance with this invention is processed as disclosed by Travis, U.S. Ser. No. 256,071 filed May 23, 1972, entitled "Process for Developing Photographic Elements," now U.S. Pat. 3,765,891. In this process the photographic element in accordance with this invention which has been imagewise-exposed is developed to convert the developable silver halide into metallic silver and form image dye. With negative emulsions the exposed areas will be developable, whereas with direct-positive emulsions or reversal emulsions the unexposed areas will be developed. The photographic element containing undeveloped silver halide and an imagewise distribution of metallic silver is then contacted with a suitable metal complex, such as a cobalt(III) complex having a coordination number of 6, in the presence of a color-developing agent which is preferably imbibed into the element during the color-development step and carried into the bath containing the cobalt metal complex. The color-developing agent can be the same developing agent used to convert the latent image to silver and remain in the coating in transit to the treatment with the metal complex or the color developer can be provided after formation of the silver. Preferably, the photographic element is treated with a liquid bath containing the suitable metal complex and which also contains a silver halide development restrainer, thus allowing this step to proceed in roomlight. By using this process one can observe the dye formation and stop dye formation at the desired dye density.

The elements of this invention can also be processed by using a physical developing agent such as described in Dipple et al., U.S. Pat. 2,750,292 issued June 12, 1956. By treating imagewise-exposed elements of this invention with a solution containing only the color-developing agent and the physical developing agent, rather than the solution described by Dipple et al., it is possible to obtain the multicolor image record.

Additionally, the elements of this invention can be developed by using a variation of the process described in Weber, U.S. Pat. 2,173,739. The elements of this invention which have been imagewise-exposed can be developed in a color developer to produce a low-density dye, bleached partially with a solution as described in Weber, such as a potassium ferricyanide bleach, redeveloped in color developer to intensify the image, etc., until the desired dye density is obtained. Peroxy treatments such as used in British Pat. 1,268,126 could also be adapted in a manner similar to the next above process for use in development of a multicolor element according to this invention.

In still another embodiment, the elements of this invention can be designed for use in and can be processed by the color negative or color reversal processes referred to in U.S. Pat. 3,046,129 by Graham issued July 24, 1962, 3,547,640 by Beckett, and 2,944,900.

The present invention is particularly suitable with multilayer, multicolor photographic elements comprising a support having coated thereon silver halide emulsion layers sensitive to blue, green and red radiation and which

contain, respectively, yellow, magenta and cyan dye-forming photographic couplers. Preferably, at least the green- and red-sensitive layers are coated at the low silver and hydrophilic colloid binder coverages described herein. In certain preferred embodiments of the invention, all three layers contain the silver, coupler and hydrophilic binder coverages and ratios featured in this invention. Particularly useful are photographic elements which have a white-reflective support and which have coated thereon, in the order given, blue-, green- and red-sensitive silver halide emulsion layers. The layers in the multilayer photographic elements described herein can be separated by conventional hydrophilic colloid interlayers or protective overcoating layers, and such layers can contain various other useful addenda, such as ultraviolet absorbers.

Cyan dyes formed in layers having low coverages of hydrophilic colloid exhibit a surprising increase in heat stability over cyan dye images formed in prior-art layers having conventional coverages of hydrophilic colloid. Most yellow and magenta photographic dyes deteriorate faster than cyan dyes in the presence of oxygen. Hence, an especially preferred embodiment of the invention features photographic elements in which the yellow and magenta dyes are formed in layers between the support and the layer which forms the cyan dye. A relatively thick interlayer, such as a hydrophilic colloid layer coated at about 3230 mg. per square meter, can be present between the cyan dye-forming layer and the underlying yellow and magenta dye-forming layers. This thick interlayer protects the yellow and magenta dyes from oxygen-induced deterioration.

In one preferred embodiment of the invention, the total quantity of hydrophilic colloid in the silver halide-containing, image dye-providing layer units is less than about 3230 mg., and preferably less than about 2700 mg., hydrophilic colloid per square meter.

The coverage of the hydrophilic colloid interlayers and overcoatings can vary over a wide range. Generally, the most useful range is from about 540 to 1080 mg. of hydrophilic colloid per square meter although somewhat higher coverages, on the order of from about 1600 to 3230 mg. per square meter, are sometimes desirable when substantial quantities of ultraviolet absorber are to be included in the layer.

The multilayer, multicolor photographic elements of this invention advantageously contain a total of less than about 8100 and more preferably less than about 7000 mg. of hydrophilic colloid binder per square meter. This represents reductions of nearly 50%, in both the total amount of hydrophilic colloid and in the image dye-providing layer units, over the quantities of hydrophilic colloid employed in typical photographic color papers which are in commercial use.

As indicated above, the silver halide emulsions are coated in accordance with this invention at silver coverages of up to about 320 mg. silver per square meter, such as from 11 to 320 mg. per square meter or preferably from about 11 to 270 mg. silver per square meter. Especially good results are obtained with coverages on the order of from about 22 up to about 110 or 160 mg. per square meter of silver for the green- and red-sensitive layers in typical multilayer color films.

In certain embodiments of this invention, the silver halide is coated at coverages less than that which will give undesirable background images, thus avoiding the necessity of bleaching or fixing. In these embodiments, the silver halide is coated at a coverage less than that amount which, if the silver halide were fully exposed and developed, would result in a maximum silver density less than 0.4, and preferably less than 0.2 (such as by using silver halide at silver coverages of less than about 215 and preferably less than 110 mg. per square meter).

Thea photographic elements of this invention contain at least sufficient silver halide to provide a latent image, or at least photolytic silver, upon imagewise exposure.

In one preferred embodiment, the photographic elements of this invention comprise an image dye-providing layer unit wherein the silver halide and the coupler are coated together with the hydrophilic colloid as one layer. Preferably, the photographic element contains three separate image-recording layers with one layer containing silver halide having an effective blue sensitivity, one layer containing silver halide having an effective green sensitivity and one layer containing silver halide having an effective red sensitivity. By effective sensitivity it is understood that the layer as incorporated in the element will record light in that region of the spectrum which may be accomplished by use of spectral-sensitizing dyes, filter layers, etc.

In another embodiment, the color couplers are coated in layers adjacent and preferably contiguous to the silver halide emulsion. In this embodiment, the silver halide emulsion layer and the layer or layers containing the color coupler can be considered to function together to provide an image dye-providing layer unit. Preferably, the silver halide emulsion layer has associated contiguous therewith a coupler-containing layer on each side thereof. In a typical multicolor photographic element at least two image dye-providing layer units will be provided which each record light dominantly in different regions of the light spectrum and have color couplers associated therewith which will produce a dye having a predominant visible light absorption in the region of the visible spectrum corresponding to the effective spectral sensitivity of the associated silver halide emulsion. In this embodiment, the dye image-providing layer unit contains the silver halide, coupler and hydrophilic colloid in the ratios specified in accordance with this invention. The image dye-providing layer units can be separated from each other by interlayers, barrier layers, etc. However, good image discrimination can be obtained where the respective image-dye-providing layer units of a multicolor element are coated contiguous to each other.

Silver halide emulsions which can be used in the image dye-providing layer units in accordance with this invention can comprise, for example, silver chloride, silver bromide, silver bromiodide, silver chlorobromide, silver chloriodide, silver chlorobromiodide crystals or mixtures thereof. The emulsions may be coarse- or fine-grain emulsions prepared by any of the well-known techniques, e.g., single-jet emulsions such as those described in Trivelli and Smith, *The Photographic Journal*, vol. LXXIX, May, 1939 (pp. 330-338), double-jet emulsions such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in U.S. Pats. 2,222,264 by Nietz et al. issued Nov. 19, 1940, 3,320,069 by Illingsworth issued May 16, 1967, and 3,271,157 by McBride issued Sept. 6, 1966. Surface-image emulsions may be used or internal-image emulsions may be used such as those described in U.S. Pats. 2,592,250 by Davey et al. issued May 8, 1952, 3,206,313 by Porter et al. issued Sept. 14, 1965, 3,367,778 by Berriman issued Feb. 6, 1968, and 3,447,927 by Bacon et al. issued June 3, 1969. If desired, mixtures of surface- and internal-image emulsions may be used as described in U.S. Pat. 2,996,382 by Luckey et al. issued Aug. 15, 1961. The emulsions may be regular-grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, vol. 12, No. 5, Sept./Oct., 1964, pp. 242-251. Negative-type emulsions may be used or direct-positive emulsions may be used such as those described in U.S. Pats. 2,184,013 by Leermakers issued Dec. 19, 1939, 2,541,472 by Kendall et al. issued Feb. 13, 1951, 3,367,778 by Berriman issued Feb. 6, 1968, 3,501,307 by Illingsworth issued Mar. 17, 1970, 2,563,785 by Ives issued Aug. 7, 1951, 2,456,953 by Knott et al. issued Dec. 21, 1948, and 2,861,885 by Land issued Nov. 25, 1958, British Pat. 723,019 by Schouwenaars issued Feb. 2, 1955, and French Pat. 1,520,821 by Illingsworth

et al. issued Mar. 4, 1968. Preferably, the emulsions are negative, developing-out-type silver halide emulsions.

Generally, each of the color-providing layer units of the photographic elements of this invention contains a light-sensitive silver salt which is preferably a silver halide. In one preferred embodiment, at least two of the color-providing layer units each comprise a silver salt at a concentration of up to 320 mg. of silver/m.². However, while the developable silver is preferably present at concentrations based on silver of less than 320 mg./m.², it is possible to coat blended emulsions at higher coverages within this embodiment as long as no more than 320 mg./m.² of silver develops; for example, such emulsions may contain silver halide grains which are relatively light-insensitive or may contain development 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, emulsions containing relatively light-insensitive grains or development inhibitors 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 of this invention contain at least two color-providing layer units, each containing a silver halide emulsions, defined in terms of "effective coverage" and developability as one which, when it is fully exposed and processed for about 1 minute at 100° F. in Developer A, as follows:

Benzyl alcohol	-----ml.	10
K ₂ SO ₃	-----g	2
KBr	-----g	0.4
Hydroxylamine sulfate	-----g	2
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-		
paratoluenesulfonate	-----g	5
K ₂ CO ₃	-----g	30
Na ₄ EDTA	-----g	5
Water to 1 liter		
pH 10.1 at 24° C.		

will provide less than 320 mg. of metallic silver/m.² and preferably less than 160 mg./m.². It is understood that the term "effective silver" refers to that amount of silver which is developed 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, 3000° K. lamp for about 10 seconds (total exposure at the film plane=11.3×10⁴ ergs./cm.²).

Photographic color couplers are employed in accordance with the invention at a concentration of at least 2 times, such as from 3 to 20 times, the weight of the silver in the silver halide emulsion. Weight ratios of coupler-to-silver coverage which are particularly useful are from 3 to 15 parts by weight coupler to 1 part by weight silver. Advantageously, the coupler is present in an amount sufficient to give a density of at least 1.7 and preferably at least 2.0. Preferably, the difference between the maximum density and the minimum density (which can comprise unbleached silver) is at least .6 and preferably at least 1.0.

As used herein, the term "photographic color coupler" includes any compound which reacts (or couples) with the oxidation products of primary aromatic amino developing agent on photographic development to form a dye, and are nondiffusible in a hydrophilic colloid binder (e.g., gelatin) useful for photographic silver halide. The couplers can form diffusible or non-diffusible dyes. Typical useful color couplers include phenolic, 5-pyrazolone and open-

chain ketomethylene couplers. Specific cyan, magenta, and yellow color couplers which can be employed in the practice of this invention are described in Graham et al., U.S. Pat. 3,046,129 issued Jan. 24, 1962, 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 the techniques described by U.S. Pats. 2,322,027 by Jelley et al. issued June 15, 1943, or 2,801,171 by Fierke et al. issued July 30, 1957. 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. The useful couplers include Fischer-type incorporated couplers such as those described in Fischer, U.S. Pat. 1,055,155 issued Mar. 4, 1913, and particularly non-diffusible Fischer-type couplers containing branch carbon chains, e.g., those referred to in the references cited in Frohlich et al., U.S. Pat. 2,376,679 issued May 22, 1945, column 2, lines 50-60. Particularly useful in the practice of this invention are the nondiffusible color couplers which form nondiffusible dyes.

In one highly preferred embodiment of the invention, the photographic elements comprise a support having thereon at least one image dye-providing layer unit containing a light-sensitive silver salt, preferably silver halide, having associated therewith a stoichiometric excess of coupler of at least 40 percent and at least preferably 70 percent. The equivalency of color couplers is known in the art; for example, a 4-equivalent coupler requires 4 moles of oxidized color developer, which in turn requires 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 invention, 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 on a stoichiometric basis with the developable silver and preferably a 70 percent excess of said coupler. In one highly preferred embodiment, at least a 110 percent excess of the coupler is present in said dye image-providing layers based on silver. Preferably, the coupler-to-silver ratio is based on effective silver as defined herein. The ratio can also be defined as an equivalent excess with a coupler-to-silver ratio of at least 1.4:1, and preferably at least 1.7:1 (i.e., 2:1 being a 100 percent excess). In certain 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. Weight ratios of coupler-to-silver coverage which are particularly useful are from 4 to 15 parts by weight coupler to 1 part by weight silver. Advantageously, the coupler is present in an amount sufficient to give a density of at least 1.7 and preferably at least 2.0. Generally, the couplers utilized in the elements of this invention will have an equivalent weight of less than 1500 and preferably less than 1000 (i.e., molecular weight divided by number of functional coupling sites).

It is realized that the density of the dye may vary with the developing agent combined with the respective coupler, and accordingly the quantity of coupler can be adjusted to provide the desired density. Preferably, each layer unit contains at least 1×10^{-4} moles/m.² of color coupler.

Advantageously, the photographic color couplers utilized are selected so that they will give a good neutral dye image. Preferably, the cyan dye formed has its major visible light 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.

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 materials 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.

The light-sensitive silver halide grains and photographic color couplers can be dispersed in colloids, which can be employed alone or in combination. Suitable hydrophilic materials include both naturally occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like, and synthetic polymeric substances such as water-soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like. Suitable thickening agents can be added to the coating melts.

The described photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also be used alone or in combination with other hydrophilic, water-permeable colloids or synthetic polymeric compounds.

The light-sensitive layers of this invention are coated in such a manner that the hydrophilic colloid binder for the silver halide is coated at a concentration less than about 1080 mg./m.², such as about 215 to 970 mg./m.² or, preferably, from about 215 to 800 mg./m.².

It is desirable to maintain a weight ratio of photographic color coupler to hydrophilic colloid of from about 1:½ to 1:2. In addition, it is desirable to maintain a weight ratio of silver to hydrophilic colloid of from 1:2 to 1:20, and preferably from 1:3 to 1:15. These ratios provide coatings having suitable physical properties. When weight ratios of silver to hydrophilic colloid of less than about 1:2 and coupler to hydrophilic colloid ratios of less than about 1:½ are utilized, the coatings become extremely soft. When ratios of silver to hydrophilic colloid higher than about 1:20 are utilized, the advantages of the invention with respect to increased sharpness, improved granularity, developability, higher speed and reduced fog tend to be minimized. Weight ratios of coupler to hydrophilic colloid higher than 1:2 tend to result in a loss of sharpness and granularity and decrease the improved dye stability.

The ratios of silver to coupler referred to above are desirable to obtain a suitable sensitometric photographic curve shape and sufficient dye density.

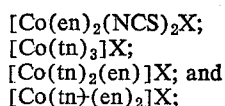
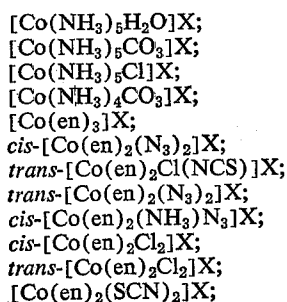
The elements of this invention are advantageously processed in accordance with the procedures described in aforementioned U.S. Ser. Nos. 189,289 by Bissonette filed Oct. 14, 1971, and 256,071 by Travis filed May 23, 1972, now U.S. Pat. 3,765,891, which are both incorporated by reference. The various oxidizing agents, or oxidants, which can be utilized in combination with photographic aromatic primary amino color-developing agents to develop the elements of this invention should have a reactivity with the color-developing agent generally similar to cobalt hexammine(III). The preferred oxidants are the metal complexes, such as a transition metal complex, e.g., a Group VIII metal complex, or a complex of a metal of Series 4 of the Periodic Table appearing on pp. 54 and 55 of Lange's *Handbook of Chemistry*, 8th edition, published by Handbook Publisher, Inc., Sandusky, Ohio, 1952. Such complexes feature a molecule having a metallic atom or ion. This metallic atom or ion is surrounded by a group of atoms, ions of other molecules which are generically referred to as ligands. The metallic atom or ion in the center of these complexes is a Lewis acid; the ligands are Lewis bases. Werner complexes are well-known examples of such complexes. The useful metal salts are typically capable of existing in at least two valent states. In a preferred aspect of the invention, the metal complexes are those referred to by American chemists as "inert" and by European chemists as "robust." Particularly useful are complexes of a metal ion with a ligand which, when a test sample thereof is dissolved at .1 molar concentration at 20° C. in an inert solvent solution also containing .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 minute and preferably for at least several hours, such as up to 5 hours 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 about 8 to 13. Many 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 radioactive isotopes to tag ligands, are well-known in the art. See, for example, Taube, *Chem. Rev.*, vol. 50, p. 69 (1952) and Basolo and Pearson, *Mechanisms of Inorganic Reactions, 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. 4789 (1951). 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 minute. 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.

Preferred metal complexes in accordance with this invention have coordination numbers of 6 and are known as octahedral complexes. Cobalt complexes are especially useful in the practice of this invention. Most square planar complexes (which have a coordination number of 4) are rather labile, although some Group VIII metal square planar complexes, particularly platinum and palladium square planar complexes, exhibit inertness to rapid ligand exchange.

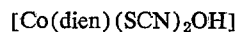
A wide variety of ligands can be used with a metal ion to form suitable metal complexes. Nearly all Lewis bases (i.e., substances having an unshared pair of electrons) can be ligands in metal complexes. Some typical useful ligands include the halides, e.g., chloride, bromide, fluoride, nitrite, water, amino, etc., including 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), diethylenetriamine (dien), triethylenetetraamine (trien), ammine (NH_3), nitrate, nitrite, azide, chloride, thiocyanate, isothiocyanate, water, carbonate and propylenediamine (tn). 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:



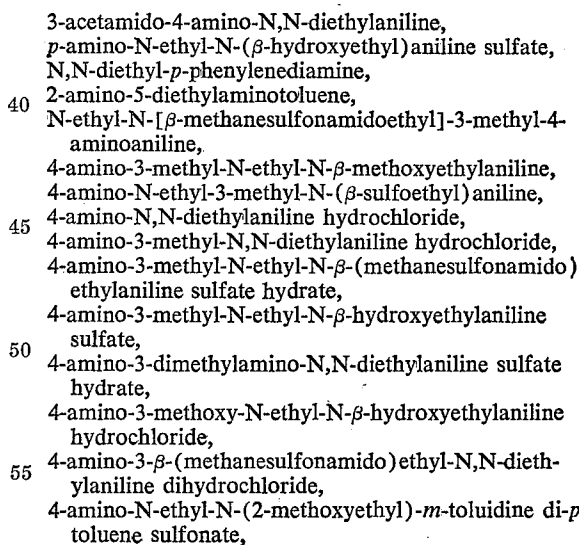
wherein X represents one or more anions determined by the charge neutralization rule. Complexes containing oxidized noble metals or ferromagnetic metals such as complexes of Cr^{III} , Fe^{III} , Rh^{III} , Pt^{IV} , Pd^{IV} and Ir^{III} , which have reactivities similar to the complexes listed above, could be used in the practice of this invention. The redox equilibria published in *Stability Constants of Metal-Ion Complexes*, Sillen and Martell, published by The Chemical Society, Burlington House, London, England (1964), indicate that other complexes have reactivities similar to the cobalt complexes mentioned above.

With many complexes, such as cobalt hexammine, the uncoordinated anions selected can substantially effect the reducibility of the complex. The following anions are listed in the order to those which give increasing stability to cobalt hexammine complexes: bromide, chloride, nitrite, perchlorate, acetate, carbonate, sulfite and sulfate. Other anions will also effect the reducibility of the complex. These uncoordinated anions should, therefore, be chosen to provide complexes exhibiting the desired degree of reducibility. Some other uncoordinated anions include hydrochloride, nitrate, thiocyanate, dithionate and hydroxide. Neutral complexes such as



are useful, but positively charged complexes are generally preferred.

The most useful aromatic primary amine color-developing agents include



and the like. See Bent et al., *JACS*, vol. 73, pp. 3100-3125 (1951) for further typical, useful color-developing agents. It will be appreciated that many of the subject reducing agents are most effective at high pH, such as a pH from about 8 to 13.

The elements of this invention can be processed to provide negative or reversal dye images, for example, using a procedure generally similar to that described in Graham et al., U.S. Pat. 3,046,129. In reversal processes, it is desirable to remove or deactivate the initial negative silver image prior to contacting the film with color-developer solution containing metal complex in order to prevent undesired interaction between developer, metal complex and the initial silver image.

The image dye-providing layer units as described herein are also useful in diffusion transfer elements. The image

dye-providing layer unit can contain initially immobile couplers or releasable dyes, or the couplers can be initially mobile. Typical image transfer systems where the image dye-providing layer units can be used include U.S. Pats. 2,983,606 by Rogers issued May 9, 1961; 3,227,552 by Whitman issued Aug. 27, 1964, 3,443,940 by Bloom and 3,443,943 by Rogers, both issued May 13, 1969, and 3,415,644, 3,415,645 and 3,415,640, all by Land issued Dec. 10, 1968, Belgian Pat. 757,959 by Cole issued Apr. 23, 1971, and U.S. Ser. No. 176,751 by Fleckenstein filed Aug. 8, 1971, now abandoned, and the like.

The photographic emulsions employed herein can be washed in accordance with conventional procedures and can contain sensitizers, antifoggants, stabilizers, hardeners, plasticizers, lubricants, surfactants, spectral-sensitizing dyes and other similar photographic addenda. The photographic elements can also contain layers which may contain various antistatic or conducting layers, filters, brightening agents and the like. The photographic layers can be coated by typical procedures including dip coating, air-knife coating, curtain coating, or extrusion coating using hoppers of the type described in Beguin, U.S. Pat. 2,681,294 issued June 15, 1954, or by other coating procedures. The elements of this invention are also suitable for use in colloid transfer and color image transfer processes of the type heretofore described in the art.

The photographic image dye-providing layer units can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly (vinyl acetal) film, polystyrene film, poly (ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an α -olefin polymer, particularly a polymer of an α -olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like. The color-providing layer units can be coated on the same side of the support or on opposite sides of the support where desired, such as when using a transparent film support. Photographic elements can be coated with layer arrangements as used for many multicolor elements or they can be coated in the format used for X-ray elements and the like. In the latter case, the effective spectral sensitivity of the image dye-providing layer units may be the same or it may be different, depending on which areas of the electromagnetic spectrum are desired to be recorded.

The following examples are included for a further understanding of the invention.

Example 1 illustrates the increase in speed, contrast and dye density, and the reduced fog obtained using the photographic elements and processes of this invention.

Example 1

A series of gelatin silver chlorobromide emulsions (15 mole percent Cl^- and 85 mole percent Br^-) containing a phenolic cyan dye-forming photographic coupler, such as 2 - [α - (2,4 - di - *tert*-amylphenoxy)butyramido]-4,6-dichloro - 5 - methylphenol, is coated on a paper support at a silver coverage 5.25 mg./ft.² and a coupler coverage of 35 mg./ft.². The coupler is dispersed in 17.5 mg. of a coupler solvent, such as dibutyl phthalate, per ft.². The amount of gelatin varies as shown in the following table:

	Gelatin, mg./ft. ²	Ratio of Ag^+ to gelatin	Ratio of coupler to gelatin
Coating 1 (prior art).....	240	1:46	1:6.5
Coating 2 (invention).....	60	1:11.5	1:1.6
Coating 3 (invention).....	40	1:8	1:1.1

The coatings are given a stepped exposure to red light and then are developed for 7 minutes at 30° C. in the following developer:

Water	ml.	800
Benzyl alcohol	ml.	10
Na_2SO_3	g.	2
NaCl	g.	0.5
NaBr	g.	0.5
Hydroxylamine sulfate	g.	2
4 - amino - 3 - methyl-N-ethyl-N- β -methoxyethyl-aniline - di - paratoluene sulfonate salt	g.	5
Na_2CO_3 (anh.)	g.	30
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	g.	1.6
Water to 1 liter		
pH 10.1 at 75° F.		

The elements are then bleached, fixed and dried, and the coatings in accordance with the invention are compared with the prior-art coating (Coating 1) with the following results:

TABLE 1

	Fog	Speed	Contrast	D_{max}
Coating 2.....	-.23	+13	+1.02	+2
Coating 3.....	-.24	+15	+1.92	+2

A visual comparison shows that the images in Coating 1 (prior-art, high gelatin concentration) are more granular and less sharp than in Coatings 2 and 3 of the invention which employ low gelatin concentrations. Generally, similar results are obtained in each layer of multilayer coatings, such as the typical red-, green- and blue-sensitive silver halide emulsion layers containing, respectively, cyan, magenta and yellow dye-forming photographic color couplers. Also, generally similar results are obtained when the photographic couplers utilized are the Fischer-type couplers, e.g., the nondiffusible Fischer-type couplers containing branch carbon chains, such as those described in Frohlich et al., U.S. Pat. 2,371,679 issued May 22, 1945. Also, generally similar results are obtained when other colloids are substituted for gelatin.

The unexpected increase in heat stability of dyes formed in the low vehicle emulsions of the invention is illustrated in Example 2.

Example 2

A series of coatings is prepared as described in Example 1, but using the gelatin, silver and coupler concentration shown in Table 2. The dye loss, at a density of 1.0, is measured after storage in a dry oven at 77° C. for 2 weeks. The percentage dye loss is reported in Table 2 for each coating:

TABLE 2

Coating No.	Gelatin (mg./m. ²)	Silver (mg./m. ²)	Coupler (mg./m. ²)	Dye stability (percent loss)
1 (prior art).....	2,600	185	375	39
2 (prior art).....	1,300	185	375	39
3.....	640	185	375	33
4.....	440	185	375	28
5 (prior art).....	2,600	55	375	39
6 (prior art).....	1,300	55	375	35
7.....	640	55	375	31
8.....	350	55	320	23
9.....	235	55	215	22

The results in the above table show the increase in cyan dye stability obtained when the vehicle coverage is reduced to amounts below about 970 mg./m.². This is unexpected since gelatin is generally regarded as contributing to dye stability.

Example 3

Two multilayer coatings are prepared at the concentrations (in mg./m.²) as shown in Table 3. The silver halide in the light-sensitive layers is silver chlorobromide (about 15 mole percent chloride and 85 mole percent bromide) having an average grain size of about .3 micron in the magenta and cyan layers and an average grain size of

13

about 1.2 in the yellow layer. The cyan coupler is the same as the one identified in Example 1. The yellow dye-forming coupler is α -[4 - (4 - benzyloxyphenylsulfonfyl)phenoxy]- α -pivalyl - 2 - chloro - 5 - [α -(2,4-di-*tert*-amylphenoxy)butyramido]acetanilide and the magenta coupler is 1 - (2,4,6 - trichlorophenyl) - 3 - [2 - chloro-5-(α -{4-hydroxy - 3 - *tert*-butylphenoxy}tetradecanamido)amino]-5-pyrazolone. The cyan and yellow couplers are dissolved in dibutyl phthalate coupler solvent at a weight ratio of about 1:½ and 1:¼ (coupler:solvent) respectively, and the magenta coupler is dissolved in tricresyl phosphate coupler solvent at a weight ratio of 1:½ (coupler:solvent).

TABLE 3

Layer	Gelatin		Coupler		Silver	
	Coat-ing #1	Coat-ing #2	Coat-ing #1	Coat-ing #2	Coat-ing #1	Coat-ing #2
Overcoat.....	1,080	860				
Cyan.....	1,700	650	375	375	55	55
Interlayer.....	2,500	1,700				
Magenta.....	2,300	900	540	540	85	85
Interlayer.....	1,080	860				
Yellow.....	2,150	970	800	800	215	215
Support.....						

The coatings are given red-, green- and blue-sensitometric exposure, developed with the developer solution used in Example 1, bleached, fixed, washed and dried. The fog values are given in Table 4:

TABLE 4

	Prior-art coating 1	Invention coating 2	Δ Fog
Red.....	.24	.18	-.06
Green.....	.17	.16	-.01
Blue.....	.22	.19	-.03

The above data show a significant reduction in fog when the vehicle concentration is lowered in photographic emulsion layers having low coverages of silver. The images in Coating 2 of the invention have less granular images than those of prior-art Coating 1 which contains conventional coverages of colloid. Generally similar results are obtained when couplers utilized are Fischer-type couplers, such as those described in Frohlich et al., U.S. Pat. 2,376,679 issued May 22, 1945. Also, generally similar results are obtained with different oxidants, such as

[Co(en)₂dien]Cl₂·HCl,
[Co(NH₃)₄(H₂O)₂](ClO₃)₃,
[Co(NH₃)₅H₂O](ClO₄)₃,
trans-NH₄[Co(NH₃)₂(NO₂)₄],
[Co(NO₂)₃(NH₃)₃],
[Co(NH₃)₄CO₃]NO₃,
[Co(NH₃)₅CO₃]NO₃,
trans-[Co(en)₂Cl₂]Cl·HCl,
trans-[Co(en)₂(N₃)(NO₂)]S₂O₈,
[Co(en)₂(N₃)₂]NO₃,
[Co(dien)(SCN)₂(OH)],
[Co(trien)(NO₂)₂]NO₃·H₂O,
cis-[Co(trien)Cl₂]Cl,
[Co(en)₂(NO₂)₂](ClO₄)₃,
[Co(trien)(N₃)₂]NO₃, and
[Co(en)₂(NH₃)₂]Cl₃.

Example 4

One sample of each of the two multilayer coatings prepared and exposed as described in Example 3 are processed in the following sequence:

Color-develop 0.5 min.—40° C.
Amplify 1.5 min.—40° C.
Bleach-fix 1 min.—40° C.
Wash 1.5 min.—26° C.

14

The processing baths are as follows:

Color Developer

Benzyl alcohol ml. 15
K₂SO₃ g. 4
KBr g. 0.4
Hydroxylamine sulfate g. 2
4-amino-N-ethyl-N-(2-methoxyethyl)-*m*-toluidine di-
para-toluenesulfonate g. 7.5
K₂CO₃ g. 30
Diaminopropanol tetraacetic acid g. 5
Water to 1 liter
pH 10.1

Amplifier

Benzyl alcohol ml. 15
[Co(NH₃)₆]Cl₃ g. 10
KBr g. 2
K₂CO₃ g. 7.5
K₂SO₃ g. 2.0
Diaminopropanol tetraacetic acid g. 10.0
Water to 1 liter
pH 10.1

Bleach-Fix

Diaminopropanol tetraacetic acid g. 3
Acetic acid ml. 20
60% (NH₄)₂S₂O₃ ml. 150
Na₂SO₃ g. 15
[Co(NH₃)₆]Cl₃ g. 3
Water to 1 liter
pH 4.5

The low gelatin coating (Coating 2) shows improvements over the high gelatin coating (Coating 1) when processed as above which are similar to those mentioned in Example 3.

Example 5

The coatings of Example 3 are kept for 1 year under average room keeping at a temperature of 24° C. and then processed as described in Example 4. The same advantages are observed as listed in Example 3, especially with regard to the cyan image. In particular, it is observed that the minimum densities of the image dyes in the high-gelatin coating are much higher than in the low-gelatin coating as shown in the following table:

TABLE 5

	High-gelatin coating, D _{min.}	Low-gelatin coating, D _{min.}
50 Cyan.....	.22	.17
Magenta.....	.26	.20
Yellow.....	.30	.23

In certain embodiments of this invention it is desirable to coat the silver halide layer separately and to have contiguous on each side thereof a layer containing the color coupler, which layers form the image dye-providing layer unit. Examples 6 and 7 set forth structures of this type where improved photographic properties such as speed, granularity and the like are observed.

Example 6

Three film elements containing magenta image dye-providing layer units are coated on a cellulose acetate film support containing a carbon black antihalation layer. The elements are prepared as follows:

Element A (control):

1. support;
2. layer containing 24 mg./ft.² of AgClBr based on Ag, 133 mg./ft.² of 1-(6-chloro-2,4-dimethylphenyl) - 3 - [α -(*m*-pentadecylphenoxy)butyramido]-5-pyrazolone (coupler A) dispersed 1:1 in tricresyl phosphate, and 220 mg./ft.² of gelatin.

Element B:

1. support;

15

2. layer containing 66 mg./ft.² of coupler A dispersed 1:1 in tricresyl phosphate and 73 mg./ft.² of gelatin;
3. layer containing 24 mg./ft.² of AgClBr based on Ag and 73 mg./ft.² of gelatin;
4. layer containing 66 mg./ft.² of coupler A dispersed 1:1 in tricresyl phosphate and 73 mg./ft.² of gelatin.

Element C:

1. support;
2. layer containing 66 mg./ft.² of coupler A dispersed 1:1 in tricresyl phosphate and 66 mg./ft.² of gelatin;
3. layer containing 24 mg./ft.² AgClBr based on Ag and 10 mg./ft.² of gelatin;
4. layer containing 66 mg./ft.² of coupler A dispersed 1:1 in tricresyl phosphate and 66 mg./ft.² of gelatin.

Each of the elements is exposed in a sensitometer and processed at 38° C. as follows:

Element A

	Minutes
Develop -----	2
Bleach-fix -----	2
Wash -----	2
Stabilize -----	2

Elements B and C

	Minutes
Developer-amplifier -----	2
Bleach-fix -----	2
Wash -----	2
Stabilizer -----	2

The developer has the formula:

	G./l.
Na ₂ SO ₃ -----	1.0
4 - amino - 3 methyl - N,N - diethylaniline hydrochloride -----	3.0
Na ₂ CO ₃ -----	20.0
NaBr -----	1.0
Ethylenediaminetetraacetic acid, sodium salt -----	1.0
H ₂ O to 1 liter	
pH 10.75 at 75° F.	

The developer-amplifier has the same formula as the developer next above with the addition of 1.6 g./l. of [Co(NH₃)₆]Cl₃.

The bleach-fix is:

Diaminopropanol tetraacetic acid -----g--	3
Acetic acid -----ml--	20
60% (NH ₄) ₂ S ₂ O ₃ -----ml--	150
Na ₂ SO ₃ -----g--	15
[Co(NH ₃) ₆]Cl ₃ -----g--	3
Water to 1 liter	
pH 4.5	

The speeds of the developed images are substantially identical and the fog is within 0.06 density unit for all samples. The gamma in all cases is approximately 1.0. The RMS granularity is measured at equal density points by the procedure described by Altman, *Applied Optics*, "The Measurements of RMS Granularity," pp. 35-38, 1963, and is recorded for each sample as $\sigma(D)$.

RMS Granularity— $\sigma(D)$

Element A -----	.0065
Element B -----	.0044
Element C -----	.0045

There is a substantial improvement in granularity with Elements B and C with equivalent speed and sharpness.

Similar improvements in granularity are obtained when the yellow image dye-providing layer, the cyan image dye-providing layer and the magenta image dye-providing layer of a multicolor integral-layer photosensitive silver

16

halide element are coated with layers containing the respective coupler contiguous on each side of the silver halide emulsion layer.

Example 7

Two film elements containing magenta image dye-providing layer units are coated on a paper support as follows:

Element A (control):

1. support;
2. layer containing 159 mg./ft.² of gelatin, 35 mg./ft.² of a-[α -(2,4-di-*tert*-amylphenoxy)butyramido]-4,6-dichloro-5-methyl phenol dispersed 1:1 in tricresyl phosphate, and 5.25 mg./ft.² of AgClBr based on silver.

Element B:

1. support;
2. layer containing 80 mg./ft.² of gelatin and 18 mg./ft.² of 2-[α -(2,4-di-*tert*-amylphenoxy)butyramido] - 4,6 - dichloro-5-methyl phenol dispersed 1:1 in tricresyl phosphate;
3. layer containing 5.25 mg./ft.² of AgClBr based on silver and 2 mg./ft.² of gelatin;
4. layer containing 80 mg./ft.² of gelatin and 18 mg./ft.² of 2-[α -(2,4-di-*tert*-amylphenoxy)butyramido] - 4,6 - dichloro-5-methyl phenol dispersed 1:1 in tricresyl phosphate.

The elements are given a red-light exposure on a sensitometer and developed to identical gamma and fog by the process of Example 1. Element B is 0.3 log exposure faster than Element A.

Example 8

Multilayer coatings are made as described in Example 3 wherein the blue-, green- and red-sensitive silver halide emulsions contain respectively 16, 10 and 6 mg. of silver/ft.² of coating. The concentrations of the couplers are varied according to the matrix as follows:

	Coupler concentration, mg./ft. ²	Coupler equivalency/Ag equivalents
Cyan-----	21, 35	1.52-2.54
Magenta-----	25, 30, 55	1.28-3.0
Yellow-----	55, 60, 75, 90, 109, 120	.82-1.76

Imagewise-exposed samples are processed by the procedures of Examples 3 and 4. Good color reproduction is obtained with all samples with the best results occurring when the coupler-to-actual-silver ratio is 1:1.4 or greater, especially using this ratio in the cyan and magenta layers.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. In a photographic element comprising a support having coated thereon at least one image dye-providing layer unit containing a light-sensitive photographic silver halide emulsion coated at a coverage of up to 320 mg. silver/m.² and a photographic color coupler at a concentration of at least two times the weight of the silver, the improvement wherein said silver halide and said coupler are dispersed in said layer unit in a hydrophilic colloid with said hydrophobic colloid coated at a coverage of from about 215 to 970 mg./m.², the weight ratio of silver to hydrophilic colloid being from 1:2 to 1:20 and the weight ratio of said coupler to said hydrophilic colloid being from 1:½ to 1:2.

2. A photographic element as defined in Claim 1 wherein said hydrophilic colloid is coated at a coverage of about 215 to 800 mg./m.², said silver halide is coated at a silver coverage of about 55 to 270 mg./m.² and said

coupler is coated at a concentration of about 215 to 1080 mg./m.².

3. In a photographic element comprising a support having coated thereon separate, overlying image dye-providing layer units which respectively contain silver halide emulsion sensitive to blue, green and red radiation and, respectively, yellow, magenta and cyan dye-forming photographic color couplers, and said green and red light-sensitive silver halide emulsion layers are each coated at a silver coverage of up to about 270 mg./m.² and contain photographic color coupler at a concentration of from 3 to 15 times the weight of the silver therein, the improvement wherein said green and red silver halide-containing layer units each comprise a hydrophilic colloid coated at a coverage of from about 215 to 1080 mg./m.², the weight ratio of said silver to said hydrophilic colloid being from about 1:2 to 1:20 and the weight ratio of said coupler to said hydrophilic colloid is from about 1:½ to 1:2.

4. A photographic element according to Claim 1 wherein said image dye-providing layer unit is a single layer containing said silver halide emulsion and said coupler coated together with said hydrophilic colloid.

5. A photographic element according to Claim 1 wherein said image dye-providing layer unit comprises a layer containing a silver halide emulsion having layers contiguous on each side thereof containing said coupler.

6. A photographic element according to Claim 1 wherein said image dye-providing layer contains at least a 40% stoichiometric excess of image dye-providing color coupler based on effective silver.

7. A multicolor photographic element according to Claim 1 which contains a cyan image dye-providing layer unit and a magenta image dye-providing layer unit wherein the respective color coupler in said layer unit is present in at least a 40% stoichiometric excess based on silver coverage.

8. In a photographic element comprising a support having coated thereon separate, overlying silver halide emulsion layers sensitive to blue, green and red radiation, respectively, each of said emulsion layers being coated at a coverage of up to about 320 mg. silver/m.², said layers containing, respectively, yellow, magenta and cyan dye-forming photographic color couplers in a concentration, in each of said layers, of at least three times the weight of the silver therein, the improvement wherein each of said silver halide emulsion layers contains from about 215 to 970 mg. of a hydrophilic colloid binder/m.², the weight ratio of silver to hydrophilic colloid in each of said layers being from 1:2 to 1:20, and the weight ratio of the coupler to hydrophilic colloid in each of said layers is from 1:½ to 1:2.

9. A photographic element as described in Claim 8 wherein said hydrophilic colloid is gelatin, said hydrophilic colloid is coated, in each layer, at a coverage of about 215 to 800 mg./m.², the silver coverage in each of said layers is from about 22 to 160 mg./m.², and said blue- and green-sensitive layers are coated between said support and said red-sensitive layer.

10. A photographic element comprising a support having coated thereon, in the order given, separate, overlying silver halide emulsion layers sensitive to blue, green and red radiation, respectively, each of said emulsion layers being coated at a silver coverage of up to about 320 mg./m.², said layers containing, respectively, yellow, magenta and cyan dye-forming couplers in a concentration, in each of said layers, of from 3 to 15 times the weight of the silver therein, each of said silver halide emulsion layers containing from about 215 to 970 mg. of gelatin binder/m.² and a weight ratio of coupler to hydrophilic colloid of from 1:½ to 1:2.

11. A photographic element as described in Claim 10 wherein the total amount of gelatin in said light-sensitive silver halide layers is less than about 2700 mg./m.².

12. A photographic element as described in Claim 11 wherein said photographic element contains a gelatin interlayer between said blue- and green-sensitive silver halide emulsion layers, said gelatin interlayer being coated at a coverage of from about 540 to 1080 mg. gelatin/m.², an ultraviolet-absorbing layer comprising gelatin and an ultraviolet absorber coated between said green- and red-sensitive silver halide emulsion layers, said ultraviolet-absorbing layer containing from about 1500 to 2150 mg. gelatin/m.², and a gelatin overcoat coated at a coverage of from about 540 to 1080 mg./m.², the total amount of gelatin in said photographic element being less than about 8100 mg./m.².

13. A process for providing photographic images in an exposed photographic element comprising a support having coated thereon at least one image dye-providing layer unit comprising a light-sensitive photographic silver halide emulsion coated at a coverage of up to about 320 mg. silver/m.² and a color coupler at a concentration of at least two times the weight of the silver, the silver halide and the coupler being dispersed in a hydrophilic colloid coated on said support at a coverage of from about 215 to 970 mg./m.², the weight ratio of silver to hydrophilic colloid being from 1:2 to 1:20 and the weight ratio of said coupler to said hydrophilic colloid being from 1:½ to 1:2, which comprises developing said exposed photographic element with a developer solution comprising a photographic aromatic primary amino color-developing agent and an oxidizing agent which undergoes redox reaction with said color developing agent in the presence of metallic silver, said color-developing agent and said oxidizing agent being essentially inert to redox reaction in the absence of a catalytic material, said oxidizing agent and said color-developing agent being so chosen that the reaction products thereof are noncatalytic for said redox reaction.

14. A photographic process as defined in Claim 13 wherein said oxidizing agent is a metal complex.

15. A photographic process as defined in Claim 14 wherein said oxidizing agent is a cobalt complex having a coordination number of 6.

16. A process according to Claim 13 wherein said photographic element comprises at least one layer unit wherein said color coupler is present in at least a 40% stoichiometric excess based on silver.

17. A process according to Claim 13 wherein said image dye-providing layer unit comprises a layer containing a silver halide emulsion having layers contiguous on each side thereof containing said coupler.

18. A process according to Claim 13 wherein said image dye-providing layer unit is a single layer containing said silver halide emulsion and said coupler coated together with said hydrophilic colloid.

19. A process of providing photographic images in an exposed photographic element comprising a support having coated thereon separate, overlying silver halide emulsion layers sensitive to blue, green and red radiation and containing, respectively, yellow, magenta and cyan dye-forming photographic color couplers, each of said light-sensitive silver halide emulsion layers being coated at a silver coverage of up to about 270 mg. silver/m.² and containing said photographic color couplers in an amount of from about 3 to 15 times the weight of the silver, each of said light-sensitive layers comprising a hydrophilic colloid coated at a coverage of from about 215 to 1080 mg./m.², the weight ratio of silver to hydrophilic colloid being from 1:2 to 1:20 and the weight ratio of coupler to hydrophilic colloid being from about 1:½ to 1:2 in each of said layers, which comprises developing said exposed photographic element in a photographic developing solution comprising a photographic aromatic primary amino color-developing agent and an oxidizing agent which undergoes redox reaction with said color-developing agent in the presence of silver catalyst, said color-developing agent and said oxidizing agent being essentially inert to

19

oxidation-reduction reaction in the absence of catalytic material, and said oxidizing agent and said color-developing agent being so chosen that the reaction products thereof are noncatalytic for said oxidation-reduction reaction.

20. A photographic process as defined in Claim 19 wherein said oxidizing agent is a cobalt complex having a coordination number of 6.

21. A photographic process as defined in Claim 15 wherein said cobalt complex comprises a ligand selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetraamine, amine, nitrate, nitrite, azide, chloride, thiocyanate, isothiocyanate, water and carbonate, said complex comprising (1) at least 2 ethylenediamine ligands or (2) at least 5 amine ligands or (3) at least 1 triethylenetetraamine ligand.

22. A photographic process as defined in Claim 19 wherein said cobalt complex is cobalt hexammine(III) chloride.

23. A photographic element as defined in Claim 3 wherein silver halide in said green- and red-sensitive layers is coated at a coverage of up to about 110 mg. silver/m.².

24. A process for providing photographic images in an exposed photographic element comprising a support having coated thereon at least one image dye-providing layer unit comprising a light-sensitive photographic silver halide emulsion coated at a coverage of up to about 320 mg. silver/m.² and a color coupler at a concentration of at least two times the weight of the silver, the silver halide and the coupler being dispersed in a hydrophilic colloid coated on said support at a coverage of from about 215 to 970 mg./m.², the weight ratio of silver to

20

hydrophilic colloid being from 1:2 to 1:20 and the weight ratio of said coupler to said hydrophilic colloid being from 1:½ to 1:2, which comprises developing said exposed photographic element to form an imagewise distribution of developed metallic silver and undeveloped silver halide and providing contact of said element with an aqueous liquid in the presence of an aromatic primary amino color-developing agent and an oxidizing agent which undergoes a redox reaction with said color-developing agent in the presence of metallic silver, said color-developing agent and said oxidizing agent being essentially inert to redox reaction in the absence of a catalytic material, said oxidizing agent and said color-developing agent being so chosen that the reaction products thereof are noncatalytic for said redox reaction.

25. A photographic process as defined in Claim 24 wherein said oxidizing agent is a metal complex.

26. A photographic process as defined in Claim 24 wherein said oxidizing agent is a cobalt complex having a coordination number of 6.

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U.S. Cl. X.R.

96—55, 60 R, 60 BF, 66 R, 74

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,822,129

Dated July 2, 1974

Inventor(s) Joseph S. Dunn and Rowland G. Mowrey

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 52, after "obtain", "the" should read --a--.
Column 5, line 13, "accomplishd" should read --accomplished--.
Column 9, line 54, "nitrie" should read --nitrite--; line 58, "1-" should read -- 1 --. Column 10, line 4, "[Co(tn)(en)₂]X" should read --[Co(tn)(en)₂]X--; line 9, "PtIV" should read --PtIV--; line 20, after "order", "to" should read --of--; line 65, "form" should read --for--. Column 11, line 64, after "coverage", --of-- should be inserted. Column 12, line 39, "genereally" should read --generally--. Column 17, line 11, after "from", --about-- should be inserted. Column 19, line 15, "ligans" should read --ligands--. Column 20, line 25, "Edith" should read --Weyde--; line 26, "Rodwick" should read --Malau--.

Signed and sealed this 26th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents