Sept. 10, 1974 V. L. BISSONETTE 3,834,907
PHOTOGRAPHIC ELEMENTS CONTAINING COLOR-PROVIDING LAYER UNITS FOR AMPLIFICATION PROCESSES
Filed May 23, 1972 2 Sheets-Sheet 1

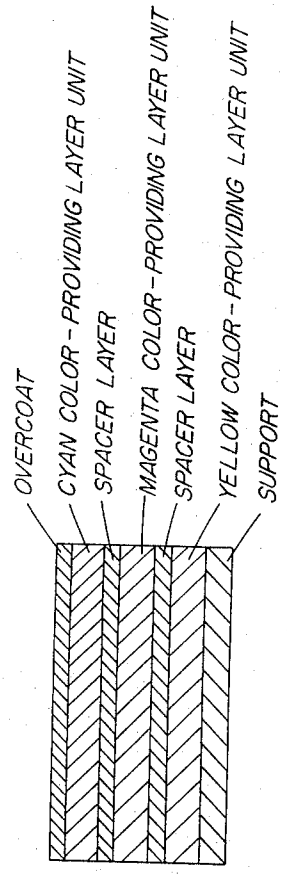


FIG. 1

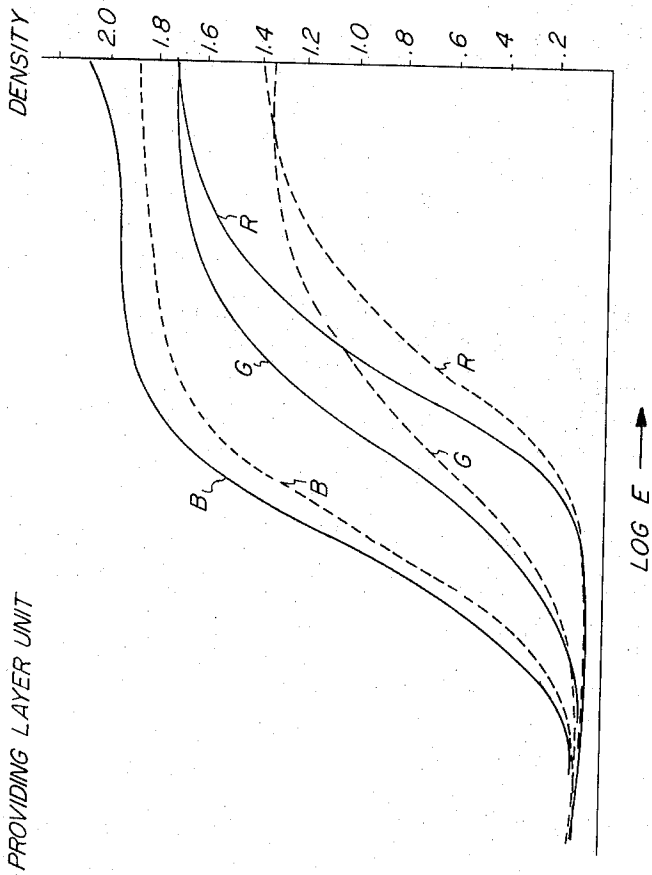


FIG. 2

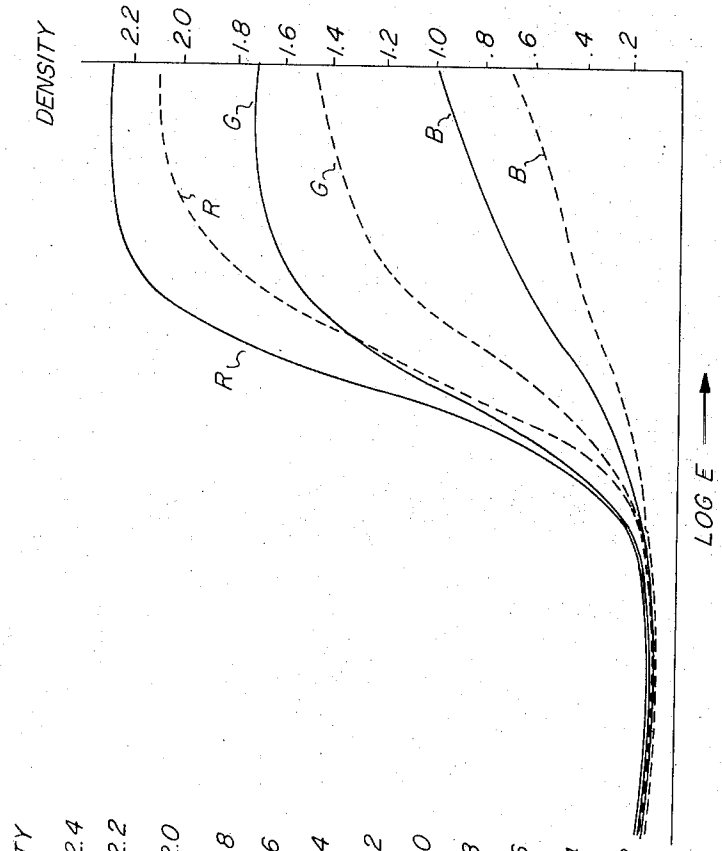

DENSITY
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
R
G
B
LOG E

FIG. 4

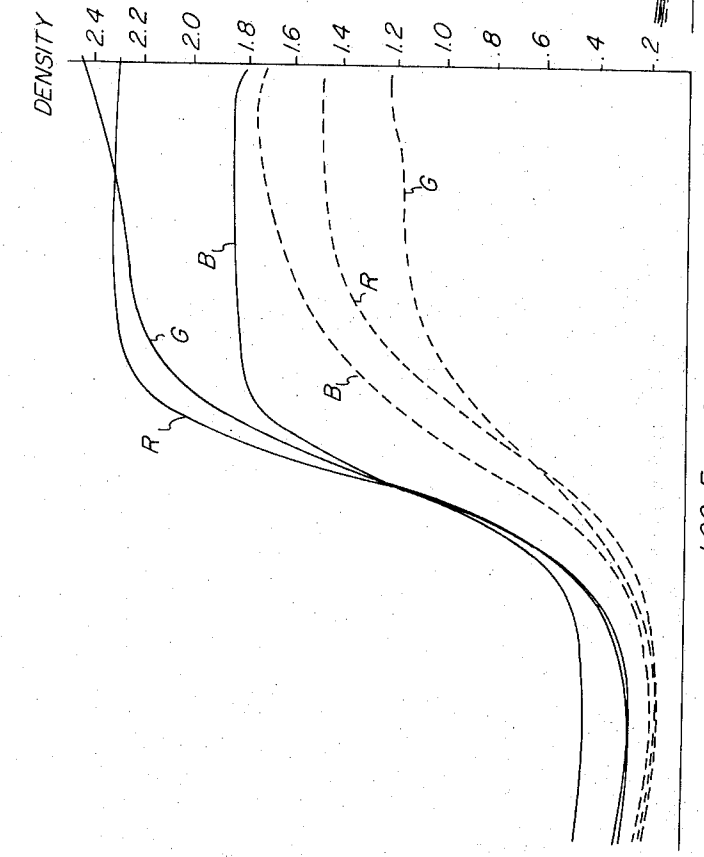

DENSITY
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
R
G
B
LOG E

FIG. 3

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3,834,907

PHOTOGRAPHIC ELEMENTS CONTAINING COLOR-PROVIDING LAYER UNITS FOR AMPLIFICATION PROCESSES

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Continuation-in-part of applications Ser. No. 150,741, June 7, 1971, now abandoned, and Ser. No. 189,289, Oct. 14, 1971. This application May 23, 1972, Ser. No. 256,072

Int. Cl. G03c 1/30, 1/40
U.S. Cl. 96—74 50 Claims

ABSTRACT OF THE DISCLOSURE

Photographic elements are disclosed which comprise a support having thereon at least one dye image-providing layer unit which contains a light-sensitive silver salt and a stoichiometric excess of an image dye-providing color coupler. In one aspect, the photographic elements of this invention are multicolor photographic elements wherein at least two distinct colors are produced in two separate layer units of the element. In another aspect, multicolor photographic elements are disclosed which comprise at least two image dye-providing layer units containing a silver halide emulsion in a concentration of up to 30 mg./ft.^{2} of silver and an image dye-providing color coupler in at least a 40 percent stoichiometric excess based on silver.

This application is a continuation-in-part of my copending application U.S. Ser. No. 150,741 filed June 7, 1971, now abandoned, and my copending application U.S. Ser. No. 189,289 filed Oct. 14, 1971.

This invention relates to photography and more particularly to photographic elements containing light-sensitive silver salts. In one aspect, the photographic elements of this invention contain color-providing layer units comprising a light-sensitive silver salt having associated therewith a photographic color coupler in a stoichiometric excess based on silver. In another aspect, the protographic elements of this invention comprise color-providing layer units which contain a light-sensitive silver salt at a concentration of under 30 mg. of silver per square foot. In another aspect, this invention relates to multicolor photographic elements which comprise at least two separate color-providing layer units which each effectively record light primarily in different regions of the light spectrum and provide image dyes, wherein said layer units comprise a light-sensitive silver salt having associated therewith a photographic color coupler in at least a 40 percent stoichiometric excess based on silver.

Photographic elements comprising light-sensitive silver salts having associated therewith a photographic color coupler are well known in the art for producing color image records, such as the color-recording elements described in *American Scientists*, Vol. 58, No. 6, November-December 1970, pp. 648–660, and the multicolor elements described by Thirtle and Zwick, *Kirk-Othmer Encyclopedia of Chemical Technology*, vol. 5, pp. 812–845, 1964. Generally, the density of the dye or amount of dye which could be produced in these photographic elements was directly dependent on the amount of oxidized color developer produced in the development of the latent image; the oxidized color developer reacts with the color coupler to form the image dye. Extensive work has been done to increase the efficiency of the system by reducing the required number of equivalents of oxidized developer which were necessary to react with the color coupler to produce 1 mole of image dye. Thus, the couplers which require for the production of 1 mole of dye 2 equivalents of oxidized developer and likewise 2 equivalents of silver are often

preferred over the 4 equivalent couplers which require 4 equivalents of oxidized developer to produce a mole of image dye, especially where one is trying to improve the efficiency of the system, i.e., maximum density image from the minimum of image-recording material.

In decreasing the equivalency of the coupler (i.e., the amount of oxidized developer necessary to form a mole of image dye), the production of oxidized developer remains directly dependent on the amount of silver salt present. Thus, photographic elements known in the prior art comprise color image-forming layers which have typically been coated at coverages of at least 100 mg. of silver per/ft.^{2} and up to substantially higher coverages such as 400 mg./ft.^{2} or higher. Generally, the couplers were incorporated in each layer unit in about a stoichiometric amount based on silver or occasionally in a small excess. There are also instances where one layer of the element may have contained excess color coupler, apparently to achieve a balanced system.

In other attempts to increase the efficiency of the system, color developers having increased efficiency in developing silver were used to try to develop a higher percentage of the exposed silver halide grains. Systems of this type are disclosed, for example, in Bent and Mowrey, U.S. Ser. No. 94,993 filed Dec. 31, 1970, now abandoned. Even in systems of this type, the maximum oxidized developer obtainable is limited by the amount of silver present and, thus, the color couplers were generally incorporated in the stoichiometric amount necessary for dye formation in the silver halide development reaction process.

In still other prior art, there is maintained the use of systems wherein a silver image is intensified using a color developer to developer the silver and a color coupler is present to form dye images in addition to silver, as mentioned in British Pat. 614,808 by Dimsdale and U.S. Pat. 2,173,739 by Weber. More recently, a disclosure also appeared in Belgian Pat. 742,768 issued June 8, 1970, disclosing the dye intensification of a low-coverage silver image.

Systems have also been disclosed for the physical development of latent images by treating an exposed light-sensitive element with a physical developing agent, a color coupler and a color developer as mentioned in Dipple et al., U.S. Pat. 2,750,292 issued June 12, 1956. However, systems of this type are generally limited to production of one color since the same coupler and developer will diffuse into each layer of the element.

In still other systems, the use of competing couplers is disclosed, such as in U.S. Pats. 2,689,793 by Weller et al., 2,742,832 by Salminen, 2,808,329 by Whitmore, 2,998,314 by Puschel, and the like. In systems of this type, the efficiency of the silver recording material appears to be reduced in an attempt to improve graininess, sharpness, contrast and the like. The efficiency is apparently lost since more oxidized developer is produced than is actually used in forming the image dye.

In accordance with this invention, I have found that photographic elements having certain image-recording unit layers can be made to produce a highly efficient image-recording system having highly improved image characteristics. Generally, a photographic element is provided which will produce a high quantity of an image dye in each layer unit from a relatively small amount of a light-sensitive silver salt. This feature is especially important in photographic elements, such as two- or three-color elements which produce a different color in each layer unit, where image dyes having specific absorption characteristics are desired for each layer unit in order to provide overall image clarity and exactness in reproduction of color.

In certain highly preferred embodiments, color-providing layer units of this invention comprise a stoichiometric excess of color coupler based on effective silver in said layer unit. The term "effective silver" is understood to mean the developable silver in said layer unit which, when it is fully exposed and processed for about 1 minute at 100° F. in a silver halide developer such as Developer A in Example 7, will provide a given amount of metallic silver which corresponds to the developable silver halide.

In one preferred embodiment, this invention relates to multicolor photographic elements comprising a support having thereon at least two color-providing layer units which each contains a light-sensitive silver salt having associated therewith an image dye-providing color coupler in an equivalent excess of at least 40 percent and preferably at least 70 percent above that required for a stoichiometric overall reaction with effective silver (i.e., developable silver) in said layer unit. In highly preferred embodiments, the image dye-providing color coupler is present in said layer units in a weight concentration of at least three times that of silver and preferably the light-sensitive silver, such as silver halide, is present in said layer units at a coverage of up to 30 mg. silver/ft.^{2}.

In another preferred embodiment of this invention, multicolor photographic elements are provided which comprise a support having thereon at least two separate layer units which contain light-sensitive silver salts, such as silver halide emulsions, which are spectrally sensitized to record light exposure primarily in different regions of the visible light spectrum and wherein each of said layers has associated therewith a photographic color coupler, which is a precursor for an image dye, and said coupler is present in a stoichiometric excess at an equivalent ratio of at least 1.4:1 and preferably greater than 1.7:1 based on effective silver in said layer unit (i.e., 2:1, 3:1, etc.). While it is now generally desirable to coat all image-recording layer units with a stoichiometric excess of the coupler, some elements such as photographic papers depend on large silver grain size and higher silver concentration for differential light sensitivity of the blue recording layer unit compared with the other recording layer units. Nevertheless, the image-recording layer units other than the blue recording layer units can be coated in accordance with this invention to produce highly improved results. Improved results are also obtained in the blue recording layer with large-grain silver salts in achieving matched developability, but the efficiency is not as readily apparent from mere analysis of the components of this layer unit.

In another embodiment of this invention, light-sensitive photographic elements are provided which comprise a support having coated thereon separate, superposed silver halide emulsion layers sensitive to blue, green and red radiation, at least two of the silver halide emulsion layers being coated at a coverage of from 1 to 25 mg. of silver/ft.^{2} and containing a photographic color coupler which will produce a dye having a predominant spectral absorption in the region of the visible spectrum corresponding to the effective spectral sensitivity of the associated silver halide and wherein said coupler is present in at least a 40 percent stoichiometric excess based on effective silver and preferably at a concentration of from 4 to 15 times the weight of the silver. Particularly good results are obtained when at least the green- and red-sensitive layers each contains from 1 to 25 mg. silver/ft.^{2} and (1) color coupler in at least a 40 percent stoichiometric excess based on effective silver and preferably 70 percent or (2) color coupler in a concentration of 4 to 10 times the weight of the silver.

The light-sensitive silver salt layers in accordance with this invention are preferably at silver coverages of up to about 30 mg. silver/ft.^{2} (325 mg./m.^{2}), such as from 1 to 30 mg./ft.^{2} (10–325 mg./m.^{2}) and more preferably from about 1 to 25 mg. silver/ft.^{2} (10–270 mg./m.^{2}). Especially good results are obtained with coverages on the order of from about 2 to 15 mg./ft.^{2} of silver (20–160 mg./m.^{2}) 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 20 and preferably less thn 10 mg./ft.^{2}).

The photographic elements of this invention contain at least sufficient light-sensitive silver salt to provide a latent image, or at least photolytic silver, upon imagewise exposure.

In another preferred embodiment in accordance with this invention, especially where the elements are designed to be developed with a *p*-phenylenediamine color developer, photographic elements are provided which contain a support having thereon at least two separate layer units, each containing a silver halide emulsion which will develop at least 50 percent of its image silver in 30 percent of the time it takes to develop the layer to 95 percent of the developable silver in said layer, and said layer has associated therewith at least a 40 percent stoichiometric excess and preferably 70 percent stoichiometric excess of color coupler based on effective developable silver. Generally, this requirement defines the emulsion as being a fine-grain emulsion, i.e., of less than 0.8 micron in mean grain size; however, it will also include those emulsions which have been coated with larger grain sizes, but the large grains do not develop to a practical extent under conditions of use.

In another preferred embodiment, this invention relates to photographic elements which comprise a support having at least one layer thereon containing a silver halide emulsion which has associated therewith a photographic color coupler, in at least a 40 percent stoichiometric excess based on silver, and certain antifoggants.

In another preferred embodiment, the photographic elements of this invention comprise silver halide emulsions wherein the halide is less than 6 mole percent iodide and preferably less than 3 mole percent iodide. While high-iodide emulsions can be processed in fresh amplifying solutions with good results, it is preferred to have an iodide content of less than 3 mole percent and most preferably less than 0.25 mole percent to prevent buildup of iodide ions in the amplifying and/or developing solutions, as described later herein.

In certain embodiments, it may be desirable to use silver halide emulsions wherein the grains have a high percentage of silver iodide in the core of a core shell structure such as disclosed in Beckett, U.S. Pat. 3,505,068 issued Apr. 7, 1970. Silver halide emulsions of this type can be used effectively in those processes where buildup of iodide ions is undesirable as long as the shell of the emulsion contains low concentrations of iodide as specified above. However, in certain preferred embodiments, all of the silver halide emulsion contained in the image dye-providing layer has the halide constituency as defined above.

In another highly preferred embodiment, this invention relates to an improved photographic element designed for use in an image-forming process which utilizes an oxidizing agent and a reducing agent which undergo a redox reaction in the presence of silver catalyst, and wherein the reducing agent and the oxidizing agent produce redox reaction products which are substantially noncatalytic for the redox reaction, the improvement comprising at least one and preferably at least two image dye-providing layer units in said photographic element which each contains a silver halide emulsion and an image dye-providing coupler in at least a 40 percent stoichiometric excess based

on effective silver. Preferably, the elements are designed for use where the oxidizing agent is a cobalt complex.

In certain other embodiments, this invention relates to photographic elements comprising at least one image dye-providing layer unit containing a light-sensitive photographic silver halide emulsion in a concentration up to 30 mg. of silver/ft.^{2} and having associated therewith an image dye-providing photographic color coupler in at least a 40 percent stoichiometric excess based on effective silver and preferably at least a 110 percent excess based on effective silver. Photographic elements of this type can include elements such as X-ray recording elements with one or more layer units wherein spectral sensitivity may be similar when more than one layer is present, or the elements can be multicolor elements wherein a different color is produced in each layer unit.

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 my copending 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, entitled "Process for Developing Photographic Elements," filed on even date herewith, 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 underdeveloped 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.

In still another embodiment, the elements of this invention can 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 a multicolor image record. Moreover, with the elements of this invention, the stability of the physical developer solution may be somewhat improved since autocatalytic dye formation is reduced in the bath since color coupler is not an essential ingredient of the bath which in turn can cause severe color contamination.

In still another embodiment, 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. Pats. 3,046,129 by Graham issued July 24, 1962, 3,547,640 by Beckett, and 2,944,900.

Certain preferred embodiments and features of the invention are set forth in the drawings of this application. FIG. 1. is a representative schematic diagram of a preferred photographic reflection print material according to this invention. The essential layers of one preferred embodiment are shown as a white opaque support with superposed layers comprising a yellow color-providing layer and which generally comprises a blue-sensitive silver salt, a spacer layer to prevent contamination by reaction products, a magenta color-providing layer unit which generally comprises a green-sensitive silver salt, another spacer layer, a cyan color-providing unit which generally comprises a red-sensitive silver salt and a protective overcoat. Elements of this general type are described in more detail in Van Campen, U.S. Pat. 2,956,879.

FIG. 2 shows an H and D curve according to Example 7 wherein the dashed lines show the dye image produced at substantially optimum development conditions for the emulsion and the solid lines show the added dye produced by use of an amplification bath after silver development. B is the curve of the respective blue-sensitive layer unit, G is the curve of the respective green-sensitive layer unit and R is the curve of the respective red-sensitive layer unit in this figure, as well as in FIGS. 3 and 4.

FIG. 3 shows an H and D curve according to Example 8 wherein the first color development step is limited in time to 1 minute. The dashed lines show the color produced by the 1-minute development and the solid lines show the color produced by the color development plus amplification.

FIG. 4 shows an H and D curve for samples prepared and processed according to Example 10 wherein a short development time with a *p*-phenylenediamine was used to demonstrate that coarse-grain emulsions with slow developability rates (blue-sensitive layer) are not amplified as efficiently as smaller-grain emulsions (green- and red-sensitive layers).

The silver salts useful in this invention can be any of the light-sensitive silver salts known in the art which includes those of U.S. Pats. 3,446,619 by Gilman, 3,206,-309 by Haist, and the like. In certain preferred embodiments, the silver salt is a silver halide emulsion.

The silver halide emulsions used in accordance with this invention can comprise, for example, silver chloride, silver bromide, silver bromoiodide, silver chlorobromide, silver chloroiodide, silver chlorobromoiodide crystals or mixtures thereof. They 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 Luckey et al., U.S. Pat. 2,996,382 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 September/October 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 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 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 eash comprise a silver salt at a concentration of up to 30 mg. of silver/ft.^{2}. However, while the developable silver halide is preferably present at concentrations based on silver of less than 30 mg./ft.^{2}, it is possible to coat blended emulsions at higher 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 development restrainers, such as with 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 coatng 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 emulsion, 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 described in Example 7, 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 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 $D_{max.}$ 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 phane$=11.3\times10^4$ ergs/cm.^{2}).

The silver halide emulsions of the layer units preferably contain fine-grain emulsions (i.e., less than 0.8 micron mean silver halide grain size) which will provide a high amount of catalytic silver in a short amount of time. This feature is especially advantageous since it allows for very rapid processing of the photographic emulsion, especially when using color-developing agents such as *p*-phenylenediamines. Moreover, fast development times allow for rapid development of the exposed areas without the buildup of background fog. This feature is further described in Examples 9 and 10. Additionally, if development times can be substantially reduced, the emulsion sensitivity can be increased by using a higher degree of chemical sensitization without substantial $D_{min.}$ buildup on development.

In certain preferred embodiments, the emulsions of certain color-providing layer units as described herein have a mean grain size of less than 0.8 micron. Grain sizes can be measured by methods commonly used in the art for this purpose. A typical procedure is set forth by Loveland, "Methods of Particle-Size Analysis," *ASTM Symposium on Light Microscopy*, 1953, pp. 94–122, or in chapter 2 of *The Theory of the Photographic Process*, Mees and Jones, 3rd Ed. (1966), published by MacMillan Co. The grain size can be measured using the projected areas of the grains or approximate diameter. When the grains are substantially uniform in shape, the size distribution can be expressed quite accurately as either diameter or projected area. The size-frequency relationship can be determined as disclosed in an article by Trivelli and Smith entitled "Empirical Relations Between Sensitometric and Size Frequency in Photographic Emulsion Series," *The Photographic Journal*, Vol. LXXIX, 1949, pp. 330-338.

The light-sensitive silver salts are generally coated in the color-providing layer units in the same layer with the photographic color coupler. However, they can be coated in separate adjacent layers as long as the coupler is effectively associated with the respective silver halide emulsion layer to provide for immediate dye-providing reactions to take place before substantial color developer oxidation reaction products diffuse into adjacent color-providing layer units.

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 nondiffusible in a hydrophilic colloid binder (e.g., gelatin) 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 preferred 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 in U.S. Pat. 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 March 4, 1913, and particularly nondiffusible Fischer-type couplers containing branched 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 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 sol-

vent. Typical useful solvents include tri-*o*-cresyl phosphate, di-*n*-butyl phthalate, diethyl lauramide, 2,4-diarylphenol, liquid dye stabilizers as described in an article entitled "Improved Photographic Dye Image Stabilizer-Solvent," *Product Licensing Index,* vol. 83, pp. 26–29, March 1971, and the like. The elements containing coupler solvents appear also to aid in imbibing color developer in those processes where it is carried from a developer bath into an amplifier bath.

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 photographic elements of this invention, as defined above, comprise a support having thereon image dye-providing layer units. A multicolor photographic element comprises at least two of said image dye-providing layer units which each 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 preferred embodiments, the color-providing layer units are continuous layers which 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. In other embodiments, the layer units are discontinuous layers comprising mixed packets which are effectively isolated from each other, as disclosed in Godowsky, U.S. Pat. 2,698,794 issued Jan. 4, 1954. The effective isolation of the layer units is known in the art and is utilized to prevent contamination in many commercial color products.

The photographic elements of this invention 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. 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.

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^{-5} moles/ft.^{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 photographic elements in certain preferred embodiments of this invention preferably contain various addenda to obtain the desired development characteristics and image properties. In certain highly preferred embodiments where developed silver is used as a catalyst, it is desirable to use addenda which do not absorb so strongly to the silver surface whereby the available surface would be substantially reduced. Generally, it is desirable to avoid using substantial quantities of iodide salts and organic compounds having free mercapto groups which have a high heat of adsorption such as, for example, substantial quantities of phenylmercaptotetrazole, alkali metal iodide salts and the like, which form silver salts more insoluble in water than silver bromide.

Generally, it is desirable to add silver halide antifoggants to the light-sensitive layers of the photographic elements. In certain preferred embodiments, it is desirable to use only those antifoggants which do not adsorb strongly to silver formed after development. Useful antifoggants include heterocyclic organic compounds such as tetrazoles, azaindines, triazoles and the like.

Typical heterocyclic organic compounds which can be used as antifoggants include tetrazoles, azaindines, triazoles and the like which are free of free mercaptan or ionic iodide groups. Specific useful antifoggants include, for example, methyl benzotriazole, benzotriazole, 3-methyl-1,3-benzothiazolium bromide, 5-nitrobenzimidazole, decamethylene bis(benzothiazolium bromide), and the like. Other useful antifoggants include nitron, nitroindazoles, and antifoggants mentioned in Abbott, U.S. Ser. No. 149,815, filed June 3, 1971 (French Pat. 2,084,-802); Abbott, U.S. Ser. No. 37,323, filed May 14, 1970 (French Pat. 2,091,544); U.S. Pats. 2,131,038 by Brooker et al., 2,694,716 by Allen et al., 2,886,437 by Piper, 2,444,605 by Heimbach, and 3,287,135 by Anderson et al.; and British Pat. 623,448 by Carrol et al.; and the like. Generally, the useful antifoggants are incorporated in the silver halide emulsion at about 20 mg. to about 2 g./mole of silver.

The light-sensitive silver salts 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(N-vinylpyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of a photographic element employed in the practice of this invention can also contain alone or in combination with hydrophilic, water-permeable colloids, other synthetic polymeric compounds such as dispersed polyvinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials.

In certain embodiments, the hydrophilic colloids employed herein are useful as coverages of at least 100 mg./ft.^{2}, such as from 100 to 400 mg./ft.^{2}.

The silver halide emulsions used with this invention may be unwashed or washed to remove soluble salts. In the latter case, the soluble salts may be removed by chill-setting and leaching or the emulsion may be coagulation-washed, e.g., by the procedures described in U.S. Pat. 2,618,556 by Hewitson et al. issued Nov. 18, 1952, 2,614,-928 by Yutzy et al. issued Oct. 21, 1952, 2,565,418 by Yackel issued Aug. 21, 1951, 3,241,969 by Hart et al. issued Mar. 22, 1966, and 2,489,341 by Waller et al. issued Nov. 29, 1949.

The silver salts used with this invention may be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compounds; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in U.S. Pat. 1,623,499 by Sheppard et al. issued Apr. 5, 1927, 2,399,-083 by Waller et al. issued Apr. 23, 1946, 3,297,447 by McVeigh issued Jan. 10, 1967, and 3,297,446 by Dunn issued Jan. 10, 1967.

The photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly (vinylacetal) 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 in the same side of the support or on opposite sides of the support where desired, such as when using a transparent film support.

Spectral-sensitizing dyes can be used conveniently to confer additional sensitivity to the light-weight silver halide emulsion of the multilayer photographic elements of the invention. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye may be added in the the form of a dispersion as described in Owens et al., British Pat. 1,154,781 issued June 11, 1969. For optimum results, the dye may either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in U.S. Pats. 2,526,632 by Brooker et al. issued Oct. 24, 1950, 2,503,776 by Sprague issued Apr. 11, 1950, 2,493,748 by Brooker et al. issued Jan. 10, 1950, and 3,384,486 by Taber et al. issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri- or tetranuclear) merocyanines, complex (tri- or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g., enamine hemicyanines), oxonols and hemioxonols.

Dyes of the cyanine classes may contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei may contain alkyl, alkylene, hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and may be fused to carbocylic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl, alkyl, haloalkyl, cyano or alkoxy groups. The dyes may be symmetrical or unsymmetrical and may contain alkyl, phenyl, enamine or heterocyclic substituents on the methine or polymethine chain.

The merocyanine dyes may contain the basic nuclei mentioned above, as well as acid nuclei such as thiohydantoins, rhodanines, oxazolidenediones, thiazolidenediones, barbituric acids, thiazolineones and malononitrile. These acid nuclei may be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, alkylamino groups or heterocyclic nuclei. Combinations of these dyes may be used, if desired. In addition, supersensitizing addenda which do not absorb visible light may be included, for instance, ascorbic acid derivatives, azaindenes, cadmium salts, and the like.

The various layers, including the photographic layers, employed in the practice of this invention can contain light-absorbing materials and filter dyes such as those described in U.S. Pats. 3,253,921 by Sawdey issued May 31, 1966, 2,274,782 by Gaspar issued Mar. 3, 1942, 2,527,-583 by Silberstein et al. issued Oct. 31, 1950, and 2,956,-879 by Van Campen issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in Jones et al., U.S. Pat. 3,282,699 by Jones et al. issued Nov. 1, 1966.

The sensitizing dyes and other addenda used in the practice of this invention may be added from water solutions or suitable organic solvent solutions may be used. The compounds can be added using various procedures including those described in U.S. Pats. 2,912,343 by Collins et al. issued Nov. 10, 1959, 3,342,605 by McCrossen et al. issued Sept. 19, 1967, 2,996,287 by Audran issued Aug. 15, 1961, and 3,425,835 by Johnson et al. issued Feb. 4, 1969.

The layers of the photographic elements of this invention can contain hardeners, plasticizers, lubricants, surfactants, brightening agents and other addenda as provided in the photographic art, as long as these compounds do not substantially deleteriously affect the elements as provided for in the description of this invention.

The photographic layers used in the practice of this invention may be coated by various coating 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. If desired, two or more layers may be coated simultaneously by the procedures described in U.S. Pats. 2,761,791 by Russell issued Sept. 4, 1956, and 3,508,947 by Hughes issued Apr. 28, 1970, and British Pat. 837,095 by Wynn issued June 9, 1960. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat. 968,453 issued Sept. 2, 1964, and Lu Valle et al., U.S. Pat. 3,219,451 issued Nov. 23, 1965.

This invention may be used with elements designed for color image transfer processes such as described in Rogers, U.S. Pats. 3,087,817 issued Apr. 30, 1963, 3,185,567 issued May 25, 1965, and 2,983,606 issued May 9, 1961, U.S. Pats. 3,253,915 by Weyerts et al. issued May 31, 1966, 3,227,550 by Whitmore et al. issued Jan. 4, 1966, 3,227,-551 by Barr et al. issued Jan. 4, 1966, 3,227,552 by Whitmore et al. issued Jan. 4, 1966, and Land, U.S. Pats. 3,415,644, 3,415,645 and 3,415,646 all issued Dec. 10, 1968; and imbibition transfer processes as described in Minsk, U.S. Pat. 2,882,156 issued Apr. 14, 1959. When splittable couplers containing a preformed dye molecule or redox couplers are used in the element, at least two of the color-providing layer units comprise at least a 40 percent stoichiometric excess of said coupler based on silver in said layer.

The photographic elements of this invention are particularly useful in the processes disclosed in my aforementioned copending application. Ser. No. 189,289, entitled "Image-Forming Processes and Compositions," filed Oct. 14, 1971, and incorporated herein by reference. Generally, in this process a redox reaction between an oxidizing agent and a reducing agent is utilized to produce a change in light value. This change in light value can come about directly by a change in the light value of either the oxidizing agent or reducing agent. Alternatively, the redox reaction can result in one or more reaction products which can react with each other or with another component, such as a reactive species, to produce a change in light value. In another variation, the reactivity of the reactive species can be reduced imagewise by one of the reaction products of the redox reaction.

The redox reaction which takes place when the elements are processed by this procedure occurs at a

catalytic surface. The catalyst is metallic silver which, of course, can be produced by development of silver halide which contains a latent image. The catalyst appears to promote redox reaction in true catalytic fashion. The amount of redox reaction products is not limited by the amount of catalyst present, since the catalyzed redox reaction of this invention does not proceed on a stoichiometric basis with respect to the catalyst.

Oxidants preferred in the practice of this process 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 or 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 over about 8. 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.

Preferred metal complexes in accordance with this process 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., as well as such common ligands as those referred to on p. 44 of Basolo et al., supra. The liability 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 two ethylenediamine ligands or (2) at least five ammine ligands or (3) one 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 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 equilibra 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 generally similar to the cobalt complexes mentioned above.

With many complexes, such as cobalt hexammine, the anions selected can substantially effect 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 effect 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.

Numerous reducing agents can be utilized in carrying out the same process. The reducing agents utilized herein undergo redox reaction with the oxidizing agent at a catalytic surface. Especially preferred reducing 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. Depending upon the particular oxidizing agent utilized, the reducing agent can be selected from such reducing agents as hydroquinones, catechols, aminophenols, 3-pyrazolidones, such as 1-phenyl-3-pyrazolidone, l-, d- or iso-ascorbic acid, reductones and phenylenediamines. Dye developers, such as those described and referred to in Rogers, U.S. Pat. 2,983,606 issued May 9, 1961, are also reducing agents which are preferably used in combination with an auxiliary developing agent. In certain aspects, the reducing agent used in this process is an aromatic primary amine color-developing agent such as *p*-aminophenols (which form particularly stable redox combinations with certain complexes, e.g., $[Co(en)_3]Cl_3$) or *p*-phenylenediamines. Color-developing agents which can be used include 3-acetamido-4-amino-N,N-diethylaniline, 4 - amino-N-ethyl-N-β-hydroxyethylaniline sulfate, N,N-diethyl-*p*-phenylene-

diamine, 2 - amino-5-diethylaminotoluene, N-ethyl-N-β-methanesulfonamidoethyl - 3 - methyl-4-aminoaniline, 4-amino-N-ethyl-3-methyl-N-(β-sulfoethyl)aniline, and the like. See Bent et al., *JACS*, Vol. 73, pp. 3100–3125 (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.

In one highly preferred embodiment, aromatic primary amino color-developing agents which provide good results in this process 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-3-β-(methanesulfonamido)ethyl-N,N-diethylaniline dihydrochloride, and
4-amino-N-ethyl-N-(2-methoxyethyl)-*m*-toluidine di-p-toluene sulfonate.

Any suitable means can be utilized to contact the oxidizing agent, reducing agent and silver catalyst. For example, an imagewise pattern of silver can be contacted with a solution containing oxidant and reductant. In one convenient embodiment of the invention, a hydrophilic colloid layer, coated on a suitable support, contains a pattern of silver catalyst and is contacted with an aqueous solution containing oxidant and reductant. The concentration of reductant and oxidant in such solutions can vary over a wide range. Optimum concentrations depend on such variables as time of contact, amount of catalyst present and reactivity of the particular oxidizing agent-reducing agent-catalyst combination chosen. Typical useful concentrations of oxidant and reductant each range from about .1 to 50, and preferably 1 to 15, g./l. of solution, using contact or residence times of about 30 seconds up to 2 hours or longer. The oxidizing agent and reducing agent can also be contained in and released from rupturable pods or pressure-sensitive capsules.

This process is admirably suited to amplify faint or even invisible quantities of catalyst which occur with low silver coverages in the certain preferred elements of this invention. The invention is highly effective with light-sensitive silver halide materials, wherein latent image silver or a low-density silver image can be utilized to generate a visible image. In addition, this process is useful in supplementing an image, for example, a silver image, or replacing preformed images with other images such as image dyes.

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

EXAMPLE 1

A photographic element is prepared having the following composition:

Layer 6	100 mg. gelatin
Layer 5	150 mg. gelatin containing red-sensitive, silver chlorobromide grains at about 5 mg. silver/ft.², 35 mg. of the 2-equivalent coupler 2-[α-(2,4-di-*tert*-amylphenoxy)-*n*-butyrylamino]-4,6-dichloro-5-methylphenol dissolved in dibutyl phthalate (coupler solvent) at a weight ratio of 1:½ coupler to coupler solvent (stoichiometric ratio of silver to coupler is 1:3.1)
Layer 4	240 mg. gelatin
Layer 3	200 mg. gelatin containing green-sensitive silver chlorobromide grains at about 10 mg. silver/ft.², 45 mg. of the 4-equivalent coupler 1-(2,4,6-trichlorophenyl)-3-[2-chloro-5-(α-(4-hydroxy-3-*tert*. butylphenoxy) tetradecanoamido) anilino]-5-pyrazolone dissolved in tricresyl phosphate (coupler solvent) at a weight ratio of 1:¼ coupler to coupler solvent (stoichiometric ratio of silver to coupler is 1:2.5)
Layer 2	100 mg. gelatin
Layer 1	200 mg. gelatin containing blue-sensitive silver chlorobromide grains at about 40 mg. silver/ft.²,150 mg. of the 2-equivalent couplerα-[4-(4-benzyloxyphenylsulfonyl)phenoxy]-α-pi valyl-2-chloro-5-[γ-(2,4-di-*tert*-amylphenoxy)butyramido] acetanilide dissolved in dibutyl phthalate (coupler solvent) at a weight ratio of 1:¼ coupler to coupler solvent (stoichiometric ratio of silver to coupler is 1:0.9)
	support

In the above element, the support is a paper support having coated thereon a polyethylene layer containing titanium dioxide. All concentrations given above are in mg./ft.². The material thus obtained is given color exposures so that the element would give, upon reversal processing, a neutral scale (formed from cyan dye, magenta dye and yellow dye). Processing is conducted as follows: black-and-white development in Kodak Developer D–19 for 1.5 minutes at 30° C., stop, a dichromate bleach, clear for 1 minute in an aqueous solution containing about 100 g./l. of sodium sulfite, uniformly re-expose to light, color-develop for 10 minutes at 24° C. in Color Developer B, which is as follows:

Benzyl alcohol	ml./l. 10
Na_2SO_3	g./l. 2.0
Hydroxyl amine sulfate	g./l. 2.0
NaBr	g./l. 0.5
NaCl	g./l. 0.5
4 - amino - 3 - methyl-N-ethyl-N-β-methoxyethyl-aniline-di-*p*-toluene sulfonate	g./l. 5.0
Na_2CO_3 (anhydrous)	g./l. 30.0
$[Co(NH_3)6]Cl_3$	g./l. 1.6

pH 10.75 at 75° F.

Thereafter, the film is bleached, fixed and dried in the normal manner. The minimum and maximum densities, respectively, for the red (cyan dye) are .19 and 1.6; for the green (magenta dye), .18 and 2.4; and for the blue (yellow dye), .20 and 1.8.

Similar results can be obtained when other nonhalogenating bleaches are used after the black-and-white development such as ferric nitrate, cobaltic hexammine nitrate, quinone and sulfuric acid, and the like.

EXAMPLE 2

Example 1 is repeated except that $[Co(NH_3)_6]Cl_3$ chloride is replaced by an equivalent amount of one of the following metal complex oxidizing agent:

$[Co(en)_2(dien)]Cl_2 \cdot HCl$,
$[Co(NH_3)_5(H_2O)](ClO_4)_3$,
$[Co(NO_2)_3(NH_3)_3]$,
$[Co(NH_3)_4(CO_3)]NO_3$,
trans-$[Co(en)_2(Cl)_2]Cl \cdot HCl$,
trans-$[Co(en)_2(N_3)(NO_2)]S_2O_6$,
$[Co(trien)(NO_2)_2]NO_3 \cdot H_2O$,
cis-$[Co(trien)(Cl)_2]Cl$,
$[Co(en)_2(N_3)_2]NO_3$,
$[Co(en)_2(NO_2)_2](ClO_4)_3$,
$[Co(trien)(N_3)_2]NO_2$,
$[Co(en)_2(NH_3)_2]Cl_3$,
$[Co(tn)_3]Cl_3$,
$[Co(tn)_2(en)]Cl_3$, or
$[Co(tn)(en)_2]Cl_3$.

With each of the oxidizing agents a useful but somewhat less dense dye image is obtained.

EXAMPLE 3

Three photographic elements, Films A, B and C, are prepared by coating cellulose acetate film supports with gelatin silver bromoiodide (0.77 mole percent of the halide being iodide) emulsions at a silver coverage of 10 mg./ft.² and 300 mg./ft.² of gelatin. Film A contains 150 mg./ft.² of the cyan dye-forming 4-equivalent coupler 5 - [α - (2,4-di-*tert*-amylphenoxy)hexamido]-2-hepta-

fluorobutyramidophenol dissolved in dibutyl phthalate coupler solvent at a weight ratio of 1:½ coupler to coupler solvent (the stoichiometric ratio of silver to coupler is 1:10). Film B is the same as Film A except that the coupler used is the yellow dye-forming coupler α-(4-carbocarboxyphenoxy)-α - pivalyl - 2 - chloro-5-[γ-(2,4-di - *t* - amylphenoxy)butyramido]acetanilide. Film C is the same as Film A except that the coupler used is the magenta dye-forming coupler 1 - (2,4,6-trichlorophenyl)-3 - { - [α-3-pentadecylphenoxy)butyramido]benzamido}-5-pyrazolone. The films thus obtained are sensitometrically exposed to white light and developed for 32 minutes at 24° C. in the following developer solution:

	G.
4-amino-N-ethyl-N-β-hydroxyethylaniline sulfate	20.0
1-phenyl-3 - pyrazolidone	0.1
Na_2SO_3	40.0
Kbr	0.5
Na_4EDTA[1]	8.0
$[Co(NH_3)_6]Cl_3$	2.5
Borax	10.0

H_2O to 1 liter.
pH 11.0.

[1] EDTA as used herein means ethylenediamine tetraacetic acid.

After development, the films are washed in water for 10 minutes; the films are not bleached or fixed. The minimum and maximum cyan, yellow and magenta dye densities for Films A, B and C, respectively, are .6 and 2.6, .2 and .8, and .2 and 1.1. Comparison of these films with control coatings prepared and processed in the same manner, but including conventional bleaching and fixing after development, shows that the silver images remaining in the elements of the invention do not contribute measurable density to the dye images. The overall density of the silver image in the unbleached films is less than 0.4. Good multicolor images are obtained without bleaching or fixing when the light-sensitive coatings of Films A, B and C are coated on a common support and the silver halide grains in the layers are made sensitive to red, blue and green radiation with the green-sensitive layer preferably being coated between the red- and blue-sensitive layers.

EXAMPLE 4

A reversal-type multicolor photographic element is prepared by coating a polyethylene-coated titanium dioxide pigmented paper with the following layers (all weights are in mg./ft.^{2}):

Layer 1: an emulsion of gelatin, 200 mg.; blue-sensitized silver chlorobromide, 40 mg.; having dispersed therein a solution of 120 mg. of the yellow dye-forming coupler α - [4-(4-benzyloxyphenylsulfonyl)phenoxy] - α - pivalyl - 2 - chloro-5 - [γ-(2,4-di-*tert*-amylphenoxy)butyramido]acetanilide dissolved in 30 mg. of di-*n*-butyl phthalate;

Layer 2: gelatin, 100 mg.;

Layer 3: an emulsion of gelatin, 200 mg.; green-sensitized silver chlorobromide, 8 mg.; having dispersed therein a solution of 30 mg. of the magenta dye-forming coupler 1 - (2,4,6 - trichlorophenyl)-3-{5-[α-(3-*tert*-butyl-4-hydroxyphenoxy)tetradecanamido] - 2 - chloroanilino}-5-pyrazolone dissolved in 15 mg. of tricresyl phosphate;

Layer 4: gelatin, 241 mg.; having dispersed therein a solution of 65 mg. of the filter dye 2-(2'-hydroxy-3',5'-di-*tert*-amylphenyl)benzotriazole dissolved in 2-(2-butoxy-ethoxy)ethyl acetate, 32.5 mg.;

Layer 5: an emulsion of gelatin, 150 mg.; red-sensitized silver chlorobromide at 5.25 mg. of silver; having dispersed therein a solution of 23.4 mg. of the cyan dye-forming coupler 2-[α-2,4-di-*tert*-amylphenoxy) butyramido]-4,6-dichloro-5-methylphenol dissolved in 11.7 mg. of di-*n*-butyl phthalate;

Layer 6: gelatin, 100 mg.

A control Strip (1) of the above multicolor photographic element is exposed through a neutral density step tablet in an intensity sensitometer and processed at 30° C. (85° F.) as follows:

	Min.
Develop in black-and-white developer [1]	1.5
Acid stop bath	1
Wash	1
Re-expose to white light color-develop [2]	10
Bleach-fix	1.5
Wash	1
Stabilize	1

[1] Black-and-white developer solution:

	G.
N-methyl-*p*-aminophenol	2
Sodium sulfite, anhydrous	90
Hydroquinone	8
Sodium carbonate, monohydrate	52.5
Potassium bromide	5

Water to make 1 liter.

[2] Color-developer solution:

Benzyl alcohol	ml. 10.0
Sodium sulfite, anhydrous	g. 2.0
Hydroxylamine sulfate	g. 2.0
Sodium bromide	g. 0.5
Sodium chloride	g. 0.5
4 - amino-N-ethyl-N-(2-methoxyethyl)-*m*-toluidine di-*p*-toluene sulfonate	g. 5.0
Sodium carbonate, anhydrous	g. 30.0

Water to make 1 liter.
pH 10.75 at 75° F.

Strip (2) of the above multicolor photographic element is exposed and processed in the same manner as Strip (1) except that 1.6 g./1. of $[Co(NH_3)6]Cl_3$ is added to the color-developer solution.

Strip (3) of the same multicolor photographic element is exposed in the same manner as Strips (1) and (2). Strip (3) is processed at 30° C. (85° F.) in the following sequence:

	Min.
Develop (above black-and-white developer)	1.5
Acid stop bath	1
Wash	1
Bleach [1]	1
Clear [2]	1
Wash	1
Re-exposed to white light color-develop (above color developer containing 1.6 g./1. of $[Co(NH_3)6]Cl_3$)	10
Bleach-fix	1.5
Wash	2
Stabilize	1

[1] Bleach formula:

	G.
Potassium dischromate	10
Sodium sulfate	50
Sodium bisulfate	50

Water to make 1 liter.

[2] Clearing bath formula:

	G.
Sodium sulfite (anhydrous)	101.07

Water to make 1 liter.

The $D_{max.}$ and $D_{min.}$ of the dye images obtained with Strips (1), (2) and (3) are set forth in Table 1 below:

TABLE 1

	Strip (1) (control)		Strip (2)		Strip (3)	
	$D_{min.}$	$D_{max.}$	$D_{min.}$	$D_{max.}$	$D_{min.}$	$D_{max.}$
Red	0.15	0.72	1.6	1.6	0.19	1.6
Green	0.17	1.03	2.4	2.4	0.18	2.4
Blue	0.18	1.27	1.8	1.8	0.20	1.8

From the data in Table 1 it can be seen that a reversal-type multicolor photographic element (Strip 3) can be processed to produce dye images of low $D_{min.}$ and higher $D_{max.}$ than an element (Strip 1) processed according to conventional methods. Strip (2) having $D_{min.}$ values equal to $D_{max.}$ shows that a bleach step is necessary after the black-and-white development step and before the color-development step when using the specified color developer solution, because the developed silver from the black-and-white development step catalyzes the oxidation-reduction reaction between the hexammine cobalt(III) chloride and the primary amine color developer.

EXAMPLE 5

A first supported multilayer photographic element is prepared having the following composition. This element is identified as Element A (quantities of components in mg./ft.²).

Layer No.	
6	Overcoat ..... 100 mg. gelatin.
	(Red-sensitive silver halide emulsion layer) 35 mg. silver/159 mg. gelatin/35 mg. of 2-equivalent cyan dyeforming coupler identified in Layer 5 of Example 4, dissolved in 17.5 mg. di-*n*-butyl phthalate
4	Interlayer ..... 231 mg. gelatin.
	(Green-sensitive silver halide emulsion layer) 54 mg. silver/222 mg. gelatin/55 mg. of 4-equivalent magenta dyeforming coupler identified in Layer 3 of Example 4, dissolved in 27.5 mg. tricresyl phosphate
2	Interlayer ..... 100 mg. gelatin.
	(Blue-sensitive silver halide emulsion layer) 50 mg. silver/200 mg. gelatin/120 mg. of 2 equivalent yellow dyeforming coupler identified in layer 1 of Example 4, dissolved in 30 mg. di-*n*-butyl phthalate
	/ / / / / / / / / paper support / / / / / / / / /

A second element is prepared whose composition differs from that of Element A in that the silver halide calculated as silver is reduced to 10.0 mg. in Layer 1, 10.8 mg. in Layer 3, and 7.0 mg. in Layer 5. This element is identified as Element B.

Processing.—(A) A sample of Element A is sensitometrically exposed to a multicolor, graduate-density test object and then processed at a temperature of 27° C. in the following sequence:

	Min.
Color development	3.5
Bleach-fix	1.5
Wash	2
Stabilizer	1
Dry.	

The bleach-fix and stabilizer are as described in Example 4. The color developer is as follows:

Water	ml	800
Potassium sulfite (anhydrous)	g	5
Hydroxylamine sulfate	g	3
Potassium bromide	g	1
4-amino - N - ethyl - N - (2-methoxyethyl)-*m*-toluidine, di-*p*-toluene sulfonic acid	g	10
Potassium carbonate (anhydrous)	g	50

Water to 1 liter.
pH 10.8

The characteristics of the yellow, magenta and cyan dye images produced in Layers 1, 3 and 5 respectively are tabulated in Table 2.

TABLE 2

	$D_{min.}$	$D_{max.}$	Gamma
Yellow	0.12	2.02	2.1
Magenta	0.14	2.26	2.4
Cyan	0.11	2.20	2.3

The results indicate that when conventionally color-developed, the conventional color photographic Element A produces a good reproduction of the photographed object.

(B) When the procedure described in (A) above is repeated with a sample of the low-silver element, Element B, of this invention, yellow, magenta and cyan dye images are produced which are of very low maximum densities ($D_{max.}$) and contrast (gamma).

(C) When the development time in the procedure described in (B) above is increased from 3½ to 7 minutes, the produced dye images have marginal, but in practice still very low, maximum densities and contrast, as is shown by the data in Table 3.

TABLE 3

	$D_{min.}$	$D_{max.}$	Gamma
Yellow	0.14	1.16	0.7
Magenta	0.14	1.54	1.5
Cyan	0.12	1.76	1.6

(D) When the procedure described in (C) above is repeated (Element B, 7 minutes' development) with the above-identified color-developing solution to which have been added 1.6 g. of $[Co(NH_3)_6]Cl_3$ and 1 g. EDTA (ethylenediamine tetraacetic acid, tetrasodium salt), the sensitometrically determined values of the three dye images are essentially like those tabulated in Table 2, as shown in Table 4.

TABLE 4

	$D_{min.}$	$D_{max.}$	Gamma
Yellow	0.11	*1.52	*1.3
Magenta	0.12	2.24	2.4
Cyan	0.12	2.24	2.8

*The still somewhat low $D_{max.}$ and gamma values for the yellow dye image as shown in Table 4 are improved with similar photographic elements wherein the silver content in the initially blue-sensitive silver halide emulsion layer (Layer 1) is increased to concentrations ranging up to about 30 mg. of silver per square foot of coating. It is apparent that photographic elements comprising low silver coverages and high ratios of color coupler can be processed to provide very good image records.

EXAMPLE 6

The photographic elements of Example 5 are exposed to a multicolor, graduated-density test object and then processed at a temperature of 27° C. in the same sequence and the same time periods as in Example 5, except 4-amino-3-methyl-N,N-diethylaniline, hydrochloride, is used as the color-developing agent in the color-developing solution in place of the specified color-developing agent. Results similar to those described in Example 5 are obtained.

EXAMPLE 7

The improvements in amplifying the image record in the red and green recording layer of a photographic element are readily apparent when processing by first developing the element in a color developer and then inserting it into an amplifier bath.

A photographic element is prepared by coating the following layers in order on a paper support:

(1) a layer containing a blue-sensitive AgClBr emulsion at 16 mg. Ag/ft.², gelatin at 150 mg./ft.² and a 2-equivalent coupler, yellow dye-forming coupler, α-pivalyl - α - [4-(4-benzyloxyphenylsulfonyl)phenoxy]-2 - chloro-5-[γ-(2,4-di-*tert*-amylphenoxy)butyramido] acetanilide, at 75 mg./ft.², dissolved in di-*n*-butyl phthalate coupler solvent at 18.75 mg./ft.²;
(2) a gelatin interlayer at 80 mg./ft.² and a scavenger for oxidized developer;
(3) a layer containing a green-sensitive AgClBr emulsion at 10 mg. of Ag/ft.², gelatin at 60 mg./ft.² and a 4-equivalent magenta coupler, magneta dye-forming 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 tricresyl phosphate coupler solvent at 12.5 mg./ft.²;
(4) a gelatin interlayer containing 231 gelatin/ft.² and a scavenger for oxidized developer;
(5) a layer containing a red-sensitive AgClBr layer at 6 mg. Ag/ft.², gelatin at 65 mg./ft.² and a 2-equivalent cyan coupler, cyan dye-forming 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) a gelatin overlayer at 80 mg./ft.² of gelatin.

Samples of the coating are sensitometrically exposed to a graduated-density step tablet and then processed at a temperature of 32° C. in the following sequence:

	Minutes	
	Test 7A (Control)	Test 7B
Color development	3.5	3.5
Amplify		1
Bleach-fix	1.5	1.5
Wash	2	1
Stabilize	1	1

The respective baths have the following compositions:

Color Developer A

Benzyl alcohol	ml.	10
K_2SO_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_2CO_3		30
Na_4EDTA	g.	5

Water to 1 liter.
pH 10.1 at 24° C.

Amplifier

$[Co(NH_3)6]Cl_3$	g.	10
KBr	g.	2

Water to 1 liter.

Bleach-Fix

$(NH_4)_2S_2O_3$	g.	92.5
$NH_4[Fe(EDTA)]$	g.	50.6
EDTA	g.	2.9
Na_2SO_3	g.	12.0

Water to 1 liter.
pH 6.8 at 80° F.

Stabilizer

Citric acid	g.	6.15
Acetic acid	g.	13.1
Benzoic acid	g.	0.34
KOH	g.	5.97

Water to 1 liter.
pH 3.60 at 80° F.

Test A is run at the optimum time of development to produce $D_{max.}$ with the cyan and magenta dyes. While this amount of developed silver is more than necessary for the amplification process of Test B, the development time is not changed to show that the amplification step will generate additional dye beyond that provided in the development step.

The H and D curves of the elements of Tests 7A and 7B are produced in FIG. 2. The density of the dyes producing the red-sensitive, blue-sensitive and green-sensitive layers are reported as dashed lines for Test 7A and solid lines for Test 7B.

In the above process, sufficient color developer is carried into the amplifier bath to produce the desired dye density. If additional density is desired, more color developer can be added to the amplifier bath. The KBr in the above amplifier appears to suppress development sufficiently to allow room-light amplification. Methylbenzotriazole can also be used in the amplifier to prevent further development of silver in the amplifier bath, and preferably combinations of an organic development restrainer and an inorganic development restrainer are used to prevent further development.

EXAMPLE 8

The imagewise-erposed element of Example 7 is processed according to procedures below to provide for balanced developability.

	Minutes at 100° F.	
	Test 8A (control)	Test 8B
Develop	1	1
Amplify	0	3
Bleach-fix	1½	1½
Wash	2	2
Stabilize	1	1

The developer, bleach-fix and stabilization baths are the same as Example 7, and the amplification bath is made as follows:

Benzy alcohol	ml./l.	15
K_2SO_3	g./l.	2
KBr	g./l.	2
$[Co(NH_3)_6]Cl_3$	g./l.	10
K_2CO_3	g./l.	30
Na_4EDTA	g./l.	5

pH 10.1 at 75° C.

The results are shown in FIG. 3 wherein the H and D curves for the elements recorded in Tests 8A and 8B are reproduced. The dye density produced in the red-, green- and blue-sensitive layers is reported in dashed lines for Test 8A and solid lines for Test 8B. This amplifier is designed to give high contrast and low sensitivity to seasoning effects. Similar results are obtained with 5-methylbenzotriazole included in the amplifier at concentrations of up to 0.3 g./l. The 5-methylbenzotriazole prevents development and fog growth, thus stabilizing the overall process response.

When Test 8B is repeated in a continuous processor using a photographic element wherein the halide of the light-sensitive silver halide emulsion is about 6 to 7 mole percent iodide, the amplification is gradually shut off as the amplifier solution increases in iodide ion concentration.

EXAMPLE 9

In certain embodiments, the photographic elements of this invention preferably comprise color-providing layer units wherein the silver halide emulsion is one which has at least 50 percent of its silver developed in ⅓ of the time required to develop 95 percent of the developable silver, for example, that silver which develops within 16 minutes at 75° F. in Developer 9A. Generally, this definition defines those emulsions which will produce a high catalytic silver surface in a short time, as shown in the following.

Silver halide coatings which contain pure silver bromide, monodispersed cubic emulsions of varying grain sizes, prepared by a double-jet precipitation technique and free of chemical and spectral sensitization, are coated with the following aim coverages:

	Mg./ft.²
Gelatin	300
Silver	100
Cyan coupler, 5-[α-(2,4-di-*tert*-amylphenoxy)hexanamido]-2-heptafluorobutyramidophenyl dissolved in	150
di-n-butyl phthalate	75
Formalin	1.5

Samples of the above prepared coatings are exposed on a sensitometer, developed at 75° F. with two different developers, fixed, washed and dried. The amount of developed silver is then determined by X-ray fluorescent silver analysis and the percentage of silver developed at the longest development time is listed first for each emulsion coating. Assuming this to be the total amount of silver developable, the percentage of silver developed at each

time (Table 6) is derived from this figure tabulated in Table 5.

TABLE 5

Sample	Grain size (microns)	Percent silver developable: Developer 9A [1]	Developer 9B [2]
1	0.2	88	85
2	0.3	71	70
3	0.6	98	90
4	0.7	89	80
5	0.84	92	85

[1] Developer 9A is:

	G./l.
Na_2SO_3	2.0
4-amino-3-methyl-N-ethyl-N-β-(methane-sulfonamido) ethylaniline sesquisulfate hydrate	4.0
Na_2CO_3	40.0
$NaHCO_3$	3.7
NaBr	0.050

pH 10.2 at 75° F.

[2] Developer 9B is:

	G./l.
EDTA·4Na	1.0
Na_2SO_3	2.0
Hydroxylamine sulfate	2.0
NaCl	0.5
NaBr	0.5
Benzyl alcohol	5.0
4-amino-N-ethyl-N-(2-methoxyethyl)-*m*-toluidine di-*p*-toluene sulfonate	5.0
Na_2CO_3 (anhydrous)	30.0

pH 10.1 at 75° F.

TABLE 6

Sample	Percent silver developed as percent of developable grains: Min. at 75° F. of Developer 9A: 2	4	8	16	Min. at 75° F. of Developer 9B: 0.5	1	3	6	12
1	85	83	91	100	34	58	88	94	100
2	76	86	98	100	36	50	79	92	100
3	59	94	96	100	11	27	77	88	100
4	41	85	95	100	6	13	50	90	100
5	28	73	94	100	12	17	34	82	100

The correlation between developability of the emulsion layer and the results produced in an amplification system are apparent from an analysis of the developability rates of two different emulsions used in separate layers of the element of Example 7, as shown in the following example.

EXAMPLE 10

(A) The emulsion of the red-sensitized layer and the emulsion of the blue-sensitive layer, which are prepared in accordance with Evans, U.S. Ser. No. 21,467 filed Mar. 20, 1971, now abandoned (Belgian Pat. 764,356 issued May 14, 1971), are examined for development characteristics. The emulsions are coated as follows:

Sample 1

AgX emulsion (0.2μ 15/85 Cl/Br) __mg. Ag/ft.^{2}__ 50
Gelatin _____mg./ft.^{2}__ 250
Cyan dye-forming coupler, 2 - [α-2,4-di-tert-amylphenoxy)butyramido] - 4,6-dichloro-5-methylphenol (1:½ with di-*n*-butyl phthalate) __mg./ft.^{2}__ 49.5

Sample 2

AgX emulsion (1.2μ 12/88 Cl/Br) __mg. Ag/ft.^{2}__ 50
Gelatin _____mg./ft.^{2}__ 250
Yellow coupler, α-[4-(4-benzyloxy-phenylsulfonyl) phenoxy] - α - pivalyl - 2-chloro-5-[α-(2,4-di-*tert*-amylphenoxy)butyramido]-acetanilide (1:1/10 in *n*-phthalate) _____mg./ft.^{2}__ 90.9

The above prepared coatings are then exposed and developed for various times at 85° F. in Developer C identified below. Developability measurements are made according to the procedure described above with the following results wherein it is apparent that fine-grain emulsions yield a high amount of silver with short development times.

TABLE 7

Sample	Emulsion	Percent silver developed as percent of developable grains: Minutes of development time: 1	2	3	4	5	6
1	.2 μ 15/85 ClBr	68	75	82	87	98	100
2	1.2 μ 12/88 ClBr	45	82	91	100	100	

Developer C is:

Water	ml__	800
Diaminopropanol tetraacetic acid	g./l__	2.75
Na_2SO_3	g./l__	1.60
NaBr	g./l__	0.29
NaCl	g./l__	0.60
Benzyl alcohol	g./l__	13.5
Hydroxylamine sulfate	g./l__	3.40
4 - amino - 3-methyl-N-ethyl-N-β-(methanesulfonamido)ethylaniline sesquisulfate hydrate	g./l__	4.3
H_3BO_3	g./l__	20.4
KOH	g./l__	20

Water to 1 liter.
pH 10.1 at 75° F.

(B) The photographic three-color element of Example 7 contains the silver halide emulsions of Sample 1 in the red-sensitive layer and the green-sensitive layer and the silver halide emulsion of Sample 2 in the blue-sensitive layer. The silver halide concentrations and concentrations for all ingredients are as specified in Example 7.

The coated photographic elements are subjected to various tests using the developing bath, bleach-fix bath and stabilizing bath of Example 7 and the amplifier bath of Example 8.

	Minutes: Test 8A	Test 8B	Test 10A	Test 10B
Develop	1	1	[1] 15	[1] 15
Amplify	0	3	1	3
Bleach-fix	1½	1½	1½	1½
Wash	2	2	2	2
Stabilize	1	1	1	1

[1] Seconds.

The sensitometric results are reported in FIGS. 3 and 4 for the respective samples processed according to the tests.

With 1-minute development at 100° F. (Test 8A), substantially all of the developable grains in each layer have been developed as shown in FIG. 3 by the dashed lines. Dye formation appears to have stopped at this time of development.

With the 15-second development time and amplification, the cyan layer appears to provide full contrast since it is fully developed, whereas the yellow layer is apparently substantially undeveloped as shown by Tests 10A and 10B in FIG. 4. Test 10A is represented by dotted lines and Test 10B is represented by solid lines. Even an amplification time of 3 minutes does not appear to provide high amounts of dye in the yellow layer, whereas the cyan and magenta layers contain substantial image dye. The yellow layer does not appear to provide full contrast through amplification until at least 1 minute is given in the developer as shown by Test 8B in FIG. 3. Even though the yellow layer is coated at about twice the silver spread as the cyan layer, high amounts of catalytic silver surface are apparently not obtained with a large-grain emulsion at the short development times.

EXAMPLE 11

A photographic film element is prepared as follows (with all ingredients as listed in mg./ft.^{2}):

(1) cellulose acetate support;
(2) a layer containing a blue-sensitive silver bromoiodide emulsion (1.14% iodide) at 61 mg. of Ag (1.0 micron grain), the yellow dye-forming coupler α-pivalyl-α-(4-

carboxyphenoxy)-2-chloro - 5 - [γ-(2,4-di-*tert*-amylphenoxy)butyramido]acetanilide at 132 mg. dissolved 1:1 in tricresyl phosphate, and gelatin at 253 mg.;

(3) layer containing gelatin at 43 mg.;

(4) layer containing a red-sensitive silver chlorobromide (80/20) emulsion (0.25 micron grain size) at 10 mg. of silver, the cyan dye-forming coupler 2-[α-(2,4-di-*tert*-amylphenoxy)butyramido]-4,6-dichloro - 5 - methylphenol at 79 mg. dissolved 1:3 in di-*n*-butyl phthalate, and gelatin at 207 mg.;

(5) layer containing gelatin at 43 mg.;

(6) layer containing green-sensitive silver chlorobromide (80/20) emulsion (0.25 micron grain size) at 20 mg., the magenta dye-forming coupler 1-(2,4-dimethyl-6-chlorophenyl)-3-[α-(3 - *n* - pentadecylphenoxy)butyramido]-5-pyrazolone at 139 mg. dissolved 1:1 in di-*n*-butyl phthalate, and gelatin at 162 mg.;

(7) layer containing gelatin at 68 mg.

Samples of the film element are exposed on a sensitometer and developed in Developers 11A and 11B for 8 minutes at 75° F., fixed, washed, dichromate-bleached, washed, fixed and stabilized.

Developer 11A is:	G./l.
Na_4EDTA	4
K_2CO_3	40
KBr	2
K_2SO_3	4
4-amino - 3 - methyl-N,N-diethylaniline hydrochloride	3.0

Water to 1 liter.
pH 10.65 at 75° F.

Developer 11B is the same as Developer 11A except 1.6 g./l. of $[Co(NH_3)_6]Cl_3$ are added to the solution.

The densities for the samples processed in Developers 11A and 11B are as follows:

	Developer A		Developer B	
	$D_{min.}$	$D_{max.}$	$D_{min.}$	$D_{max.}$
Yellow	0.1	3.1	0.1	>4.6
Cyan	0.1	1.6	0.1	>4.6
Magenta	0.1	1.2	0.1	>4.8

It is apparent that photographic film elements having low silver coverages can be processed to provide good image records where cyan, yellow and magenta dyes have high densities in the $D_{max.}$ areas.

EXAMPLE 12

A photographic element, referred to herein as Film A, is prepared by coating on a transparent cellulose acetate film support a gelatin silver bromoiodide (about 0.6% of the halide being iodide) emulsion at 300 mg. gelatin/ft.², 150 mg. of the 4-equivalent photographic color coupler 5-[α-(2,4-di-*tert*-amylphenoxy)hexamido] - 2 - heptafluorobutyramidophenol dissolved in 75 mg./ft.² of the coupler solvent dibutyl phthalate, the silver halide being coated at a coverage of 10 mg. of silver/ft.². The coated layer contains silver to coupler at about a 1:2.5 stoichiometric ratio. Two samples of Film A are then sensitometrically exposed and processed at 24° C. in the following developer:

	G.
4-amino - N - ethyl-N-β-hydroxyethylaniline sulfate (color-developing agent)	20.0
1-phenyl-3-pyrazolidone	0.1
Na_2SO_3	40.0
KBr	0.5
Ethylenediamine tetraacetic acid (EDTA)	8.0
Cobalt hexamine chloride	2.5

H_2O to 1 liter.
pH 11.0.

One sample of the exposed film is developed for 4 minutes and the other is developed for 16 minutes. The developed films are then bleached, fixed and dried in the usual manner. The results obtained show that excellent dye images are produced with low minimum densities (under about 0.4). At the 16-minute and 4-minute development times, the highest maximum densities achieved are approximately 1.5 and 1.1, respectively. Slightly higher silver and coupler coverages produce dye images having maximum densities over 1.7.

EXAMPLE 13

Example 12 is repeated except that the cobalt hexamine chloride is replaced by an equivalent amount of one of the following metal complex oxidizing agents:

$[Co(en)_2(dien)]Cl_2 \cdot HCl$,
$[Co(NH_3)_5(H_2O)](ClO4)_3$,
$[Co(NO_2)_3(NH_3)_3]$,
$[Co(NH_3)_4(CO_3)]NO_3$,
trans-$[Co(en)_2(Cl)_2]Cl \cdot HCl$,
trans-$[Co(en)_2(N_3)(NO_2)]S_2O_6$,
$[Co(trien)(NO_2)_2]NO_3 \cdot H_2O$,
cis-$[Co(trien)(Cl)_2]Cl$,
$[Co(en)_2(NO_2)_2](ClO4)_3$,
$[Co(trien)(N_3)_2]NO_2$ or
$[Co(en)_2(NH_3)_2]Cl_3$.

With each of the oxidizing agents a useful but somewhat less dense dye image is obtained.

EXAMPLE 14

A light-sensitive silver dye emulsion is prepared according to Gilman et al., U.S. Pat. 3,446,619, and coated on a grey support which has a density through a red filter of 0.30. The coated emulsion contains per square foot 400 mg. of gelatin, 130 mg. of the cyan dye-forming coupler 5-[α-(2,4-di - *tert* - amyl-phenoxy)hexamido] - 2 - heptafluorobutyramidophenol dissolved in 65 mg. of the coupler solvent dibutyl phthalate and 0.066 mg. of the sensitizing dye 1 - carboxymethyl-5-[3-ethyl-2-benzoxazolinylidene) ethylidene]-3-phenyl-2-thiohydantoin reacted with 5.6 mg. of $AgNO_3$.

Test strip 1 of the photographic element is exposed through a graduated-density test object and developed in processing solution I for 15 minutes at 30° C. (85° F.), washed, fixed, washed and dried.

Processing Solution I

4 - amino-N-ethyl - N - β - hydroxyethylaniline sulfate	g.	10.0
Sodium sulfite	g.	10.0
Sodium bromide	g.	1.0
Sodium carbonate (anhydrous)	g.	30.0
Tetrasodium salt of ethylenediaminetetraacetic acid	g.	1.0
Benzyl alcohol	ml.	5.0

Water to make 1 liter.
pH 10.8.

The above procedure is repeated with test strips 2–9 except that 1.6 g./l. of $[Co(NH_3)_6]Cl_3$ is added to the processing solution I and the pH of processing solution I is adjusted to 9.3, 9.5, 10.0, 10.2, 10.4 and 10.8. These test strips are developed for 15 minutes except where the pH is 10.8, in which instance separate strips are developed for 5, 10 and 15 minutes. Further, the above procedure is repeated with test strip 10 developed in processing solution I at pH 10 at 38° C. (75° F.) for 15 minutes. The above procedure is again repeated except that the test strips 11 and 12 are developed for 15 minutes at 30° C. (85° F.) respectively, in processing solution II and in processing solution II with 1.6 g./l. of $[Co(NH_3)6]$ added.

Processing Solution II

4-amino-3-methyl-(N-ethyl-N - 2 - methoxyethyl)-aniline debenzene sulfonate	g.. 5.0
Sodium sulfite	g.. 10.0
Sodium bromide	g.. 1.0
Sodium carbonate (anhydrous)	g.. 30.0
Tetrasodium salt of ethylenediamine tetraacetic acid	g.. 1.0
Benzyl alcohol	ml.. 5.0

Water to make 1 liter.
pH 10.8.

The dye densities of the test strips read through a red filter are recorded in the table below:

Test strip	Processing solution	$[Co(NH_3)_6]Cl_3$ (g.)	pH	Dev. time, min.	Temp. (° C.)	$D_{min.}$	$D_{max.}$
1	I	0	10.8	15	30	0.30	0.50
2	I	1.6	9.3	15	30	0.34	0.78
3	I	1.6	9.5	15	30	0.38	1.14
4	I	1.6	10.0	15	30	0.40	1.35
5	I	1.6	10.2	15	30	0.44	1.50
6	I	1.6	10.4	15	30	0.48	1.70
7	I	1.6	10.8	5	30	0.45	1.08
8	I	1.6	10.8	10	30	0.60	1.60
9	I	1.6	10.8	15	30	0.77	2.18
10	I	1.6	10.0	15	38	0.62	2.60
11	II	0	10.8	15	30	0.28	0.32
12	II	1.6	10.8	15	30	0.69	1.72

From the above example, it is apparent that dyes reacted with $AgNO_3$ can also be used as the light-sensitive medium to produce good dye images when the cobalt complex is added to the processing solution.

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.

I claim:

1. A photographic element comprising a support having thereon at least two separate color-providing layer units which each contains a light-sensitive silver salt having associated therewith an image dye-providing photographic coupler in at least a 40 percent stoichiometric excess based on effective silver.

2. A photographic element according to Claim **1** wherein each of said color-providing layer units comprises said silver salt in a concentration of up to 30 mg. of silver/ft.^{2}.

3. A photographic element according to Claim **1** wherein one of said color-providing layer units comprises a green-sensitive silver halide emulsion and said coupler associated therewith is a magenta dye-forming coupler, and another of said color-providing layer units comprises a red-sensitive silver halide emulsion and said coupler associated therewith is a cyan-dye-forming coupler.

4. A photographic element according to Claim **1** wherein said color-providing layer units comprise a silver halide emulsion at a silver concentration of from 1 to 30 mg./ft.^{2} and said coupler at a concentration of from 3 to 20 times the weight of said silver.

5. A photographic element according to Claim **1** wherein each of said color-providing layer units contains silver halide emulsion which, when fully exposed and processed for about 1 minute in Developer A at 100° F., will provide less than 30 mg. of metallic silver/ft.^{2}, wherein Developer A has the composition:

Benzyl alcohol	ml.. 10
K_2SO_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_2CO_3	g.. 30
Na_4EDTA	g.. 5

Water to 1 liter; pH 10.1 at 24° C.

6. A photographic element according to Claim **1** wherein said image dye-providing coupler is associated with said silver salt in at least one of said image dye-providing layer units in at least a 70 percent stoichiometric excess based on effective silver.

7. A photographic element according to Claim **1** comprising superposed color-providing layer units containing silver halide emulsion layers sensitive to blue, green and red radiation, respectively, at least two of said color-providing layer units each containing a dye image-providing coupler in at least a 40 percent stoichiometric excess based on silver.

8. A photographic element according to Claim **7** wherein at least two of said color-providing layer units each contains a dye image-providing coupler in at least a 70 percent stoichiometric excess based on silver.

9. A photographic element according to Claim **7** wherein said coupler provides an image dye having predominant spectral adsorption in the same region of the visible spectrum as the primary effective light sensitivity of the silver halide in said layer unit.

10. A photographic element according to Claim **1** wherein each of said color-providing layer units comprises a silver halide emulsion which will develop at least 50 percent of its image silver in 30 percent of the time it takes to develop the layer to 95 percent of the developable silver in said layer.

11. A photographic element according to Claim **1** wherein each of said color-providing layer units comprises a silver halide emulsion having a mean grain size of less than 0.8 micron.

12. A photographic element according to Claim **1** wherein said color-providing layer units contain a silver halide and antifoggant concentrations of an azole or azide antifoggant which is substantially free of ionic iodide groups or free mercapto groups.

13. A photographic element according to Claim **1** wherein the light-sensitive silver salt of said color-providing layer units is a silver halide wherein the halide of said silver halide is less than 3 mole percent iodide.

14. A photographic element according to Claim **1** wherein said photographic coupler is a nondiffusible coupler.

15. A photographic element according to Claim **1** wherein said couplers in each of said color-providing layer units are nondiffusible couplers dissolved in a photographic coupler solvent.

16. A photographic element according to Claim **15** wherein said coupler solvent is dibutyl phthalate.

17. A photographic element according to Claim **15** wherein said coupler solvent is tricresyl phosphate.

18. A photographic element according to Claim **1** wherein each of said color-providing layer units contains silver halide emulsion coated at a coverage which, when fully exposed and fully developed, will provide a maximum silver density of less than 0.2 and said layer units comprise said coupler in a concentration sufficient to produce a dye density of at least 2.0.

19. A photographic element according to Claim **1** wherein said support is a transparent film support.

20. A photographic element according to Claim **1** wherein said support is a white opaque support.

21. A photographic element according to Claim **1** wherein the silver salt of said dye image-providing layers is a direct-positive silver halide.

22. A photographic element according to Claim **1** wherein the silver salt of said dye image-providing layers is a negative, silver halide.

23. A photographic element according to Claim **1** wherein said photographic coupler forms a nondiffusible image dye upon reaction with oxidized color developer.

24. In a photographic element comprising a support having coated thereon separate, overlying silver halide emulsion layers sensitive to blue, green and red radiation, respectively, said emulsion layers containing, respectively, yellow, magenta and cyan dye-forming couplers, the improvement wherein at least two of said silver halide emul-

sion layers are coated at a coverage of less than 30 mg./ft.² and which produces a maximum silver density of less than 0.4 when fully exposed and developed, and said dye-forming couplers are present in each layer at a concentration sufficient to produce a maximum dye density of at least 1.7.

25. A photographic element comprising a support having coated thereon, in the order given:

(a) a blue-sensitive silver halide gelatin emulsion layer having associated therewith a yellow dye-forming coupler;

(b) a green-sensitive silver halide gelatin emulsion layer coated at a coverage of less than about 15 mg. of effective silver per square foot, having associated therewith a magenta dye-forming coupler in at least a 40 percent stoichiometric excess based on effective silver;

(c) a red-sensitive photographic silver halide gelatin emulsion layer coated at a coverage less than about 15 mg. of effective silver/ft.², having associated therewith a cyan dye-forming coupler in at least a 40 percent stoichiometric excess based on effective silver.

26. A photographic element comprising a support having thereon at least two separate image dye-providing layer units which each contains a light-sensitive silver salt at a coverage of up to 30 mg. of silver/ft.² and an image dye-providing coupler associated with said silver salt in at least a 40 percent stoichiometric excess based on effective silver.

27. A photographic element according to Claim 26 wherein said coupler is associated with said silver salt in at least a 110 percent stoichiometric excess based on silver and said support is a transparent film support.

28. A photographic element according to Claim 26 wherein one of said image dye-providing layer units comprises a silver halide emulsion having an effective predominant spectral sensitivity to red light and another of said image dye-providing layer units comprises a silver halide emulsion having an effective predominant spectral sensitivity to green light.

29. A photographic element comprising a support having thereon at least two separate image dye-providing layer units which each contains a light-sensitive silver halide emulsion wherein the halide of said silver halide is less than 3 mole percent iodide and wherein said silver halide emulsion has associated therewith an image dye-providing photographic coupler in at least a 40 percent stoichiometric excess based on effective silver.

30. A photographic element according to Claim 29 wherein the halide of said silver halide emulsions is less than 0.25 mole percent iodide.

31. A photographic element according to Claim 29 wherein said coupler is associated with said silver halide emulsion in at least one of said image dye-providing layers in at least a 70 percent stoichiometric excess based on effective silver.

32. A photographic element comprising a support having thereon at least two separate image dye-providing layer units which each contains a light-sensitive silver halide emulsion and a silver halide antifoggant which forms a silver salt more soluble in water than silver bromide, and wherein said silver halide emulsion has associated therewith an image dye-providing photographic coupler in at least a 40 percent stoichiometric excess based on effective silver.

33. A photographic element comprising a light-sensitive silver halide emulsion coated on a support at a silver coverage of up to 15 mg./ft.², said emulsion containing a photographic color coupler at a concentration of at least 3 times the weight of said silver.

34. A photographic element according to Claim 33 wherein said emulsion contains said photographic color coupler at a concentration of from 4 to 15 times the weight of said silver.

35. A photographic element according to Claim 33 wherein said silver halide emulsion is coated at a silver coverage of less than 15 mg./ft.².

36. A photographic element comprising a support and having thereon at least two separate color-providing layer units which each contains a light-sensitive silver halide emulsion having associated therewith an image dye-providing photographic coupler in at least a 40 percent stoichiometric excess based on effective silver, wherein each of said color-providing layer units contains silver halide emulsion which, when fully exposed and processed for about 1 minute in Developer A at 100° F., will provide less than 30 mg. of metallic silver/ft.², wherein Developer A has the composition:

Benzyl alcohol	ml	10
K_2SO_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_2CO_3	g	30
Na_4EDTA	g	5

Water to 1 liter; pH 10.1 at 24° C.

37. A photographic element comprising a support and having thereon at least two separate color-providing layer units which each contains a light-sensitive silver halide emulsion having associated therewith an image dye-providing photographic coupler in at least a 40 percent stoichiometric excess based on effective silver, wherein each of said color-providing layer units comprises a silver halide emulsion which will develop at least 50 percent of its image silver in 30 percent of the time it takes to develop the layer to 95 percent of the developable silver in said layer.

38. In a photographic element comprising a support having coated thereon separate, overlying silver halide emulsion layers sensitive to blue, green and red radiation, respectively, said emulsion layers containing, respectively, nondiffusible color couplers which form nondiffusible yellow, magenta and cyan dyes, the improvement wherein said red- and green-sensitive silver halide emulsion layers are each coated at a silver coverage of from 2 to 15 mg./ft.² and the cyan and magenta dye-forming color couplers, respectively, are present in a concentration of from 4 to 10 times the weight of the silver in said red- and green-sensitive silver halide emulsion layers.

39. A photographic element comprising a support and at least one image dye-providing layer unit thereon comprising a light-sensitive silver halide emulsion at a concentration of up to 15 mg. of silver/ft.² and having associated therewith an image dye-providing color coupler in at least a 40 percent stoichiometric excess based on effective silver.

40. A photographic element according to Claim 39 wherein said coupler is associated with said silver halide emulsion in at least a 110 percent stoichiometric excess.

41. A photographic element according to Claim 39 which comprises at least two separate image dye-providing layer units which comprise a silver halide emulsion and an image dye-providing coupler in at least a 40 percent stoichiometric excess based on effective silver.

42. A photographic element according to Claim 41 wherein each of said image dye-providing layer units comprises a silver halide emulsion having substantially different spectral sensitivity.

43. A photographic element according to Claim 39 wherein the halide of said silver halide emulsion is less than 0.25 mole percent iodide.

44. A photographic element according to Claim 39 wherein the mean grain size of said silver halide emulsion is less than 0.8 micron.

45. In a photographic element which is used in an image-forming or image-intensifying process wherein an oxidizing agent and a reducing agent undergo a redox reaction in the presence of a silver catalyst, wherein the redox re-

action products of the oxidizing agent and the reducing agent are substantially noncatalytic for the redox reaction, the improvement in said photographic element comprising at least one image dye-providing layer unit which contains a silver halide emulsion and an image dye-providing coupler in at least a 40 percent stoichiometric excess based on effective silver.

46. A photographic element according to Claim **45** wherein said image dye-providing layer unit contains said silver halide emulsion in a concentration of up to 30 mg./ft.^{2}.

47. A photographic element according to Claim **45** wherein said photographic element comprises at least two of said image dye-providing layer units.

48. A multicolor photographic element comprising a support having thereon at least two image dye-providing layer units thereon, each comprising a silver halide emulsion coated in a concentration of up to 30 mg. of silver/ft.^{2} and wherein the halide of said silver halide is less than 3 mole percent iodide and the mean grain size of said silver halide emulsion is less than 0.8 micron and said silver halide emulsion has associated therewith an image dye-providing coupler in at least a 40 percent stoichiometric excess based on silver, and the silver halide emulsions in said image dye-providing layer units have substantially different sensitivity to visible light, and said coupler associated therewith is capable of producing an image dye having a predominant spectral absorption in the same region of the visible spectrum as the effective predominant sensitivity of the silver halide emulsion.

49. A photographic element according to Claim **48** wherein said couplers are water-insoluble couplers dispersed in a coupler solvent.

50. A photographic element comprising a support and at least one image dye-providing layer unit thereon comprising a light-sensitive silver halide emulsion at a concentration of up to 30 mg./ft.^{2} and having associated therewith an image dye-providing color coupler in at least a 70 percent stoichiometric excess based on silver.

References Cited

UNITED STATES PATENTS

3,533,745 2/1971 Vanden Eyde et al. ___ 96—56.5

RONALD H. SMITH, Primary Examiner

A. T. SURO PICÓ, Assistant Examiner

U.S. Cl. X.R.

96—100

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,834,907 Dated September 10, 1974

Inventor(s) Vernon L. Bissonette

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

Column 1, line 59, "Kirk-Othmer" should read --Kirch-Othmer--. Column 2, line 13, "and" should read --on--. Column 4, line 13, "thn" should read --than--. Column 7, line 34, "eash" should read --each--; line 49, "coatng" should read --coating--; line 70, "phane" should read --plane--. Column 10, line 21, "absorb" should read --adsorb--; line 74, "as" should read --at--. Column 14, line 3, "liability" should read --lability--. Column 15, line 74, "1:1/" should read --1:1/2--. Column 16, line 47, "agent" should read --agents--. Column 17, line 10, that part of formula reading "{-[α-3" should read --{3-[α-(3 --; line 18, "Kbr" should read --KBr--. Column 18, line 48, "dischromate" should read --dichromate--. Column 19, line 11, before "(Red-sensitive" and under "6", --5-- should be inserted; line 12, "dyeforming" should read --dye-forming--; line 16, before "(Green-sensitive" and under "4", --3-- should be inserted; line 17, "dyeforming" should read --dye-forming--; line 21, "dyeforming" should read --dye-forming--. Column 20, line 62, "magneta" should read --magenta--. Column 21, line 13, under "Stabilize", --Dry-- should be inserted; line 60, "produce" should read --reproduce--. Column 22, line 2, "imagewise-erposed" should read --imagewise-exposed--; line 18, "Benzy" should read --Benzyl--; line 63, that part of formula reading "heptafluorobutyramidophenyl" should read --heptafluorobutyramidophenol--; line 64, the line of dashes should be deleted and the number "150" should be placed directly under "100". Column 23, line 66, that part of formula reading "5-[α" should read --5-[γ --; line 68, "n-phthalate" should read -- di-n-phthalate --. Column 26, line 25, that part of formula reading "(Cl04)3" should read --(Cl04)3--. Column 32, line 19, "3,533,745" should read --3,563,745--; "Eyde" should read --Eynde--.

Signed and sealed this 11th day of March 1975.

(SEAL)
Attest:

RUTH C. MASON
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