

[54] ION-PAIRED COBALTIC COMPLEXES AND
PHOTOGRAPHIC ELEMENTS
CONTAINING SAME

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96/66 R, 66.3, 76 R, 77, 92, 93, 108, 110,
111; 260/105, 45.75

[56]

References Cited

UNITED STATES PATENTS

3,748,138	7/1973	Bissonette.....	96/66.3
3,656,961	4/1972	Hayakawa et al.	96/108
3,551,406	12/1970	Idelson.....	96/66
2,839,405	6/1958	Jones	96/108
3,565,622	2/1971	Sincius.....	96/63
3,702,247	11/1972	Williams et al.....	96/55
3,701,662	10/1972	Piccotti et al.....	96/55

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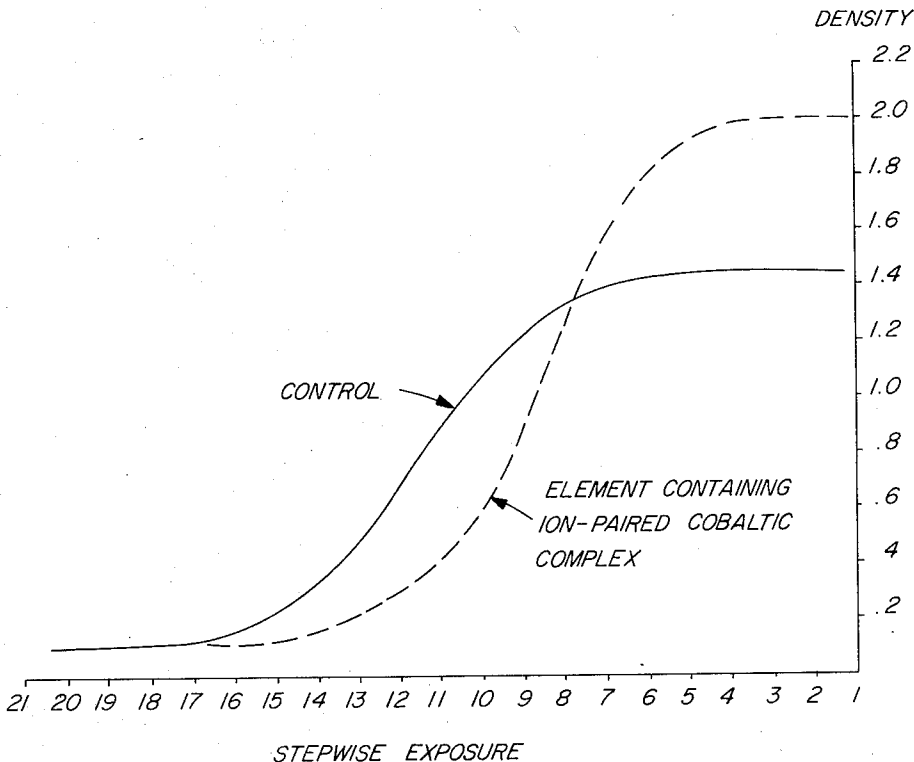
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[57]

ABSTRACT

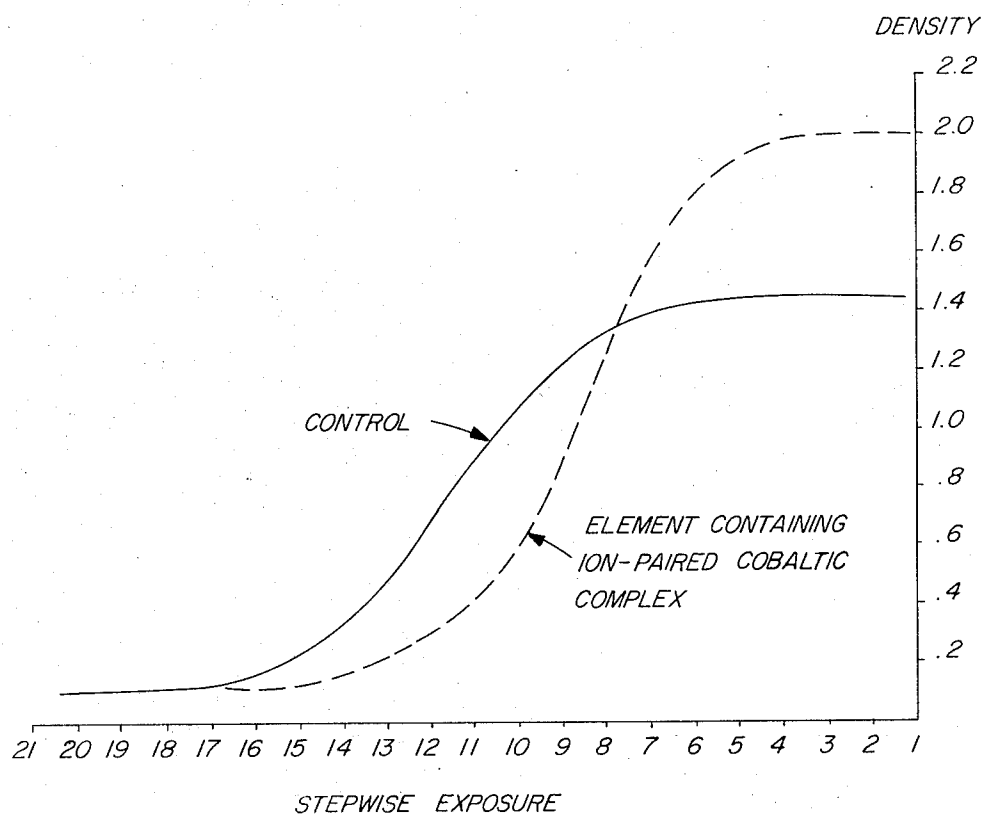
Photographic elements and photographic silver halide emulsions are disclosed which contain cobalt(III) ion complexes which are ion-paired with high-molecular-weight, anionic organic compounds.

35 Claims, 1 Drawing Figure



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3,847,619



ION-PAIRED COBALTIC COMPLEXES AND PHOTOGRAPHIC ELEMENTS CONTAINING SAME

This invention relates to cobalt(III) complex ions which are ion-paired with high-molecular-weight, organic compounds and to photographic silver halide emulsions and photographic elements containing said ion-paired cobalt complex ions. In one aspect, this invention relates to cobalt(III) complexes which are ion-paired with an anionic organic acid to form a water-insoluble compound or a relatively immobile compound when utilized in a photographic element. In another aspect, this invention relates to a method of incorporating cobalt(III) complexes into photographic silver halide emulsions and photographic elements.

Cobalt salts have been used in photographic elements in the prior art to provide stabilizers, fog inhibitors and the like, for example, as mentioned in British Pat. Nos. 1,214,982 and 239,875 and the like. Certain cobalt salts have also been mentioned as being useful in processing photographic elements, for example, as mentioned in British Pat. No. 777,635 and U.S. Pat. Nos. 3,615,508 and 2,750,292 by Dippel et al.

Certain cobalt salts have also been utilized in photographic elements in the prior art as the light-sensitive image-recording material, for example, as disclosed in U.S. Pat. Nos. 1,594,470, 3,297,440 and 3,429,760.

More recently, several photographic systems were discovered which utilize a transition metal-ion complex such as a cobalt(III) complex to amplify a prerecorded image pattern. Systems of this type are disclosed in co-pending applications U.S. Ser. Nos. 189,289 by Bissonette filed Oct. 14, 1971, and 256,072 by Travis filed May 23, 1972, now Pat. No. 3,834,907, which are both incorporated herein by reference.

In some instances, it would be desirable to incorporate the cobalt(III) complexes into a photographic element which contains another photographic, light-sensitive, image-recording material or directly into the silver halide emulsion. Generally, the direct incorporation of the cobalt(III) ion complex into the photographic element results in certain adverse effects such as, for example, substantial speed losses or desensitization occurring when the cobalt(III) ion complex is incorporated in photographic elements containing silver halide emulsions. Thus, improved methods of incorporating cobalt(III) metal-ion complexes into photographic elements would be useful in designing photographic systems.

We have now found that cobalt(III) ion complexes can be ion-paired with certain high-molecular-weight compounds and incorporated in photographic elements with a substantial reduction in adverse photographic properties. Generally, the ion pairs according to this invention can be prepared by procedures wherein substantially all of the cobalt(III) ion complex incorporated in the photographic element is ion-paired to form a water-insoluble or relatively immobile compound. The ion pair appears to remain relatively stable in the photographic elements under coating conditions and storage conditions and releases the cobalt(III) ion under processing conditions.

While we do not wish to be bound by any theoretical explanation for the stability of the ion pair as incorporated in a photographic element and the relative ease of release of the cobalt(III) ion under certain condi-

tions, it appears that metal-ion concentrations present in processing solutions and/or pH conditions in some instances may be responsible for the release of cobalt(III) ion under photographic processing conditions.

Generally, the ion pairs of this invention are formed with cobalt(III) ion complexes and anionic organic acids which generally have an equivalent weight of at least 70 and preferably between 100 and 300 based on acid groups. In one preferred embodiment, the anionic organic compound contains at least 2 carbon atoms for each acid present on the compound. The anionic acid groups are preferably sulfonic acid groups or carboxylic acid groups, but can include acid groups such as phosphonic acid groups, sulfinic acid groups, phosphate groups, sulfate groups and the like.

The ion pairs of this invention are generally incorporated in photographic elements at a concentration per a layer of silver halide emulsion of about 1 mg./ft.² to about 200 mg./ft.² and preferably from about 2 mg./ft.² to about 50 mg./ft.² based on cobalt. Generally, a photographic element comprises multiple image dye-providing layer units and contains the ion pairs at concentrations of from 3 mg./ft.² to about 600 mg./ft.² and preferably from about 5 mg./ft.² to about 150 mg./ft.² based on cobalt. In another aspect, the ion pairs can be incorporated in the silver halide emulsions or in elements containing silver halide emulsions to provide at least 0.25 mole of cobalt and preferably at least 0.5 mole of cobalt for each mole of silver.

The cobalt(III) ion pairs of this invention can generally be used in photographic elements where a cobalt(III) ion complex is desired during processing. The ion pairs are useful in photographic elements which are to be bleach-fixed in accordance with U.S. Pat. No. 3,615,508 issued Oct. 26, 1971, where cobalt can be released in the bleach-fix bath.

In one preferred embodiment, the photographic elements which are processed in accordance with Bissonette, U.S. Ser. No. 189,289 filed Oct. 14, 1971, contain the ion pairs whereby the cobalt(III) ion can be released during processing.

In another embodiment, the photographic elements containing the cobalt(III) ion pairs are processed as described in Bissonette, U.S. Ser. No. 189,331, now Pat. No. 3,748,138, where the cobalt can be released to provide an increase in the rate of metallic silver formation.

In still other embodiments, the cobalt(III) ion pairs can be utilized in photographic elements where cobalt(II) ion complexes are desired. After release of the cobalt(III) ion, it can be reduced in situ to provide the cobalt(II) ion complex for uses such as, for example, the processes described in U.S. Pat. No. 3,565,622 issued Feb. 23, 1971.

In another embodiment, the water-insoluble ion-paired cobalt(III) metal complexes of this invention are incorporated into silver halide emulsions. Silver halide emulsions of this type can be used in photographic elements or can be used for application to articles for non-destructive testing, such as by radioactive exposure and development wherein dense image records can be produced with very little radiation-sensitive silver.

In yet another embodiment, the water-insoluble ion pairs of this invention can be used in photographic elements at high concentrations sufficient for hardening or crosslinking polymeric binder vehicles or hydrophilic colloids by generation of oxidized tanning devel-

opers or use of the reduction products of the cobalt(III) ion complex.

The drawing accompanying this application contains a reproduction of an H and D curve of Elements A and E of Example 6. The curves demonstrate that the cobaltic complex is incorporated in the element by means which still allow it to participate in the image dye-producing reaction. Further details are provided in Example 6.

Generally, the ion pairs of this invention comprise a transition metal-ion complex which is preferably a cobalt(III) complex. Such complexes feature a metallic ion which 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 0.1 molar concentration at 20° C. in an inert solvent solution also containing 0.1 molar concentration of a tagged ligand of the same species which is uncoordinated, exhibits essentially no exchange of uncoordinated and coordinated ligands for at least 1 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.

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 chloride, bromide, fluoride, nitrite, water, amino, etc., as well as such common ligands as those referred to on p. 44 of Basolo et al., supra. The lability of a complex is influenced by the nature of the ligands selected in forming said complex.

Particularly useful cobalt complexes have a coordination number of 6 and have a polyatomic ligand selected from the group consisting of ethylenediamine(en), diethylenetriamine(dien), triethylenetetraamine(trien), ammine(NH₃), nitrate, nitrite, azide, 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. Some other specific highly useful cobalt complexes include those having one of the following formulas: [Co(NH₃)₅H₂O]X; [Co(NH₃)₅CO₃]X; [Co(NH₃)₅Cl]X; [Co(NH₃)₄CO₃]X; [Co(en)₃]X; cis-[Co(en)₂(N₃)₂]X; trans-[Co(en)₂Cl(NCS)]X; trans-[Co(en)₂(N₃)₂]X; cis-[Co(en)₂(NH₃)N₃]X; cis-[Co(en)₂Cl₂]X; trans-[Co(en)₂Cl₂]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.

The metal-ion complexes contain anions which are generally referred to as outer sphere complexed ions or ion pairs, and are to be distinguished from the ligands which are sometimes referred to as the inner sphere complexes. While the exact mechanism by which the cobalt compounds are retained in the element is not completely understood, it is believed that the acid group of the high-molecular-weight compounds described herein forms an ion pair, outer sphere complex, or salt with the metal-ion complex as described on pp. 34-38 of Basolo et al., supra. The term "ion pair" is thus used herein to refer to the metal-ion complex associated in what is believed to be an ion pair with the high-molecular-weight compound containing acid groups thereon.

The ion pairs of this invention are those which are substantially insoluble in distilled water at room temperature at a neutral pH, i.e., those which are completely insoluble, or at least less soluble than 1 percent by weight.

In one highly preferred embodiment, substantially all of the acid groups of the high-molecular-weight compound are ion-paired with the metal-ion complex so that there is no substantial increase in viscosity when dispersed in gelatin. The ion pairs of this embodiment provide for wide coating latitude and ease of coating in high-speed coating operations. Thus, the viscosity depends more on the concentration of solids than on the compatibility of the ion pair with the make-up binder vehicle.

The ion pairs according to this invention can be made by mixing the cobalt(III) ion complex with the anionic organic acid, imbibing the cobalt(III) ion complex in a layer containing the organic acid wherein the ion pair is formed in situ, etc., In some embodiments, the anionic organic compound is dispersed in gelatin or another hydrophilic colloid before addition of the cobalt(III) ion complex, especially when the ion pair is to be used in a photographic element or when the anionic or-

ganic compound is not wholly adequate as the carrier vehicle. The cobalt (III) ion complex is generally added to the anionic organic compound in at least a stoichiometric amount wherein the acid groups of the organic compound can replace all anions of the cobalt(III) ion complex. The conditions are maintained at the temperatures and for the duration necessary to obtain the desired amount of ion pairing. Generally, room temperatures can be used, but elevated temperatures can also be used to expedite the replacement reaction.

After the desired amount of ion pairing is achieved, the mixture is generally washed thoroughly to remove the unreacted cobalt(III) ion complex. This step is very desirable when the ion pair is to be utilized in a photographic element wherein adverse photographic properties occur as a result of cobalt(III) ion complex which is not ion-paired.

In order to wash the ion pair substantially free of cobalt(III) ion complex, it is desirable to select an anionic organic compound which will form an ion pair which is insoluble in the wash solution, such as an ion pair which is substantially water-insoluble. However, it is also desirable to use a compound which can be readily dispersed for coating.

When the ion pairs are to be utilized in photographic elements, it is very desirable to form ion pairs which are relatively immobile or nondiffusible to avoid premature reactions of the ion pair within the element, such as with ingredients in other layers of the photographic element.

In certain embodiments, polymeric compounds are used to form the ion pairs of this invention. Generally, these polymeric compounds contain acid groups thereon and have an equivalent weight of at least 70 and less than 800 and preferably between about 100 and 300 based on the acid groups. Higher equivalent-weight polymers are also useful, but they are not as efficient for incorporating the cobalt(III) ion complex since the weight percentage of cobalt in the ion pair is lower. Polymers useful in forming the ion pairs generally include any polymer which contains the acid groups thereon. In certain preferred embodiments, the polymers used to form the ion pairs are water-soluble polymers, i.e., those which are soluble to the extent of at least a 3 percent and preferably at least a 5 percent by weight solution in distilled water at room temperature.

Typical polymers which can be used include those containing units of styrene sulfonic acid; 3-methacryloyloxypropane-1-sulfonic acid, sodium salt; methacrylic acid; acrylic acid; and the like; and preferably units of acrylic monomers. In certain preferred embodiments, the ion pairs of this invention are prepared with homopolymers of the above monomers.

If the polymer used to form the ion pair contains an anionic acid group and groups which are crosslinkable by photographic hardeners, the polymer may serve as the primary or sole coating vehicle. Typical hardening groups which can be incorporated into polymers of this type include 2-acetoacetoxyethylmethacrylate, 2-[2-(methacryloyloxy)ethyl]isothiuronium methane sulfonate, N-cyanoacetyl-N'-methacryloylhydrazine, N-methacryloyl-N'-glycyl hydrazine hydrochloride, 2-aminoethyl methacrylate hydrochloride and the like. Typical useful polymers of this type include poly(N-isopropylacrylamide - 3-methacryloyloxypropane-1-sulfonic acid, sodium salt-2-acetoacetoxyethyl meth-

acrylate); and the like, including polymers containing acid groups disclosed in U.S. Pat. No. 3,459,790 by Smith issued Aug. 5, 1969, etc.

It is desirable to form an ion pair which can be coated under normal coating conditions in the ion-pair state and which will release the cobalt(III) ion complex under appropriate conditions, such as conditions used in photographic processing with an alkaline processing solution. Thus, the cobalt(III) ion complex can be incorporated in a photographic element in a relatively inactive form and can then be released at the appropriate time when reaction with the cobalt(III) complex is desired. In this manner premature reactions, such as desensitization of an unexposed silver halide emulsion, are substantially reduced.

The anionic organic compounds which are generally suitable according to this invention for forming useful ion pairs with cobalt(III) ion complexes are anionic organic acids. Preferably, the acid groups on the organic compounds which are used to form the ion pairs are carboxylic acid groups or sulfonic acid groups. The compounds may be used in formation of the ion pair in either their acid form or the salt form, as long as the compounds will undergo ion exchange in the presence of the cobalt complex.

In another preferred embodiment, simple compounds such as monomeric compounds can be used to form the ion pairs of this invention. Generally, these compounds also have an equivalent weight based on acid groups of at least 70 and up to 800 and preferably have an equivalent weight of about 100 to about 300. Typical useful compounds of this type include naphthalene sulfonate; sodium naphthalene-2,5-disulfonate; sodium lauryl sulfonate; sodium decyl benzene sulfonate; sodium naphthalene-2,7-disulfonate; tri-isopropyl naphthalene sulfonate, sodium salt, and the like.

Where the cobalt(III) ion complexes are used in photographic elements containing silver halide emulsions, the cobalt (III) ion complex is preferably a complex which will undergo a redox reaction at a metallic surface, such as a metallic silver surface, in the presence of a silver halide developing agent which is capable of reducing silver halide to silver under alkaline processing conditions, for example, with a developing agent such as 4-amino-3-methyl-(N-ethyl-N- β -ethoxyethyl)-aniline, di-p-toluenesulfonate. These cobalt complexes are especially preferred where the oxidized developing agent is used to produce image dye, tan the hydrophilic colloid, etc.

In certain embodiments, it is desirable to form the ion pair with a cobalt(III) ion complex having a net positive charge and preferably a net positive charge of +3. A cobalt (III) ion with six NH_3 ligands has a net positive charge of +3. A cobalt(III) ion with five NH_3 ligands and one chloro ligand has a net positive charge of +2. A cobalt(III) ion with two (en)ethylenediamine ligands and two (N_3)azide ligands has a net positive charge of +1. Generally, we have found that the best results in terms of compatibility in a photographic system and usefulness in photographic processes occur with ion pairs containing cobalt(III) complexes having a net positive charge of +3.

The cobalt(III) ion pairs of this invention can generally be used in any photographic element or in any photographic emulsion. Generally, the cobalt(III) ion pairs are used in photographic elements comprising a sup-

port having thereon one layer containing a silver halide emulsion such as an X-ray emulsion, a single-color system, photographic elements used in lithographic systems, etc. The photographic element can also be a multicolor element containing at least two image dye-providing layer units. Typical units of this type include elements such as disclosed in U.S. Ser. Nos. 256,072 by Bissonette filed May 23, 1972, or 285,399 by Dunn et al. filed Aug. 31, 1972, which are both incorporated herein by reference. Preferably, the multicolor photographic elements which are prepared in accordance with this invention contain an image dye-providing layer unit containing a blue-sensitive silver halide emulsion having associated therewith a yellow image dye-forming coupler, an image dye-providing layer unit containing a green-sensitive silver halide emulsion having associated therewith a magenta image dye-providing color coupler, and an image dye-providing layer unit containing a red-sensitive silver halide emulsion having associated therewith a cyan image dye-providing color coupler.

In certain embodiments, the ion pairs of this invention are very useful in photographic elements which are used to produce an image transfer wherein either the transferred image can be used or the image retained in the photographic element. The ion pairs can be used in photographic elements as described in Belgian Pat. No. 757,959 by Cole, U.S. Ser. Nos. 282,796 by Fleckenstein filed Aug. 22, 1972, and 206,836 by Lestina et al. filed Dec. 10, 1971, U.S. Pat. Nos. 3,227,552 by Whitmore, 2,983,606 by Rogers, and 3,443,940 by Bloom, and the like. Generally, the image transfer film units of this type can be made thinner, require less liquid in the processing composition, etc., with high yield of image dye.

The cobalt(III) ion pair can be located in the emulsion layers, adjacent layers, interlayers, underlayers, overlayers and the like. In certain preferred embodiments, the cobalt(III) ion pairs are coated in the photographic element in layers which are substantially free of photographic silver halide emulsions.

In photographic elements which comprise image dye-providing layer units, the photographic element generally contains at least 1 mg./ft.² of the cobalt(III) ion pair based on cobalt for each image dye-providing layer unit, and preferably from 2 mg./ft.² to 50 mg./ft.². In a photographic element containing three separate image dye-providing layer units, the element contains at least 3 mg./ft.², and preferably 15 to about 150 mg./ft.², of the cobalt(III) ion pair based on cobalt.

It is understood that in certain systems the cobalt(III) ion complex will function to generate products such as oxidized color developer which in turn reacts with color coupler to form an image dye. Since oxidized color developer can also be produced by development of silver halide, the concentration of cobalt(III) ion complex can be varied in an inverse ratio to the silver halide in a photographic emulsion. Thus, a photographic element containing image dye-providing layer units containing less than 30 mg./ft.² of silver halide based on silver will generally be associated with relatively high concentrations of cobalt(III) ion complex, and image dye-providing layer units containing high silver levels such as over 60 mg. of silver halide/ft.² based on silver may contain only low concentrations of cobalt(III) ion complex, especially where image dyes are being produced.

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 each comprise a silver salt at a concentration of up to 30 mg. of silver/ft.². Generally, these layer units will be the red- and green-sensitive silver halide-containing layer units. 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 coating coverage with less precise coating equipment, as well as for other reasons. Thus, highly preferred photographic elements of this invention contain at least two color-providing layer units, each containing a silver halide 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 follows:

Color Developer A

benzyl alcohol	10	ml.
K ₂ SO ₃	2	g.
KBr	0.4	g.
hydroxylamine sulfate	2	g.
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-paratoluenesulfonate	5	g.
K ₂ CO ₃	30	g.
ethylenediamine tetraacetic acid-sodium salt	5	g.
water to 1 liter		
pH 10.1 at 24° C.		

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 Dmax as is well-known in the art, for example, by exposure to a 500-watt, 3000° K lamp for about 10 seconds (total exposure at the film plane = 11.3×10^4 ergs/cm.²).

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. No. 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. Nos. 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. No. 1,055,155 issued Mar. 4, 1913, and particularly nondiffusible Fischer-type couplers containing branched carbon chains, e.g., those referred to in the reference cited in Frohlich et al., U.S. Pat. No. 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 solvent. 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 cobalt(III) ion pairs, the couplers and the 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 certain embodiments of this invention 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. The effective isolation of the layer units is known in the art and is utilized to prevent contamination in many commercial color products.

In certain preferred embodiments, 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. 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 embodiment, the color image-providing unit can comprise 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 0.6 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.

In certain embodiments, the photographic emulsions or photographic elements used in combination with the cobalt(III) complexes comprise a binder vehicle or carrier vehicle which can be hardened or crosslinked. The hardening can occur by the cobalt(II) complex formed during processing or it can occur by an oxidized tanning silver halide developer formed in the development step or in the oxidation-reduction reaction with the co-

balt(III) complex. Typical tanning reactions of this type are disclosed in Bissonette, U.S. Ser. No. 189,289 filed Oct. 14, 1971, and incorporated herein by reference. Typical useful vehicles which can be used in this embodiment include hydrophilic colloids such as gelatin, etc., polymers having crosslinking groups or photographic hardening groups, and the like.

In some embodiments, it is desirable to incorporate a timing layer or barrier layer between the layer containing the ion pair and other layers of the photographic element to delay release of the cobalt(III) ion complex. Typical useful timing layers include gelatin or other binder layers of about 50 to 2000 mg./ft.² which may contain pigments or dyes to mask the color of the cobalt complex either before processing during exposure or after processing.

In certain embodiments, the silver halide emulsions containing cobalt(III) complexes in accordance with this invention can be coated on materials to provide a means for nondestruction testing of the material. Various sources of electromagnetic radiation, such as radioactive emission, X-ray exposure and the like, can be used to provide a latent image record of the physical or chemical properties of the material. In one embodiment, the material can then be inserted in a developing solution or swabbed with a developer such as a viscous solution containing a color developer, and a color coupler if one is not present in the emulsion, to obtain an image dye record on the material. The emulsions of this invention would enable one to obtain very dense image records with very small amounts of light-sensitive silver halide.

The invention can be further illustrated by the following examples.

Example 1

To 100 ml. of 12.5% gel are added 30 ml. of poly(3-methacryloyloxypropane-1-sulfonic acid, sodium salt) (16.5% solids). To this is added 100 ml. of a saturated solution of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. This mixture is chill-set, noodled and washed for 12 hours until there is no detectable chloride ion in the wash water. Analysis gives 0.187 wt. % Co^{+3} . The gel is 5.0%.

Example 2

To 100 ml. of 12.5% gel are added 5 g. of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and the mixture is stirred at 40° C. (120° F.) until solution is obtained. While stirring vigorously, 50 ml. of poly(3-methacryloyloxypropane-1-sulfonic acid, sodium salt) are added and the solution becomes milky. An additional 25 ml. of poly(3-methacryloyloxypropane-1-sulfonic acid, sodium salt) are added until the solution clears. This is chill-set with stirring, noodled and washed until excess chloride is removed. It is then remelted and analyzed to give 0.578 wt. % Co^{+3} in about 6% gel.

Example 3 To 200 ml. of 12½% gel are added 10 g. of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and this is stirred until solution is effected. Then 50 ml. of 16.5% poly(3-methacryloyloxypropane-1-sulfonic acid, sodium salt) are added in 2-25 ml. portions. The dispersion is chilled, noodled and washed as above. Analysis shows 0.202 wt. % cobalt.

Example 4

A 9.4% solution of copoly(N-isopropylacrylamide--3-acryloyloxypropane-1-sulfonic acid, sodium salt --2-acetoacetoxyethyl methacrylate) (7:2¼ molar ratio) is coated on a paper support at 1504 mg./ft.² with formaldehyde hardener and saponin spreading agent. This is

equivalent to about 508 mg./ft.² of a hemopolymer of the sulfonic acid unit. A saturated $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ solution is applied to the surface of the paper and then the paper is washed. The theoretical uptake of cobaltic ion is between about 40 and 125 mg./ft.². Analysis shows the strips contain about 21.2 mg./ft.² cobaltic ion.

Example 5

Photographic elements are prepared as follows:

Element A (control):

1. support;
2. layer containing a blue-sensitive silver halide emulsion at 40 mg. of Ag/ft.², a yellow dye-forming coupler, α -pivalyl-4-(4-benzyloxyphenylsulfonyl)phenoxy-2-chloro-5-[γ -(2,4-di-tert-amylphenoxy)-butyramido]acetanilide, at 100 mg./ft.² dispersed in di-n-butyl phthalate at 25 mg./ft.² and gelatin at 240 mg./ft.²;
3. layer containing gelatin at 100 mg./ft.²;
4. layer containing a green-sensitive silver halide emulsion at 8 mg. of Ag/ft.² and a magenta dye-forming coupler, 1-(2,4,6-trichlorophenyl)-3-[5-[α -(3-tert-butyl-4-hydroxyphenoxy)tetradecanamido]-2-chloroanilino]-5-pyrazolone, at 50 mg./ft.² dispersed in tri-o-cresyl phosphate at 25 mg./ft.² and gelatin at 280 mg./ft.²;
5. layer containing gelatin at 231 mg./ft.²;
6. layer containing a red-sensitive silver halide emulsion at 5 mg. of Ag/ft.², the cyan dye-forming coupler 2-[α -(2,4-di-tert-amylphenoxy)butyramido]-4,6-dichloro-5methylphenol at 35 mg./ft.² dispersed in di-n-butyl phthalate at 175 mg./ft.² and gelatin at 172 mg./ft.²;
7. gelatin overlayer containing 100 mg. gelatin/ft.².

Element B:

Same as Element A except 5.0 mg./ft.² of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ are added to layers 2, 4 and 6 just before coating.

Element C:

Same as Element A except that layers 2-7 are coated on a support which has been prepared as described in Example 4.

The elements are exposed and processed in a color developer for 7 minutes at 29° C., bleach-fixed, washed, stabilized and dried. The color developer has the formula:

water	800	ml.
benzyl alcohol	10	ml.
Na_2SO_3	2	g.
hydroxylamine sulfate	2	g.
NaBr	0.5	g.
NaCl	0.5	g.
4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic acid	5	g.
Na_2CO_3 (anhydrous)	30	g.
ethylenediamine tetraacetic acid-sodium salt	5	g.
water to 1 liter; pH 10.0 at 24° C.		

The processed elements are compared for photographic speed in the red, green and blue recording layers and found to be as follows:

	Element A	Element B	Element C
red	control	-1.0 log E	-0.3 log E
GREEN	control	no image	-0.3 log E
blue	control	-1.0 log E	-0.3 log E

The contrast and Dmax of the image dye record are much higher in Element C than in Element A. The Dmin of Element C is substantially the same as Element A.

Example 6

Photographic elements are prepared as follows:

Element A:

1. support;
2. layer containing a green-sensitive silver halide emulsion at 15 mg./ft.², a magenta dye-forming coupler, 1-(2,4,6-trichlorophenyl)-3-[5-[α -(3-tert-butyl-4-hydroxyphenoxy)tetradecanamido]-2-chloroanilino]-5-pyrazolone, at 50 mg./ft.² dispersed in trio-o-cresyl phosphate and gelatin at 250 mg./ft.².

Element B:

Same as Element A except the dispersion of Example 1 is added to layer 2 to provide 20 mg./ft.² of cobalt.

Element C:

Same as Element A except the dispersion of Example 2 is added to layer 2 to provide 20 mg./ft.² of cobalt.

Element D:

Same as Element A except the dispersion of Example 3 is added to layer 2 to provide 20 mg./ft.² of cobalt.

Element E:

Same as Element A except the dispersion of Example 4 is added to layer 2 to provide 20 mg./ft.² of cobalt.

After exposure and processing as described in Example 5, Elements B-E have higher Dmax, higher contrast, and about 0.3 log E slower speed than Element A.

The H and D curves of Element A (control) and Element E (element containing ion-paired cobaltic complex) are reproduced in the FIGURE accompanying this application. It is apparent from the FIGURE that substantially more image dye is produced in Element E than in Element A, which demonstrates that the cobaltic ion is present in an active form during the dye formation process.

Example 7

A. A dispersion is made identical to that described in Example 1, but using a 17.5% solution of noncross-linked water-soluble sulfonated polystyrene (prepared by sulfonating polystyrene having a molecular weight of 60,000-100,000). The analysis is 0.42 wt. % cobaltic ion.

B. Six magenta single-layer coatings are prepared as described in Example 6, but using a non-spectrally sensitized version of the same emulsion for convenience in handling. The six coatings contain from 14.9 to 18.9 mg./ft.² of Ag and respectively 0, 2, 4, 8 and 17 mg./ft.² of cobaltic ion from the dispersion described in Section A above.

This represents a coverage of about 22, 44, 88 and 176 mg. of the cobalt hexammine polymer ion pair/ft.²

of coating. There is a speed loss of about .2 log E in all of the experiments with increased dye density at higher levels of cobaltic ion.

Example 8

Dispersions are also made according to Example 7-A where the cobalt(III) ion complex is $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$; $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$; $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{NO}_3$; $[\text{Co}(\text{en})_2(\text{N}_3)_2]\text{NO}_3$; and $[(\text{Co}(\text{tn}))_3]\text{Cl}$. Increased dye density is observed when these dispersions are used in photographic elements prepared in accordance with Example 7-B and exposed and processed in accordance with Example 5.

Example 9

A cobalt ion pair is prepared by adding a solution of 24 g. of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in 400 g. of 5% aqueous gelatin solution to a solution of 120 g. of Alkanol XC (TM) (a triisopropyl naphthalene sulfonate sodium salt) with stirring. The mixture is then dispersed, chilled, noodled and washed. The product is analyzed to contain 0.34% cobalt and 4.75% gelatin.

Example 10

Photographic elements are prepared as follows:

Element A:

1. polyethylene-coated paper support;
2. layer containing gelatin at 390 mg./ft.², the cobalt dispersion of Example 9 at 21 mg. of cobalt/ft.² and 400 mg./ft.² of Alkanol XC (TM);
3. layer containing 200 mg./ft.² of gelatin and 1500 mg./ft.² of TiO_2 ;
4. layer containing 150 mg./ft.² of gelatin;
5. layer containing a blue-sensitive silver halide emulsion coated at 16 mg./ft.² based on silver, gelatin at 122 mg./ft.² and a yellow dye-forming coupler, α -pivalyl-4-(4-benzyloxyphenylsulfonyl)-phenoxy-2-chloro-5-[γ -(2,4-di-tert-amylphenoxy)-butyramido]acetanilide, at 60 mg./ft.² dispersed in di-n-butyl phthalate at 15 mg./ft.²;
6. layer containing gelatin at 100 mg./ft.²;
7. layer containing a green-sensitive silver halide emulsion coated at 10 mg./ft.² based on silver, gelatin at 132 mg./ft.² and a magenta dye-forming coupler, 1-(2,4,6-trichlorophenyl)-3-[5-[α -(3-tert-butyl-4-hydroxyphenoxy)tetradecanamido]-2-chloroanilino]-5-pyrazolone, at 25 mg./ft.² dispersed in tri-o-cresyl phosphate at 12.5 mg./ft.²;
8. layer containing gelatin at 160 mg./ft.²;
9. layer containing a red-sensitive silver halide emulsion coated at 6 mg./ft.² based on silver, gelatin at 90 mg./ft.² and a cyan dye-forming coupler, 2-[α -(2,4-di-tert-amylphenoxy)butyramido]-4,6-dichloro-5-methylphenol, at 35 mg./ft.² dispersed in di-n-butyl phthalate at 17.5 mg./ft.² and gelatin at 90 mg./ft.²;
10. layer containing gelatin at 100 mg./ft.².

Element B:

This element is prepared exactly as Element A except layers 2, 3 and 4 are omitted.

Elements A and B are exposed, developed for 3½ minutes at 32° C., fixed for 1½ minutes, washed and dried. The developer formula is:

benzyl alcohol	15	ml./l.
K ₂ CO ₃	30	g./l.
KBr	0.25	g./l.
hydroxylamine sulfate	2.0	g./l.
K ₂ SO ₃	4.0	g./l.
diaminopropanol tetraacetic acid	3.0	g./l.
4-amino-3-methyl-(N-ethyl-N-β-ethoxy-ethyl)aniline, di-p-toluenesulfonate	5.0	g./l.
1-phenyl-4,4-dimethyl-3-pyrazolidone	0.025	g./l.
pH 10.1 at 24° C		

Sensitometric Results

Element	Speed			Dmax			Dmin		
	Red	Green	Blue	Red	Green	Blue	Red	Green	Blue
B (control)	1.57	1.85	1.70	1.6	1.7	2.0	.20	.20	.20
A	1.53	1.70	0.86	2.2	1.9	2.4	.18	.24	.22

Example 11

A cobalt ion pair is prepared as described in Example 9 except the Alkanol XC (TM) is replaced with sodium polystyrene sulfonate. The resulting ion pair is used in layer 2 of Element A of Example 10. Sensitometric evaluation of the processed element shows results similar to Element A.

Example 12

A cobalt ion pair is prepared as described in Example 9 except the Alkanol XC (TM) is replaced with 2-sulfonaphthalene and layers 3 and 4 are omitted. The resulting product is used in layer 2 of Element A of Example 10. The sensitometric results in the processed element are substantially equivalent to Element A, but slight loss of speed is observed.

Example 13

A solution of 240 g. of [Co(NH₃)₆]Cl₃, 4800 ml. water and 160 g. of a phthalated gelatin is added with rapid stirring to a solution of 960 g. of 2,7-disulfonaphthalene disodium salt dissolved in 6 l. distilled water at 49° C. After 3 minutes, the pH is adjusted to 3.0 with dilute H₂SO₄. The temperature is then lowered to 30° C. and the dispersion is allowed to settle. After decanting, the original volume of distilled water is added and the coagulum is redispersed at 40° C., pH 6.0. The dispersion is then adjusted to pH 3.8 and allowed to settle. After decanting, 137 g. of an aqueous gelatin dispersion containing 48 g. gelatin are added to the coagulum, redispersed at 40° C., pH 5.6, chill-set, noodled and washed for 1 hour to remove any chloride ion which may remain. The dispersion is then melted and brought to final weight of 3500 g. with distilled water.

Example 14

A multicolor photographic element is prepared as follows:

1. paper support;
2. layer containing a blue-sensitive silver halide emulsion at 24 mg./ft.² of silver, gelatin at 220 mg./ft.², the coupler α-pivalyl-4-(4-benzoyloxyphenylsulfonyl)phenoxy-2-chloro-5- γ -(2,4-di-tert amylphenoxy)butyramido]acetanilide at 100 mg./ft.² dispersed in di-n-butyl phthalate at 15 mg./ft.², a cobalt dispersion prepared according to Example 12 at 21 mg./ft.² based on cobalt and 154 mg./ft.² based on sulfonated compound, and 4-hydroxy-6-methyl-1,3,3a,7-tetrazoindene at 20 g./mole of silver;
3. layer containing gelatin at 77 mg./ft.²;
4. layer containing a green-sensitive silver halide emulsion at 10 mg./ft.² of silver, gelatin at 60 mg./ft.², and the coupler 1-(2,4,6-trichlorophenyl)-3-[5-[α-(3-tert-butyl-4-

- hydroxyphenoxy)tetradecanamido]-2-chloroanilino }-5-pyrazolone at 35 mg./ft.² dispersed in tricresyl phosphate at 12.5 mg./ft.²;
5. layer containing gelatin at 80 mg./ft.²;
6. layer containing a red-sensitive silver halide emulsion at 8 mg./ft.², gelatin at 50 mg./ft.², and the coupler 2-[α-(2,4-di-tert-amylphenoxy)butyramido]-

- 4,6-dichloro-5-methylphenol at 35 mg./ft.² dispersed in di-n-butyl phthalate at 17.5 mg./ft.²;
7. layer containing gelatin at 100 mg./ft.².

The above-prepared element is exposed through a multicolor, graduated-density test object, developed for 1½ minutes at 40° C., fixed, washed and dried. The developer formula is:

benzyl alcohol	15	ml./l.
K ₂ CO ₃	30	g./l.
KBr	0.5	g./l.
hydroxylamine sulfate	2.0	g./l.
K ₂ SO ₃	4.0	g./l.
diaminopropanol tetraacetic acid	5.0	g./l.
4-amino-3-methyl-(N-ethyl-N-β-ethoxy-ethyl)aniline, di-p-toluenesulfonate	7.5	g./l.
pH 10.1 at 24° C.		

Sensitometric results, when compared with a control which does not contain a cobalt dispersion, indicate equal photographic speed in the red-sensitive layer and a 0.4 log E speed loss in the green- and blue-sensitive layers. Dmax and Dmin values are:

	Dmin	Dmax
red	0.15	2.20
green	0.24	1.98
blue	0.20	2.20

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

We claim:

1. A photographic element comprising a support having thereon at least one layer containing a silver halide emulsion and at least one layer containing a water-insoluble ion pair of a cobalt(III) ion complex ion-paired with an anionic organic acid which has an equivalent weight of at least 70 based on acid groups.
2. A photographic element according to claim 1 wherein said photographic element contains from 1 mg./ft.² to about 600 mg./ft.² of said ion pair based on cobalt.
3. A photographic element according to claim 1 wherein said anionic organic acid is a compound which contains sulfonic acid groups and has an equivalent weight from about 100 to about 800 based on acid groups.
4. A photographic element according to claim 1 wherein said anionic organic acid is a compound which contains carboxylic acid groups and has an equivalent

weight from about 70 to about 800 based on acid groups.

5. A photographic element according to claim 1 wherein said anionic organic acid is a polymeric compound.

6. A photographic element according to claim 1 wherein said cobalt(III) ion complex has a net positive charge.

7. A photographic element according to claim 1 wherein said cobalt(III) ion complex has a net positive charge of +3.

8. A photographic element according to claim 1 which comprises at least one layer containing a binder vehicle which can be hardened by photographic hardening agents.

9. A photographic element according to claim 1 wherein said layer containing said silver halide emulsion is located within an image dye-providing layer unit which comprises a color coupler.

10. A photographic element comprising a support having thereon at least one layer containing a water-insoluble ion pair of a cobalt(III) ion complex ion-paired with an anionic organic acid having an equivalent weight of at least 70 based on acid groups and at least one image dye-providing layer unit containing a silver halide emulsion.

11. A photographic element according to claim 10 which comprises three image dye-providing layer units containing a silver halide emulsion having associated therewith a color coupler.

12. A photographic element according to claim 10 which contains said ion pair in a concentration of from 2 mg./ft.² to about 50 mg./ft.² based on cobalt for each image dye-providing layer unit.

13. A photographic element according to claim 10 which contains said ion pair in a concentration of from about 5 mg./ft.² to about 150 mg./ft.² based on cobalt.

14. A photographic element according to claim 10 wherein said image dye-providing layer unit contains less than 30 mg./ft.² based on silver of said silver halide emulsion.

15. A photographic element according to claim 10 wherein said image dye-providing layer unit contains at least a 40 percent stoichiometric excess of a color coupler based on silver.

16. A photographic element according to claim 10 wherein said anionic organic compound is a polymeric compound containing sulfonic acid groups thereon and having an equivalent weight of at least 100 based on said groups.

17. A photographic element according to claim 10 wherein said anionic organic acid contains at least 2 carbon atoms.

18. A photographic element according to claim 10 wherein said anionic organic compound is a naphthalene sulfonic acid.

19. A photographic element according to claim 10 wherein said anionic organic compound is a polymeric compound containing sulfonic acid groups thereon and photographic hardening groups thereon.

20. A photographic element comprising a support having thereon (1) an image dye-providing layer unit containing a blue-sensitive silver halide emulsion having associated therewith a yellow dye-providing coupler, (2) an image dye-providing layer unit comprising a green-sensitive silver halide emulsion having associ-

ated therewith a magenta dye-providing coupler, (3) an image dye-providing layer unit comprising a red-sensitive silver halide emulsion having associated therewith a cyan dye-providing coupler and (4) at least one layer in said element containing at least 3 mg. based on cobalt of a water-insoluble ion pair of a cobalt(III) ion complex ion-paired with an anionic organic acid having an equivalent weight of at least 70 based on acid groups.

21. A photographic element according to claim 20 wherein said ion pair is present in said element in a concentration of from about 5 mg. to about 15 mg./ft.² based on cobalt.

22. A photographic element according to claim 20 wherein at least two of said image dye-providing layer units contain less than 30 mg./ft.² of effective silver halide based on silver.

23. A photographic element according to claim 20 wherein at least two of said image dye-providing layer units contain at least a 40 percent stoichiometric excess of coupler based on silver.

24. A photographic element according to claim 20 wherein said ion pair is present in at least one image dye-providing layer unit.

25. A photographic element according to claim 20 wherein said layer containing said ion pair is located adjacent said image dye-providing layer units but in water-permeable association with said image dye-providing layer units.

26. A photographic element according to claim 20 wherein said anionic organic acid is a polymeric compound having an equivalent weight of between 70 and 800 based on acid groups.

27. A photographic element according to claim 20 wherein said anionic organic acid is a naphthalene sulfonate.

28. A photographic element according to claim 20 wherein said anionic organic acid is a polymer containing units of 3-methacryloyloxypropane-1-sulfonic acid.

29. A silver halide emulsion comprising a water-insoluble ion pair of a cobalt(III) ion complex ion-paired with an anionic organic acid which has an equivalent weight based on acid groups of at least 70 and less than 800.

30. A silver halide emulsion according to claim 29 which contains said ion pair to provide a concentration of at least 0.25 mole of cobalt for each mole of silver.

31. A silver halide emulsion according to claim 29 wherein said anionic organic acid is a polymeric compound.

32. A silver halide emulsion according to claim 29 wherein said cobalt(III) ion complex is a cobaltic hexammine.

33. A silver halide emulsion according to claim 32 which contains an image dye-providing color coupler.

34. A silver halide emulsion according to claim 29 wherein said cobalt(III) ion complex will undergo a redox reaction at a metallic silver surface in the presence of a silver halide developing agent.

35. A silver halide emulsion according to claim 34 wherein said cobalt(III) ion complex has a net positive charge.

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