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PROCESS FOR DEVELOPING RADIATION-SENSITIVE ELEMENTS

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ABSTRACT OF THE DISCLOSURE

Photographic dye images can be produced by physical development of imagewise exposed elements containing a radiation-sensitive metal compound to form an imagewise distribution of catalyst. The resultant catalyst image is then treated in the presence of a color developer and a color coupler with an amplifier solution containing a cobalt(III) complex having a coordination number of six, wherein said treatment is accomplished under conditions which reduce cobalt(III) to cobalt(II) and, in turn, oxidize the color developer to thereby form image dye from the oxidized color developer and the color coupler.

This is a continuation-in-part application of Bissonette U.S. Application Ser. No. 189,289, filed Oct. 14, 1971.

FIELD OF INVENTION

This invention relates to the art of photography and more particularly, to a process for developing photographic elements which comprise layer units containing a photosensitive metal compound that forms catalytic sites for the deposition of metal from a physical developer composition and optionally contain an image dye-providing photographic color coupler associated with said compound.

DESCRIPTION OF THE PRIOR ART

It is known in the prior art to physically develop exposed silver halide emulsions to thereby render the latent image visible. Typical physical developer solutions contain a reducible metal compound and a reducing agent. In physical development, virtually all the metal in the resultant visible image is formed by the selective reduction of metal ions supplied by the reducible metal compound during development. Once a catalytic site (e.g., the latent silver image specks) is enveloped with metal deposited from the developer solution, it is essential that the reduced metal be autocatalytic, that is, it too must catalyze the decomposition of the physical developer solution.

Physical development involving silver compounds has not had any substantial commercial application due to the instability of silver physical developer solutions. Thus, shortly after a physical developer solution is prepared by mixing silver salts and reducing agent, reduced silver begins to deposit rapidly and in a few hours the developer solution is completely decomposed. This type of instability is inherent in silver physical developer solutions, since the poor autocatalytic properties of silver metal require that silver physical developer solutions be formulated so as to be capable of depositing silver very rapidly, if inordinately long development times are to be avoided.

These problems have been overcome through the use of non-silver imaging elements and appropriate developer solutions therefor. Elements and processes of this type are described, for example, in Yudelson U.S. Pat. No. 3,597,206, issued Aug. 3, 1971. However, such physical development procedures typically are neutral density monochrome systems. Dippell et al. in U.S. Pat. No. 2,750,292, issued June 12, 1956, earlier described what was referred to as a means for producing colored images by physical color development. This latter system was lengthy in that it required separate sequential exposure and development steps for each color desired. Each development step alone required anywhere from three to ten minutes. Typical solutions for color formation contain both color-developing agent and a color coupler. Solutions of this type are prone to formation of dye in the bath through aerial oxidation of the developer, causing dye contamination; additionally, systems using these solutions are often limited to one color. Moreover, where a physical developing agent is used in conjunction with a color coupler and a color-developing agent, the processing baths themselves are often autocatalytic since the reaction products of the redox reaction with the physical development provide a catalyst for more redox reactions.

New processes for developing and amplifying an image record are disclosed in Bissonette U.S. Application Ser. No. 189,289, entitled Image-Forming Processes and Compositions, filed Oct. 14, 1971, and in Travis U.S. Application Ser. No. 256,071, entitled Process for Developing Photographic Elements, filed May 23, 1972, now U.S. Pat. No. 3,765,891, both incorporated by reference herein. In one embodiment, the processes disclosed therein relate to image formation in photographic elements comprising color-providing layer units containing a silver halide emulsion having associated therewith a color coupler. While such processes are excellent for forming color images from silver halide emulsions, they typically involve the use of only chemical development in the formation of visible images.

Accordingly, there is a need in the art for a relatively simple means for obtaining colored images through the use of physical development.

SUMMARY OF THE INVENTION

I have found that photographic dye images can be produced, using physical development techniques, by first physically developing an imagewise exposed element containing a radiation-sensitive metal compound to form an imagewise distribution of catalyst. The resultant catalyst image is then treated, in the presence of a color developer and a color coupler, with an amplifier solution containing a cobalt(III) complex having a coordination number of 6, said treatment being accomplished under conditions which reduce cobalt(III) to cobalt(II) and, in turn, oxidize the color developer to thereby form image dye from the oxidized color developer and the color coupler.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The objects of the present invention are achieved through the use of a photographic element comprising a support having thereon at least one color-providing layer unit containing a radiation-sensitive compound of a first metal, which compound, upon exposure to actinic radiation, forms catalytic sites for the deposition of a second metal from a physical developer composition. In a preferred embodiment, said compound has associated therewith an image dye-providing color coupler. An element of this type is imagewise exposed to form a latent image of catalytic sites for physical development. After exposure, the element is subjected to a physical developer composition, for example, by immersing the element in an aqueous solution of the physical developer. After physical development, the resultant imagewise distribution of catalyst is treated with an amplifying bath in the presence of a color-forming reducing agent and a color coupler to effect a catalyzed redox reaction between an oxidizing agent and a color-forming reducing agent whereby said reducing agent is oxidized and combines with the color coupler to form an image dye in the areas corresponding to said catalyst.

Generally, the photographic elements in accordance with this invention comprise any suitable support such as those known in the photographic art. Carried on that support is at least one and preferably two or more color-providing layer units which can contain a wide variety of metal compounds which, upon exposure, form sites for further physical development. Materials of this type include metal compounds which yield photolytically produced metal latent image sites (such as metal images of silver, gold, copper, iron, tin, mercury, palladium, etc.), as well as those which merely form an electronic charge latent image such as various photoconductors known in the art. The former type of metal compounds include various silver salts (e.g., halides, oxalates, etc.), as known in the art as well as a variety of non-silver metal salts, such as oxalate, citrate, etc., salts of a Group VIII, Group I*b* or Group II*b* metal, e.g., palladium oxalate, ferric ammonium oxalate, mercury oxalate, ferric ammonium citrate and the like. Non-silver salts of this type and their use are described in U.S. Pat. No. 2,750,292, issued June 12, 1956, U.S. Pat. No. 3,597,206, issued Aug. 3, 1971 and British Pat. No. 1,265,844, dated Mar. 8, 1972. Various useful photoconductive compounds include metal oxides, such as titanium dioxide, antimony trioxide, zirconium dioxide, germanium dioxide, indium oxide, stannic oxide, barium titanate, lead oxide, tantalum oxide, and tellurium oxide; metal sulfides such as cadmium sulfide, zinc sulfide and stannic sulfide; and metal selenides, such as cadmium selenide. Inorganic photoconductors of this type are described further in U.S. Pat. No. 3,121,006, issued Feb. 11, 1964. Some of these materials are sensitive to radiation outside the visible region of the spectrum. For example, certain lead oxides are sensitive to X-radiation. Preferred photoconductive compounds for use in this invention are oxides and sulfides of Group II*b*, IV*b* or IV*a* metals. Highly preferred are metal oxides, with titanium dioxide providing good results. Thus, preferred photosensitive metal compounds for use herein contain a Group I*b*, II*b*, IV*b*, IV*a* or VIII metal atom as seen in the Periodic Chart of the elements found on page 30 of Cotton and Wilkinson *Advanced Inorganic Chemistry,* 1962 Edition.

In preferred embodiments, especially multicolor embodiments, there is a color coupler associated with the radiation-sensitive metal compound. The terms "photographic color coupler" and "image dye-providing color coupler" include any compound which reacts (or couples) with the oxidation products or primary aromatic amino developing agent on photographic developemnt 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. In those instances of diffusible dye formation, the resultant dye is generally imagewise transferred to a receiver sheet. 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 January 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. Pats. 2,322,027 by Jelley et al., issued June 15, 1943, or 2,801,171 by Fierke et al., issued July 30, 1957. When coupler solvents are employed, the most useful weight ratios of color coupler to coupler solvent range from about 1:3 to 1:0.1. The useful couplers include Fischer-type incorporated couplers such as those described in Fischer U.S. Pat. 1,055,155, issued Mar. 4, 1913, and particularly nondiffusible Fischer-type couplers containing branched carbon chains, e.g., those referred to in the references 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,* Volume 83, pages 26–29, March 1971, and the like.

The light-sensitive metal compounds 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 photosensitive 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. A multicolor photographic element comprises at least two of said image dye-providing layer units each of which primarily records light in a different region of the spectrum. The layer unit comprises a light-sensitive metal compound, which can be spectrally sensitized to a specific region of the spectrum, and a photographic color coupler associated with said compound. 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.

The concentration of coupler can vary widely. In preferred embodiments, the coupler concentration is in excess over the amount of photosensitive metal compound present. In certain preferred embodiments, the photographic color couplers are employed in the image dye-providing layer units at a concentration of at least about 3 times and up to about 20 times the weight of photosensitive material present in that layer unit. Weight ratios of coupler to metal compound which are particularly useful are from 4 to 15 parts by weight of coupler to 1 part by weight of metal compound. 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 metal) 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 containing coupler 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 is major absorption between about 500 and 600 nm., and the yellow dye has its major absorption between about 400 and 500 nm.

After exposure of the described elements, they are treated with a physical developer composition to deposit imagewise a catalytically active metal such as a Group VIII, Group VI*a* or Group I*b* metal which typically is different from the metal of said photosensitive compound. Useful physical developer compositions contain as the major active ingredient an ionizable salt of a Group I*b*, VI*a* or VIII metal. Physical developer solutions for use with elements containing a photosensitive metal compound which upon exposure yields photolytically produced metal latent image sites, typically comprise a reducible heavy metal salt (e.g., a reducible salt of such metals as nickel, cobalt, iron, chromium or copper), a reducing agent for the heavy metal salt (e.g., formaldehyde, sodium hypophosphite, sodium hydrosulfide or potassium borohydride), and a complexing agent for heavy metal ions derived from the reducible heavy metal salt (e.g., a carboxylic acid such as maleic acid, lactic acid, citric acid, aspartic acid or glycolic acid). Such physical developers are extremely stable under storage conditions, but in the presence of catalytic centers are reduced and deposit heavy metal on the catalytic sites. Physical developer compositions of this type as well as the formulation thereof are described, for example, in U.S. Pat. No. 3,597,206 which is incorporated herein by reference.

In those instances wherein the photosensitive metal compound used is a photoconductor as described previously, the deposition of a catalytically active Group I*b*, VI*a* or VIII metal can be accomplished in a variety of ways. For example, a solution of a suitable metal salt can be applied to the exposed element whereby the trapped electron-hole pairs produced in the exposed areas of the photoconductor interact with the metal ions in solution to cause imagewise deposition of metal. Additionally, various electrolytic deposition techniques can be used as described, for example, in U.S. Pat. No. 3,372,029, issued Mar. 5, 1968.

The term "physical development" as used in connection with this invention has reference to any means for imagewise depositing a catalytically active Group I*b*, VI*a* or VIII metal including the various means known in the art of photoconductography (e.g., see U.S. Pat. No. 3,010,883, issued Nov. 28, 1961). Physical development also refers to the physical deposition of metal to form a subvisible or only partially visible image. The resultant physically developed image need not be visible to be useful as it serves as a catalyst for a subsequent dye formation reaction. The physical developer for the photosensitive elements of this invention can, of course, be applied from a rupturable pod which optionally can be an integral part of the element.

The photographic elements described herein are subsequently treated by the processes disclosed in Bissonette U.S. 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 the catalytic surface provided by the metal deposited from the physical developer solution. 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. Preferred metal complexes in accordance with this process have coordination numbers of six and are known as octahedral complexes. 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 by Basolo and Pearson in *Mechanisms of Inorganic Reactions, a Study of Metal Complexes and Solutions,* 2nd Edition, 1967, published by John Wiley and Sons, page 44. The lability of a complex is influenced by the nature of the ligands selected in forming said complex.

Particularly useful cobalt complexes have a coordination number of 6 and have a ligand selected from the group consisting of ethylenediamine(en), diethylenetriamine(dien), triethylenetetraamine(trien), ammine(NH_3), nitrate, nitrite, azide, chloride, thiocyanate, isothiocyanate, water, carbonate, and propylenediamine(tn). The preferred cobalt complexes comprise (1) at least 2 ethylene diamine ligands or (2) at least 4 ammine ligands or (3) 1 triethylenetetraamine ligand. Especially useful are the cobalt hexammine (e.g., the chloride, bromide, sulfite, sulfate, perchlorate, nitrate, nitrite and acetate salts). Some other specific highly useful cobalt complexes include those having one of the following formulas:

$$[Co(NH_3)_5H_2O]X;\ [Co(NH_3)_5CO_3]X;\ [Co(NH_3)_5Cl]X;\ [Co(NH_3)_4CO_3]X;\ [Co(en)_3]X;\ cis[Co(en)_2(N_3)_2]X;$$

$$trans\text{-}[Co(en)_2Cl(NCS)]X;\ trans\text{-}[Co(en)_2(N_3)_2]X;$$

$$cis\text{-}[Co(en)_2(NH_3)N_3]X;\ cis\text{-}[Co(en)_2Cl_2]X;$$

$$trans\text{-}[Co(en)_2Cl_2]X;\ [Co(en)_2(SCN)_2]X;$$

$$[Co(en)_2NCS)_2]X;\ [Co(tn)_3]X;\ [Co(tn)_2(en)]X;$$

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.

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. In certain embodiments, the reducing agent used in this process is an aromatic primary amino color-developing agent such as p-phenylenediamine. 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*-phenylenediamine, 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*, Volume 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-methylamino-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*-toluenesulfonate.

In one embodiment, the amplifier solution of oxidizing and reducing agents can be imbibed into an applicator sheet, such as a gelatin coated support, and placed in face-to-face contact with the physically developed photosensitive element in the presence of an activator solution. A suitable activator would include an aqueous alkaline solution. Also, the activator solution can be a viscous medium which can be applied between the applicator sheet and the element through the use of a rupturable pod.

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

Example 1

A sample of a supported single-layer gelatinous coating containing per square foot of coating 200 mg. of gelatin and 80 mg. of the magenta-dye forming coupler 1-(2,4,6-trichlorophenyl) - 3 - {5-[α-(3-t-butyl-4-hydroxyphenoxytetradecaneamido] - 2 - chloroanilino}-5-pyrazolone (described in U.S. Pat. No. 3,519,429) dissolved in 40 mg. of tricresyl phosphate, is imbibed for 5 minutes with an aqueous solution of palladium oxalate

(0.3 g. $K_2Pd(C_2O_4)_2$ in 100 ml. H_2O).

Elemental analysis shows that a 5-minute imbibition in the above solution gives a palladium oxalate coverage of 5–10 mg./ft.². Upon drying it is exposed to a graduated-density test object using radiation in the range of 360 to 440 nm. The sample is then nickel physically developed in a solution of the following composition:

	G.
$NiCl_2 \cdot 6H_2O$	23.8
NaH_2PO_2	21.2
Gluconic Acid (50% in H_2O)	225
H_2O to 1 liter.	

(pH adjusted to 5.0 with NaOH, then to 9.0 with NH_4OH)

After physical development, the sample is washed, then color developed in developer of the following composition:

	G.
K_2CO_3	30
K_2SO_3	2.0
4 - amino - N - ethyl - N(2 - methoxyethyl) - m-toluidine di-p-toluenesulfonate	5.0
$[Co(NH_3)_6]Cl_3$	1.6
H_2O to 1 liter; pH 10.1 with 10% HCl.	

The exposure and processing conditions are as follows:

Exposure	min	[1] 3
Nickel physical development	sec	10
H_2O Wash	sec	10
Color Developer	min	10
H_2O Wash	min	3

[1] Considerably more than sufficient to fog silver chloride contact papers.

Under these exposure and processing conditions, an excellent magenta dye image of the test object is obtained, with no fog and no residual nickel metal image. The nickel image is either too faint to be seen or else it is completely bleached by the $[Co(NH_3)6]Cl_3$ contained in the color developing solution.

Example 2

A melt of the following composition is hand-coated at a wet thickness of .006 inches onto a support:

H_2O	ml	10
TiO_2	g	2
Gelatin (12.5% aqueous solution)	ml	7
Saponin (7% aqueous solution) (spreading agent)	ml	1
Formalin (5% aqueous solution) (hardener)	ml	1
Green sensitizing dye (merocyanine, .6 mg./ml.)	drops	3

The above light-sensitive layer is then overcoated at a wet thickness of .006 inches with a melt of the following composition:

	Ml.
Gelatin (12.5% aqueous solution)	9.4
Saponin (7% aqueous solution)	2.5
Coupler of Example 1 (6% dispersion in tricresyl phosphate)	5.4
H_2O	20
Formalin (5% aqueous solution)	2.5

A strip of the dual-layer element thus prepared is exposed for 15 seconds with a low-output U.V. lamp through a line-copy test sample and then immersed for 2 minutes in an approximately 1% aqueous silver nitrate solution. The strip is washed for 1.5 minutes and then treated for 2 minutes at room temperature in the developer/amplifier solution the composition of which is shown below. After fixing in a Kodak F–5 sodium thiosulfate fixing solution (see page 3315 of *Handbook of Chemistry and Physics,* 41st Edition), washing, and final drying, the strip contains a negative magenta dye image reproduction of the photographic test sample. A similar element is exposed and treated with $AgNO_3$ in the same manner as above, followed by treatment for 1 minute in the Kodak F–5 fixing solution, washing for 2 minutes and treatment in the developer/amplifier bath. A good dye image results. A repeat of the above described procedure with a developer/amplifier solution which does not contain cobalt hexammine does not yield a good visible dye image.

Composition of Developer/Amplifier Solution

Benzyl alcohol	ml	15
K_2CO_3	g	30
KBr	g	0.7
Hydroxylamine sulfate	g	2
K_2SO_3	g	4
Diaminopropanol tetraacetic acid	g	3
Color Developing Agent (4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine, di-p-toluenesulfonate)	g	7.5
$[Co(NH_3)_6]Cl_3$	g	1.6
Water	liters to	1

Example 3

A sample of a supported single-layer gelatin coating containing per square foot of coating 200 mg. gelatin, 5 mg. $K_3Fe(C_2O_4)_3 \cdot 3H_2O$, and 168 mg. of the magenta-dye-forming coupler of Example 1 dissolved in di-n-butylphthalate is exposed for 5 minutes at a distance of 12 inches to a 1000 watt quartz iodide lamp through a graduated density test object and then processed in the following manner:

	Sec.
Treatment in 1% aqueous $K_3[Fe(CN)_6]$ solution	30
Wash	30
Treatment in 1% aqueous $AgNO_3$	30
Wash	30
Treatment in the amplifier solution described in Example 2	60
Wash.	
Dry.	

This procedure results in a magenta colored reproduction of the photographed test object. A control test without $[Co(NH_3)_6]Cl_3$ in the amplifier solution produces no dye image.

Example 4

A coating dope of the following composition is prepared:

	G.
Binder—Resin Mix A	53.3
Pigment—Zinc oxide XX–78 (New Jersey Zinc Co.)	62.2
Solvent—Toluene	76.8
Surfactant—Solution B	3.92

Resin Mix A

	G.
Pliolite S–7 (Goodyear Tire & Rubber Co.)	444.5
Silicone SR–82 (General Electric Company)	27.8
Piccopale (Penn. Ind. Chem. Company)	27.8

Surfactant Solution B

A solution of eight grams of a mixture of 1 part Aerosol TR (a bis(tridecyl) ester of N-sulfosuccinic acid from American Cyanamid) and 3 parts Duomeen-S (an N-tallow trimethylene diamine salt from Armour Industrial Chemical Company) in a 4:1 solvent mixture of toluene and methanol.

The resultant dope is ball milled for 48 hours and then coated at a wet thickness of 0.008 inch on an aluminum foil-paper laminate. The coating is then exposed for 50 seconds to a Rayonet UV light source at a distance of 12 inches through a line-copy test object and then contacted with a negative electrode consisting of an 18% aqueous solution of $AgNO_3$ with a potential of 50 volts. Thereafter, the coating is immersed for 1 minute at a temperature of 24° C. (75° F.) in an amplifier-developer solution having the following composition:

Cyan-dye-forming coupler 1-hydroxy-2-[β-(2′-acetamido)-phenethyl]naphthamide	g	4.0
Ethanol	ml	50
20% NaOH	ml	50
Benzyl alcohol	ml	15
K_2SO_3	g	2
KBr	g	2.5
Na_4EDTA	g	5.0
$[Co(NH_3)_6]Cl_3$	g	5.0
Color developing agent N-ethyl-N-(β-methoxyethyl)-3-methyl-p-phenylenediamine, di-p-toluenesulfonate	g	3.0
K_2CO_3	g	30.0
H_2O to 1 liter.		

After a brief rinse with water, the coating is dried. It contains an amplified negative rendition in cyan dye of the photographed test object.

Example 5

When the procedure described in Example 4 is repeated with another sample of the coating and an amplifier-developer solution wherein the cyan-dye-forming coupler is replaced with the yellow-dye-forming coupler α-benzoyl-2-methoxyacetanilide, an amplified negative rendition in yellow dye of the photographed test object is obtained.

Example 6

When the procedure described in Example 4 is repeated with another sample of the coating and an amplifier-developer solution wherein the cyan-dye-forming coupler is replaced with the magenta-dye-forming coupler 1-(2,4,6-trichlorophenyl)-3-(4-nitroanilino) - 5-pyrazolone, an amplified negative rendition in magenta dye of the photographed test object is obtained.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be affected within the spirit and scope of the invention.

I claim:

1. A process of providing or intensifying a visible image in a photographic element which comprises at least one color-forming layer unit containing a radiation-sensitive compound of a first metal which compound upon exposure to actinic radiation forms catalytic sites for the deposition of a second metal from a physical developer composition, said process comprising the steps of (1) imagewise exposing said element to actinic radiation, (2) treating said element with a physical developer comprising a solution of an ionizable salt of a second metal to imagewise deposit said second metal on said element, (3) contacting the resultant element with an amplifier composition in the presence of a color-developing agent and a color coupler, said composition containing a cobalt(III) complex having a coordination number of six, wherein said contact is maintained under conditions which reduce cobalt(III) to cobalt(II) and, in turn, oxidize said color developing agent whereby image dye is formed from the color coupler and the oxidized color developing agent in proportion to the imagewise distribution of said second metal.

2. A process as described in claim 1 wherein said color-developing agent is an aromatic primary amino compound.

3. A process as described in claim 1 wherein said second metal is different from said first metal.

4. A process as described in claim 1 wherein said photographic element comprises at least two of said color-providing layer units.

5. A process as described in claim 1 wherein the colored coupler is associated with said compound in the color-forming layer unit.

6. A process as described in claim 5 wherein each of said color-providing layer units comprises said color coupler in a concentration sufficient to produce a dye density of at least about 1.7.

7. A process as described in claim 1 wherein said compound is a photosensitive salt of a Group VIII metal.

8. A process as described in claim 1 wherein said physical developer comprises an aqueous solution of a reducible salt of a heavy metal selected from the group consisting of a Group I*b* metal, a Group VI*a* metal, a Group VIII metal and mixtures thereof, a reducing agent for heavy metal ions derived from said salt and a complexing agent for heavy metal ions derived from said salt.

9. A process as described in claim 1 wherein said compound is a photosensitive salt of a Group I*b* metal.

10. A process as described in claim 1 wherein said compound is an oxide or sulfide of a Group II*b* metal.

11. A process as described in claim 1 wherein said compound is an oxide or sulfide of a Group IV*b* metal.

12. A process as described in claim 1 wherein said compound is an oxide or sulfide of a Group IV*a* metal.

13. A process as described in claim 1 wherein said radiation-sensitive compound is titanium dioxide.

14. A process of providing or intensifying a visible image in a photographic element which comprises at least one color-forming layer unit containing a photosensitive metal salt containing a Group I*b*, II*b* or VIII metal which upon exposure to actinic radiation forms catalytic sites for the deposition of metal from a physical developer composition, said compound having associated therewith an image dye-providing photographic color coupler, said process comprising the steps of (1) imagewise exposing said element to actinic radiation, (2) treating said element with a physical developer comprising a reducible heavy metal salt containing a Group I*b*, VI*a* or VIII metal, a complexing agent for heavy metal ions derived from said salt and a reducing agent for heavy ions derived from said salt, (3) contacting the resultant physically developed element in the presence of a color-developing agent with an amplifier composition which contains a cobalt (III) complex having a coordination number of six, wherein said contact is maintained under conditions which reduce cobalt(III) to cobalt(II) and in turn oxidize said

color developing agent whereby image dye is formed from the color coupler in said layer unit and the oxidized color developing agent in the areas corresponding to the imagewise distribution of physically deposited heavy metal.

15. A process as described in claim **14** wherein said photosensitive metal salt is a metal oxalate.

16. A process as described in claim **14** wherein said reducible heavy metal salt contains a metal different from the metal of said photosensitive metal salt.

17. A process as described in claim **14** wherein said color-developing agent is an aromatic primary amino compound.

18. A process as described in claim **14** wherein said reducible heavy metal salt is a salt of a Group VIII metal.

19. A process as described in claim **14** wherein said photosensitive metal salt is palladium oxalate.

20. A process of providing or intensifying a visible image in a photographic element which comprises at least one color-forming layer unit containing a photosensitive metal compound which, upon exposure to actinic radiation, forms catalytic sites for the deposition of metal from a physical developer solution, said compound comprising an oxide or sulfide of a Group II*b*, IV*b*, or IV*a* metal and has associated therewith an image dye-providing photographic color coupler, said process comprising the steps of (1) imagewise exposing said element to actinic radiation, (2) treating said element with a physical developer comprising a solution of an ionizable salt of a Group I*b*, VI*a* or VIII metal, (3) contacting the resultant physically developed element in the presence of a color-developing agent with an amplifier composition which contains a cobalt(III) complex having a coordination number of six, wherein said contact is maintained under conditions which reduce cobalt(III) to cobalt(II) and, in turn, oxidize said color developing agent whereby image dye is formed from the color coupler in said layer unit and the oxidized color developing agent in the areas corresponding to the imagewise distribution of physically deposited heavy metal.

21. A process as described in claim **20** wherein said photosensitive compound is an oxide of a Group II*b* metal.

22. A process as described in claim **20** wherein said photosensitive compound is an oxide of a Group IV*a* metal.

23. A process as described in claim **20** wherein said photosensitive compound is a sulfide of a Group II*b* metal.

24. A process as described in claim **20** wherein said photosensitive compound is titanium dioxide.

25. A process as described in claim **20** wherein said ionizable salt is a salt of a Group VIII metal.

26. A process as described in claim **20** wherein said color-developing agent is an aromatic primary amino compound.

27. In a process of developing an imagewise-exposed photographic element comprising a support and at least one image dye-providing layer unit thereon which contains a radiation-sensitive metal compound which, upon exposure to actinic radiation, forms catalytic sites for the deposition of metal from a physical developer composition, said compound having associated therewith a color coupler, the improvement comprising physically developing said imagewise-exposed element to provide an imagewise distribution of physically deposited metal and contacting said photographic element in the presence of a color developing agent, with an amplifier solution which contains a cobalt(III) metal complex having a coordination number of 6 under conditions which reduce said cobalt(III) to cobalt(II) and in turn oxidize said color-developing agent to provide an increase in dye density with dye produced from said coupler in the areas corresponding to the imagewise distribution of said metal.

28. A process as described in claim **27** wherein said compound contains a member selected from the group consisting of a Group I*b*, II*b*, IV*b*, IV*a*, VI*a* or VIII metal.

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