

[54] PHOTOGRAPHIC ELEMENTS AND PROCESSES FOR PROVIDING TANNED IMAGE RECORDS

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[57]

ABSTRACT

Photographic elements are disclosed which comprise a support having thereon a light-sensitive photographic metal salt and a hydrophilic colloid wherein said element also contains a cobalt(III) ion complex. In one aspect, the photographic element contains an unhardened hydrophilic colloid such as gelatin and a cobalt-(III) ion complex in a concentration of at least 0.5% by weight of unhardened hydrophilic colloid based on cobalt. In another aspect, a process of producing tanned image records is disclosed wherein a photographic element containing an imagewise distribution of a metal and an unhardened hydrophilic colloid is processed with a liquid composition comprising a cobalt(III) ion complex at a pH of above 10 wherein the hydrophilic colloid is tanned imagewise.

26 Claims, No Drawings

PHOTOGRAPHIC ELEMENTS AND PROCESSES FOR PROVIDING TANNED IMAGE RECORDS

This application is a continuation-in-part of my application U.S. Ser. No. 189,289 filed Oct. 14, 1971, now abandoned, and a continuation-in-part of U.S. Ser. No. 189,331 filed Oct. 14, 1971, now issued as U.S. Pat. No. 3,748,138.

This invention relates to photographic elements and processes for tanning hydrophilic colloids. In one aspect, this invention relates to processes for tanning gelatin imagewise. In another aspect, this invention relates to photographic elements containing a photographic metal salt, a cobalt(III) ion complex and a hydrophilic colloid.

It is known in the art to make presensitized printing plates and presensitized wash-off elements, such as disclosed in U.S. Pat. No. 3,402,045. Generally, in processes known in the art a silver halide emulsion layer is developed with a tanning developer which is oxidized and tans the hydrophilic colloid. In certain instances, it is also known that the oxidized tanning developer can diffuse imagewise to harden the hydrophilic colloid on a separate support such as, for example, by the processes disclosed in Yackel et al., U.S. Pat. No. 3,364,024 issued Jan. 16, 1968. However, in each instance the ability to tan gelatin was generally proportional to the amount of silver developed. Moreover, in another aspect the developer solutions used in the prior art for tanning were unstable over long periods of time and yielded nonuniform results over long periods of use.

I have now discovered improved processes for obtaining an image record in a photographic element and improved photographic elements which can be used to produce image records.

In one aspect of the invention, I have found that cobalt (III) ion complexes can be used under alkaline conditions of above pH 10 to imagewise-tan catalytically a hydrophilic colloid layer. Generally, in this process an imagewise distribution of a metal is formed in a photographic element. The element is treated with the cobalt(III) ion complex in the alkaline medium whereby the cobalt(III) ion complex apparently reacts imagewise on the metallic surface to produce reaction products which react with a hydrophilic colloid, such as gelatin, to harden or crosslink the hydrophilic colloid. By this process, differential hardness is obtained imagewise in the hydrophilic colloid layer. The element containing the hardened colloid layer can be used directly such as where use is made of the differential ink receptivity of the unhardened and hardened areas or the lesser hardened areas can be washed off.

In one embodiment of this invention, photographic elements are prepared which can be used advantageously in the above process or which can be used in other processes.

In another embodiment, the development of the imagewise distribution of metal can be carried out with a color developer in the presence of a photographic color coupler. Thus, image dye can be provided in the areas of development to provide opacity. The element can then be hardened with a solution of cobalt(III) ion complex at a pH of above 10 to harden the areas containing the silver and dye.

In another embodiment, this invention relates to photographic elements comprising a support having

thereon at least one layer containing a silver halide emulsion and a hydrophilic colloid wherein said element contains incorporated therein a black-and-white developing agent and a cobalt(III) ion complex. The desensitization often accompanying photographic elements containing cobalt salts such as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ developed with color developers does not appear to be as apparent when using the elements containing the black-and-white developer and the cobalt(III) ion complexes, for example, as demonstrated in Example 6.

Generally, the photographic elements comprise a support having thereon at least one layer containing a lightsensitive, photographic metal salt and a hydrophilic colloid, and said element contains a cobalt(III) ion complex having a net positive charge and preferably a net charge of +3. The elements of this type can be imagewise-exposed and developed with a reducing agent for the metal salt, whereby this developable metal salt is reduced to the metal; the development can be carried out at a high pH or the pH can be raised above 10 after development to effect imagewise tanning by the above process.

The photographic elements of this invention comprise a hydrophilic colloid which can be either a hardened hydrophilic colloid or an unhardened hydrophilic colloid. Generally, where the photographic element comprises a silver halide emulsion dispersed in a hardened hydrophilic colloid, it can be used in combination with a receiver element having thereon an unhardened hydrophilic colloid layer, for example, as disclosed in Yackel, U.S. Pat. No. 3,364,024. A photographic element in accordance with this invention and a receiver element comprising an unhardened hydrophilic colloid layer can be put in interfacial contact in the presence of a highly alkaline liquid to achieve very good imagewise tanning in the receiver element. In certain preferred embodiments, the photographic element contains an unhardened hydrophilic colloid which is itself hardened imagewise by the catalytic decomposition of the cobalt(III) ion complex.

The processes and photographic elements described above provide many advantages. The photographic element can be developed in any developer which is stable and does not require a tanning developer which may be unstable to provide imagewise tanning of the hydrophilic colloid. The photographic element need contain only low coverages of silver, such as less than 50 mg./ft.², to obtain good hardening of high coverages of the hydrophilic colloid. Improved images can be made for lithographic printing since the tanning achieved by the use of cobalt (III) ion complexes appears to provide better tenacity of the hardened areas to a hydrophobic support. Moreover, the present processes provide a mechanism whereby several wash-off image records can be made from a single photographic element.

In certain embodiments, I have found that photographic elements containing a hydrophilic colloid at levels of 2000 mg./ft.² and above can be effectively tanned imagewise. This is quite unexpected since in many prior-art systems it was quite difficult to form a good imagewise distribution of a hardened hydrophilic colloid in a receiver element which contained thick layers of hydrophilic colloid and hardening was achieved by oxidized tanning developer.

The cobalt(III) ion complexes as referred to herein generally are those complexes which feature a cobalt ion which is surrounded by a group of atoms, ions or

other molecules which are generally referred to as ligands. The cobalt ion is generally referred to as a Lewis acid and 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 cobalt complexes are those referred to by American chemists as "inert" and by European chemists as "robust". Particularly useful are complexes of a cobalt ion with a ligand which, when a test sample thereof is dissolved at 0.1 molar concentration at 20° C. in an inert solvent solution also containing .1 molar concentration of a tagged ligand of the same species which is uncoordinated, exhibit 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 cobalt complexes useful in this invention show essentially no exchange of uncoordinated and coordinated ligands for several days. The definition of inert metal complexes and the method of measuring ligand exchange using radioactive isotopes to tag ligands are well-known in the art; see, for example, Taube, *Chem. Rev.*, Vol. 50, p. 69 (1952), and Basolo and Pearson, *Mechanisms of Inorganic Reactions, a Study of Metal Complexes and Solutions*, 2nd Edition, 1967, published by John Wiley and Sons, p. 141. Further details on measurement of ligand exchange appear in articles by Adamson et al., *J. Am. Chem. Soc.*, Vol. 73, p. 4789 (1951). The inert metal complexes should be contrasted with labile complexes which, when tested by the method described above, have a reaction half-life generally less than 1 minute. Metal chelates are a special type of metal complex in which the same ligand (or molecule) is attached to the central metal ion at two or more different points. The metal chelates generally exhibit somewhat slower ligand exchange than nonchelated complexes. Labile-type chelates may have a half-life of several seconds, or perhaps slightly longer. Generally, the oxidizing agents employed are not reduced to a zero valent metal during the redox reaction.

The metal complexes preferred in accordance with this process are cobalt(III) ion complexes which numbers coordination numbers of 6 and are known as octahedral complexes. Most square planar complexes (which have a coordination number of 4) are rather labile, although some Group VIII metal square planar complexes, particularly platinum and palladium square planar complexes, exhibit inertness to rapid ligand exchange.

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

thylenetetraamine(trien), ammine(NH₃), nitrate, nitrite, azide, water, carbonate and propylenediamine(tn). Especially useful are the cobalt complexes containing ammine ligands such as the cobalt hexammine salts. Some 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; and [Co(NH₃)₄CO₃]X; wherein X represents one or more anions determined by the charge neutralization rule, and X preferably represents polyatomic organic anions.

In one preferred embodiment according to this invention where the cobalt(III) ion complexes are incorporated in the photographic element, the anions of the complexes are polyatomic anions, and in some highly preferred embodiments are polyatomic organic anions. The anions are associated with the cobalt(III) ion complex in what may be a salt, an outer sphere complex or an ion pair; see, for example, p. 34 of Basolo et al., *supra*. Typical useful polyatomic anions include sulfato groups, nitrate, and the like. Typical useful polyatomic organic anions include acetato, propionato, methanesulfonato, benzenesulfonato, hexanesulfonato, and the like.

The polyatomic anions are preferably those which in the sodium salt form are not silver halide solvents, i.e., the sodium salt of the polyatomic anion when employed in an aqueous solution (60° C.) at a 0.02 molar concentration does not dissolve more than 5 times the amount by weight of silver chloride than that which can be dissolved in distilled water at 60° C. The sodium salts of anions such as thiocyanato and thiosulfato in a 0.02 molar concentration dissolve more than 5 times the amount by weight of silver chloride than that which is dissolved by distilled water at 60° C.

In another embodiment where the cobalt(III) ion complexes are incorporated in the photographic element, they are incorporated as water-insoluble ion pairs. The use of water-insoluble ion pairs of cobalt(III) ion complexes is described in more detail in Bissonette et al, U.S. Ser. No. 307,894 entitled "Ion-Paired Cobaltic Complexes and Photographic Elements Containing Same", filed Nov. 20, 1972, which is incorporated herein by reference. Generally, these ion pairs comprise a cobalt(III) ion complex ion-paired with an anionic organic acid having an equivalent weight of at least 70 based on acid groups. Preferably the acid groups are sulfonic acid groups.

In certain highly preferred embodiments, the cobalt(III) ion complexes used in this invention contain ammine (NH₃) ligands or have a net positive charge which is preferably a net charge of +3. A cobalt(III) ion with six (NH₃) ligands has a net charge of +3. A cobalt(III) ion with five (NH₃) ligands and one chloro ligand has a net charge of +2. A cobalt(III) ion with two ethylenediamine(en) ligands and two (N₃) azide ligands has a net charge of +1. Generally, the best tanning results have occurred where the cobalt(III) complex has a net charge of +3 and/or the cobalt complex contains at least three ammine ligands.

When the cobalt(III) ion complexes are used in a liquid solution to obtain catalytic tanning, such as at a pH of over 10, the liquid composition can contain from about 10 mg. to about 50 g./l. of solution, and preferably it contains from about 100 mg. to about 10 g./l. based on cobalt. Where the cobalt(III) ion complex is incorporated in the photographic element, good tan-

ning can be achieved when the element contains the cobalt(III) ion complex in a concentration at least 0.5% by weight of unhardened hydrophilic colloid in said element based on cobalt and preferably at least 1.0%.

The hardenable hydrophilic colloids useful in certain embodiments of this invention are those generally known in the photographic art which can be hardened by photographic hardeners such as formaldehyde. In certain preferred embodiments, the hardenable hydrophilic colloid is a material, such as gelatin, which has a melting point of less than 150° F. and preferably less than 120° F., and it preferably has a melting point above about 80° F. In another embodiment, the hydrophilic colloid is a material which can be hardened by a photographic hardening agent to provide at least 100% lower water solubility of the hardened material at a temperature of 90° F.

The term "unhardened hydrophilic colloid" as used herein refers to those materials which are capable of substantial further hardening. These materials may possess a small amount of crosslinking or may have been hardened or tanned slightly. However, this term generally refers to those materials which are capable of being further hardened to provide a melting point differential between hardened and unhardened hydrophilic colloid of at least 20° F. and preferably at least 40° F. wherein the unhardened hydrophilic colloid has a melting point of less than 150° F.

Typical useful hydrophilic colloids include proteinaceous materials such as gelatin and similar materials which can be hardened by photographic hardeners, for example, such as other proteinaceous photographic vehicles.

The unhardened hydrophilic colloid is generally coated on the support at a coverage of from about 5 to about 3000 mg./ft.² and preferably from 10 to about 2000 mg./ft.².

Generally, it is preferred to use gelatin as the unhardened hydrophilic colloid but other vehicles, and especially those which contain groups which are ligands as described above, can also be used. Moreover, other photographic binding agents can be used as substituted in whole or in part for gelatin. Suitable photographic binders include colloidal albumin, cellulose derivatives, synthetic resins such as polyvinyl compounds and the like, and preferably the water-soluble and latex polyvinyl compounds. In certain instances, it is desirable to use latex polymers to improve dimensional stability such as, for example, the alkyl acrylates and alkyl methacrylate polymers. Where the binding agents are used as substitutes for all or part of the gelatin, the layer must still have the properties as defined for the unhardened hydrophilic colloid layer as set forth herein.

In certain embodiments, the photographic elements used in accordance with this invention have supports which have a hydrophobic surface. Elements of this type are desirable to provide a lithographi. plate wherein the hardened gelatin will provide a hydrophilic surface and the areas where the colloid is removed will provide a hydrophobic or oleophilic surface. Typical useful hydrophobic supports include materials such as polyethylene, polystyrene, cellulose esters such as cellulose acetate, polyesters, polytetrafluoroethylene, polystyrenebutadiene, etc.

The hydrophobic surface can be treated to obtain adhesion to the unhardened hydrophilic colloid layer by

methods known for improving the adhesion of hydrophilic materials to hydrophobic supports such as electron bombardment, flame-treating, oxidation with sulfuric acid-dichromatic solution, treatment with chlorine gas, hydrogen peroxide, nitric acid, etc.

The photographic elements of this invention may comprise incorporated developers such as black-and-white-developing agents or color-developing agents. Since the hardening of the hydrophilic colloid does not depend on a tanning developer such as 4-phenyl catechol, etc., generally any developing agent can be used to develop the silver halide. Likewise, where other photographic metal salts are used the reducing agent can be incorporated in the photographic element.

If the developing agent is incorporated in the silver halide emulsion or in a contiguous layer, development can be attained by using an alkaline activator.

Typical activator baths for the photographic element containing a developing agent include, for example, an aqueous solution of an alkaline material such as sodium carbonate, sodium hydroxide, potassium carbonate, potassium hydroxide, etc. Suitable baths can comprise, for example, an aqueous solution containing about 1% sodium hydroxide.

The developer solution or activator solution may also contain gelatin softeners such as citric acid or urea to aid in removal of the soft hydrophilic colloid during the wash-off step.

Typical of the activator solutions which can be used in my process are those disclosed in U.S. Pat. Nos. 2,596,754, 2,596,756, 2,725,298, 2,739,890, 2,763,553, 2,835,575, 2,852,371 and 2,865,745.

The development and/or tanning processes as referred to herein can be effected by bathing the photographic element in an activator solution or developing solution. Alternatively, a viscous processing solution can be placed between the photographic element and a spreading sheet for spreading in a predetermined amount across and in contact with the emulsion side of the photographic element so as to provide all of the solution required for processing. The viscous processing solution can be located in one or more pods or containers which can be readily ruptured when processing is desired.

The photographic elements used in the process of this invention which contain silver halide emulsions can be developed with black-and-white silver halide developing agents or color-developing agents such as aromatic primary amino compounds. The developing agents can be located in the photographic element or in the processing solution.

Useful black-and-white developing agents which can be used to develop the silver halide emulsion and can be incorporated in the photographic elements of this invention include those black-and-white developers disclosed in U.S. Pat. Nos. 2,315,966 by Knott issued Apr. 6, 1943, 2,592,368 by Yackel issued Apr. 8, 1952, 2,685,510 by Yackel issued Aug. 3, 1954, 2,716,059 by Yutzy et al. issued Aug. 23, 1955, 2,751,300 by James et al. issued June 19, 1956, 3,146,104 by Yackel et al. issued Aug. 25, 1964, 3,180,731 by Roman et al. issued Apr. 27, 1965, 3,276,871 by Abbott issued Oct. 4, 1966, 3,278,307 by Stewart et al. issued Oct. 11, 1966, 3,287,129 by Rees et al. issued Nov. 22, 1966, 3,291,609 by Porter et al. issued Dec. 13, 1966, and 3,301,678 by Humphlett et al. issued Jan. 31, 1967.

Typical useful black-and-white developing agents include 1-phenyl-3-pyrazolidone, 1-p-tolyl-3-pyrazolidone, 5-phenyl-3-pyrazolidone, 1-p-hydroxyphenyl-4,4-dimethyl-3-pyrazolidone, 1-phenyl-4-methyl-3-pyrazolidone, hydroquinone, catechol, pyrogallol, N-methyl-p-aminophenol, p- β -hydroxyethylaminophenol, p- α -aminoethylaminophenol, N-methyl-N-(β -sulfoamidoe-thyl)-p-aminophenol, ascorbic acid, p-hydroxyphenylglycine, morpholino hexose reductone, 2,6-dimethyl morpholino hexose reductone, piperidino hexose reductone, piperidino hexose reductone monoacetate, 4-methyl piperidino hexose reductone, pyrrolidino hexose reductone and the like.

In certain aspect, the developing agent used in developing the photographic elements of this invention are aromatic primary amino color-developing agents such as p-aminophenols or p-phenylenediamines. Representative useful color-developing agents include those mentioned in Mees and James, *The Theory of the Photographic Process*, 1966, MacMillan Co., New York, pp. 278-311.

In those embodiments where color-developing agents are used, a color coupler can be used to produce an image dye to provide a visible image in the developed areas. Useful photographic color couplers 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.

The photographic elements of this invention generally comprise a photographic light-sensitive metal salt. The metal salts are those which are capable of being imagewise-exposed to electromagnetic radiation, preferably in the ultraviolet or invisible region of the spectrum, to produce an image record which can then be contacted with a reducing agent or appropriately treated to produce an imagewise distribution of a metal which is preferably a Group Ib, VIa or VIII metal which is catalytically active for the tanning reaction and is most preferably a noble metal. The catalytically active metals are further described in U.S. Ser. No. 189,289 which is incorporated herein by reference. In certain highly preferred embodiments, the metal salt is a silver salt which is preferably a silver halide including silver chloride, silver bromide, silver iodide, mixed silver halides such as silver bromochloride, silver chlorobromiodide and the like. Other silver salts such as silver oxalates, silver-dye complexes and the like can also be used. The silver halide emulsions can, of course, be negative silver halide emulsions, direct-positive silver halide emulsions or reversal silver halide emulsions. Thus, either negative- or positive-working systems can be made in accordance with this invention.

The photographic element can also contain a light-sensitive salt other than silver. Materials of this type include metal compounds which yield photolytically produced metal latent image sites (such as metal images of 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 includes various silver salts (e.g., halides, oxalates, etc.) as known in the art, as well as a variety of nonsilver metal salts, such as oxalate, citrate, etc., salts of a Group VIII, Group Ib or Group IIb metal, e.g., palladium oxalate, ferric ammonium oxalate, mercury oxalate, ferric ammonium citrate and the like. Nonsilver salts of this type

and their uses are described in U.S. Pat. Nos. 2,750,292 issued June 12, 1956, and 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. Preferred photoconductive compounds for use in this invention are oxides and sulfides of Group IIb, IVb or IVa metals. Highly preferred are metal oxides, with titanium dioxide providing good results. Thus, preferred photosensitive metal compounds for use herein contain a Group Ib, IIb, IVb, IVa or VIII metal atom as seen in the Periodic Chart of the elements found on p. 30 of Cotton and Wilkinson, *Advanced Inorganic Chemistry*, 1962 Edition.

After exposure of the next above described elements, they are treated with a physical developer solution to deposit imagewise a catalytically active metal such as a Group VIII, VIa or Ib metal which typically is different from the metal of said photosensitive compound. Useful physical developer solutions contain as the major active ingredient an ionizable salt of a Group Ib, VIa 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 Ib, VIa 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 deposition of metal. Additionally, various electrolytic-deposition techniques can be used as described, for example, in U.S. Pat. No. 3,372,029 issued March 5, 1968. The term "physical development" as used in connection with the present invention has reference to any suitable means for imagewise depositing a catalytically active Group Ib, VIa 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).

In a highly preferred process according to this invention, a photographic element containing an imagewise

distribution of metal and a hardenable hydrophilic colloid is treated with an alkaline solution in the presence of a cobalt(III) ion complex wherein the alkaline solution has a pH of at least above 10 preferably between 11 and 13.

The hydrophilic colloid is hardened or tanned in the areas where there is an imagewise distribution of metal without any apparent effect on the metal such as oxidation, etc. Therefore, the reaction can continue as long as desired, i.e., as long as there is sufficient cobalt(III) ion complex in the element. Likewise, a photographic element containing an imagewise distribution of metal can be used to achieve hardening successively in several receiver sheets containing layers of unhardened hydrophilic colloid.

In certain embodiments, the photographic elements of this invention have a layer containing hardened hydrophilic colloid and a silver halide emulsion and at least one adjacent layer containing an unhardened hydrophilic colloid which can contain a pigment or opacifying agent. With elements of this type, it is possible to obtain a differentially hardened surface and, if desired, where the silver halide emulsion is in a layer next to the support and a transparent support is used, the element can be imagewise-exposed through the support. Additionally, since color developers can be used to develop the silver halide, a dye can be formed during the development step to provide materials in the element having opacity or at least a certain density in the visible region of the light spectrum.

In addition to preparing image records on conventional supports, my process can be used for making plates by means of stencils. An unhardened hydrophilic colloid layer is coated on a porous support such as cloth, silk or highly porous paper and, after being hardened by contacting with the photographic element as described elsewhere herein, the unhardened areas are removed by washing in warm water leaving the support pervious to a printing ink in the areas wherein the gelatin has been removed. Prints are then made from the resulting stencil in the usual manner, using a low-viscosity ink with a result that a large number of positive prints can be made.

The photographic elements can contain opacifying agents such as carbon black in the nonsilver halide-containing layer. Other pigments or dyes may also be used. When the term "pigment" is used herein and in the appended claims, it is to be understood to include, for example, any insoluble opacifying materials such that they impart density to the copy. However, the materials are preferably nonmetallic opacifying materials. While organometallic compounds or the like can be used, the term "nonmetallic opacifying agent" does not include the metals in their metallic or zero valent state.

The photographic elements of this invention can also be used in processes where the imagewise distribution of metal is bleached and removed during the tanning process. When a solvent for the metal salt is present during the reaction of the cobalt(III) ion complex on the metal surface, the mechanism of the reaction is apparently changed to the extent that the metal will be oxidized to the metal salt which can then be removed from the element. In one embodiment, a photographic element containing an imagewise distribution of silver can be treated with a liquid containing a cobalt(III) ion complex and a silver halide solvent, such as alkali metal thiosulfite, an alkali metal thiocyanate and the like,

wherein the silver will be bleached and fixed from the element. If tanning is desired in this process, it is desirable to maintain the processing solution substantially free of complexing agents for the cobalt(II) ion, i.e., such as ethylenediamine tetraacetic acid. The complexing agents appear to reduce the tanning effectiveness of the cobalt compounds.

The invention can be further illustrated by the following examples.

EXAMPLE 1

The film used in this example is a supported singlelayer gelatinous silver halide coating containing 475 mg./ft.² of a silver bromiodide emulsion and 1222 mg./ft.² of an unhardened mixture of 30% bone and 70% hide gelatin. Several strips of the film are exposed to a graduated-density test object through the support and then processed in accordance with the following procedure:

Procedure 1: Predevelopment/70° F. (21° C.)

developer* + 0.2 g./l. of 5-methylbenzotriazole	2 min.
1% acetic acid stop bath	1 min.
fix**	3 min.
wash	5 min.
dry	

After processing, the strips contain an imagewise deposit of developed silver (14 visible steps) in a uniform thickness of gelatin. All of the silver halide is removed by the fix and subsequent wash. The data are shown in Table 1.

*The developer has the formula:

water	750	cc.
N-methyl-p-aminophenol	30.0	g.
sodium sulfite	45.0	g.
hydroquinone	12.0	g.
sodium carbonate	80.0	g.
potassium bromide	2.0	g.
water to 1 liter		

**The fix bath is Kodak F-24 Fix which has the formula

water	500	cc.
sodium thiosulfate	240	g.
sodium sulfite	10.0	g.
sodium bisulfite	25	g.
water to 1 liter		

Procedure 2:

To determine if any tanning takes place in the absence of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, five strips from Procedure 1 are treated respectively as follows:

Treatment	Time
Solution 1: Na_2CO_3 — 25.0 g. H_2O to 1 liter pH 11.6	30 sec., 1, 2, 4 and 8 min. at 70° F. (21° C.) (constant N_2 agitation)
wash dry	3 min. at 100° F. (38° C.)

All of the gel is removed from the strips in the hot-water wash as is indicated in Table 1. No tanning occurs during treatment in Solution 1.

Procedure 3:

To determine if tanning occurs in the presence of Na_2CO_3 and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, five additional predeveloped silver strips are treated as in Procedure 1 with the exception that Solution 2 is used instead of Solution 1.

Solution 2

Na_2CO_3	25.0 g.
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	2.0 g.
H_2O to 1 liter; pH 11.6	

Tanning of gelatin does occur in all strips during treatment in Solution 2. The tanning is proportional to the amount of predeveloped silver and increases with increasing treatment time as is shown in Table 1.

Procedure 4:

To determine if another alkali could be substituted for Na_2CO_3 and produce the same results, an additional predeveloped silver strip is treated as in Procedure 2 with the exception that a 4-minute treatment time in Solution 3 is used instead of Solution 2.

Solution 3

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	2.0 g.
H_2O to 1 liter; pH 11.6 (NaOH)	

Tanning occurs in Solution 3 to the same degree as in Solution 2 as is shown by the data in Table 1. The experiment shows that the tanning is not a function of the alkali used.

EXAMPLE 2

Procedure 1:

To determine the effect of pH on tanning, additional predeveloped silver strips from Example 1 are processed as in Procedure 3 of Example 1 with the exception that 4-minute treatment times are used and Solution 2 (Procedure 3 of Example 1) is adjusted to the following pH values: pH 13.0 (NaOH), pH 11.6 (unadjusted), pH 11.0 (HCl), pH 10.0 (HCl), pH 9.0 (HCl), pH 5.8 (HCl).

No tanning occurs at pH 5.8, 9.0 or 10.0. All of the gelatin is removed from these strips by a hot-water wash, as is shown by the data in Table 1. Some tanning occurs at pH 11.0. However, significantly more tanning occurs at pH 11.6 and 13.0. The tanning is pH-dependent, with an optimum pH in the range of 11-13.

Similar results are obtained when the cobalt salts $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{NO}_3$, $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{NO}_3$ and $[\text{Co}(\text{NH}_3)_5(\text{H}_2)](\text{ClO}_4)_3$ are used in place of the $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ of Solution 2 of Procedure 3. Good results are obtained when the cobalt (III) complex contains at least three ammino ligands and very good results are obtained when the cobalt(III) ion complex has a net charge of +3.

EXAMPLE 3

Procedure 1: Silver Analysis - Planographic (pH 11.6)

To determine if any silver bleaching occurs in the tanning solutions, three additional predeveloped silver strips from Example 1 are processed respectively as follows:

(A) Treatment

Time

Solution 1, Procedure 2, Example 1 (Na_2CO_3 - pH 11.6)	30 sec., 2 and 8 min. at 70° F. (21° C.)
1% acetic acid rinse	5 min. at 70° F. (21° C.)
wash	5 min. at 70° F. (21° C.)
fix (F-5 of Example 1)	3 min. at 70° F. (21° C.)
wash	5 min. at 70° F. (21° C.)
dry	

B. An additional set of three predeveloped silver strips from Example 1 are processed as described in Section (A) above with the exception that Solution 2, Procedure 3, Example 1 (Na_2CO_3 + cobalt(III) - pH 11.6), is used instead of Solution 1 above.

None of the strips is washed in hot water. Thus, all of the gelatin remains on the support in these experiments. Therefore, any silver that is bleached by the $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ solutions should be removed from the film in the fix and subsequent wash steps. The strips from (A) and (B) above and an untreated predeveloped silver check strip from Example 1 are analyzed for silver by X-ray fluorescent analysis techniques.

The data in Table 2 show that no silver bleaching occurs in the tanning solutions (within experimental error of the analysis technique), thereby establishing the tanning mechanism to be catalytic with respect to silver.

EXAMPLE 4

Procedure 1:

To determine if the tanned images are ink-receptive, additional strips are exposed and processed as in Example 1 with the exception that the exposure is made through the emulsion side of the film.

A. One sample of the above predeveloped silver film is further processed as follows:

Treatment

Time

Solution 1, Test 2, Example 1 (Na_2CO_3 - pH 11.6)	1 min. at 70° F. (21° C.) (constant N_2 agitation)
wash	5 min. at 70° F. (21° C.)
dry	

B. An additional predeveloped silver sample is processed according to Section (A) with the exception that Solution 2, Procedure 3, Example 1 (Na_2CO_3 + cobalt(III) - pH 11.6), is used instead of Solution 1.

Since no hot-water wash step is included in the process, all of the gelatin remains on the support in these experiments.

The strips (matrices) are then tested through a lithographic press where water and then an oil-soluble ink are applied to the surface. The matrices are then brought in contact with a lithographic paper receiver sheet for a brief period. The strips processed through the check solution (A) are not ink-receptive. The strip processed in the presence of cobalt(III) (Solution B) is ink-receptive in proportion to the developed silver images.

This examples shows that the areas tanned in the solution containing cobalt(III) and Na_2CO_3 are ink-receptive and could be used for lithographic printing.

EXAMPLE 5

To determine the effect of constant nitrogen vs. air agitation on tanning solutions, the following experiments are performed:

A. Nitrogen agitation

1. Example 1, Procedure 2, is repeated (8-min. time only) with a freshly mixed solution.
2. The solution used in Example 5(A)(1) is held in an open cylinder with constant nitrogen agitation for 5 days. Process 5(A)(1) is repeated using this solution.

B. Air agitation

1. Example 5(A)(1) is repeated with the exception that air agitation is used instead of nitrogen.
2. Example 5(A)(2) is repeated with the exceptions that:
 - a. air agitation is used instead of nitrogen and
 - b. the pH of the solution, which has dropped to 10.1 after 5 days (probably due to CO₂ impurity in the air supply), is readjusted to pH 11.6 with NaOH.

No difference in tanning is observed between the freshly mixed solutions agitated with either nitrogen or air. However, after 5 days the solution agitated with nitrogen has lost some tanning ability. The solution agitated with air produces the same tanning effects as the fresh solutions, as shown by the data in Table 1. This example shows the tanning solutions are stable and can be used for a long period of time.

transparent support and containing 475 mg. of silver in 1222 mg. of gelatin/ft.² of coating is exposed through the support to a 0.3 log E graduated-density test object and then processed at room temperature in the following sequence:

development (developer of Example 1)	60 sec.
acid stop (1% acetic acid)	60 sec.
fix (F-24 of Example 1)	60 sec.
wash	60 sec.
dry	

The coating sample contains 5 visible steps of a silver image. Although the silver halide emulsion is unhardened, all of its remains on the support. The room-temperature processing conditions and the absence of a warm-water spray assures retention of the emulsion on its support.

B. A second sample of the control coating described above is imbibed in the dark with a solution consisting of:

Na ₂ SO ₃	2.5	g.
hydroquinone	5.0	g.
H ₂ O whose pH has been adjusted with citric acid to 5.5	1	l.

and dried. The sample is then exposed as described in Example 1 and treated for 1 min. at room temperature

Table 1

Example	Procedure	Steps Retained as Relief Image (After 38° C. Wash)
1	1	predeveloped silver (14 visible silver steps)
do.	2	Na ₂ CO ₃ check solution — 30 sec.
do.	do.	do. — 1 min.
do.	do.	do. — 2 min.
do.	do.	do. — 4 min.
do.	do.	do. — 8 min.
do.	3	Na ₂ CO ₃ + [Co(NH ₃) ₆]Cl ₃ — 30 sec.
do.	do.	do. — 1 min.
do.	do.	do. — 2 min.
do.	do.	do. — 4 min.
do.	do.	do. — 8 min.
do.	4	NaOH + Co(NH ₃) ₆ Cl ₃ — 4 min.
2	1	Na ₂ CO ₃ + Co(NH ₃) ₆ Cl ₃ (pH 11.6) - 4 min.
do.	do.	do. (pH 11.0) - 4 min.
do.	do.	do. (pH 10.0) - 4 min.
do.	do.	do. (pH 9.0) - 4 min.
do.	do.	do. (pH 5.8) - 4 min.
5	(A) (1)	nitrogen agitation (fresh) - 8 min.
do.	(A) (2)	do. (5 days) - 8 min.
do.	(B) (1)	air agitation (fresh) - 8 min.
do.	(B) (2)	do. (5 days) - 8 min.

Table 2

Example 3 - Treatment times (mg. of Silver/ft. ²)							
Exposure Step	Check*	30-Seconds		2 Minutes		8 Minutes	
		No Co(III)	+Co(III)	No Co(III)	+Co(III)	No Co(III)	+Co(III)
1	308	304	301	305	300	305	299
3	254	251	250	253	248	252	250
4	183	182	184	184	178	181	182
8	117	121	125	127	123	124	121
9	69	69	74	80	76	77	74
11	29	34	39	38	34	43	35
13	8	9	17	15	13	17	19

* Untreated predeveloped silver check

EXAMPLE 6

A. Control

A first sample of a single-layer, unhardened gelatinous silver bromoiodide emulsion coating applied to a

with an alkaline activator consisting of 40 g. Na₂CO₃, and 0.5 g. KBr dissolved in 1 liter H₂O (pH 11.6). Following this activation step, the sample is warm-water rinsed for 2 min. at a temperature of 38° C. (100° F.), and finally dried.

The entire emulsion is removed from its support during the rinse cycle. This result suggests that whatever development may occur during the activator cycle, it fails to tan the emulsion sufficiently to cause it to adhere to the support.

C. The procedure described next above is repeated with a coating sample which has additionally been imbibed prior to the activation step with a solution consisting of 5 g. of $[\text{Co}(\text{NH}_3)_6](\text{OAc})_3$ dissolved in 1 liter H_2O , whose pH is adjusted with citric acid to 5.5. The cobalt hexammine is present at a concentration of about 110 mg./ft.² of coating. Good silver development and simultaneous imagewise tanning is observed. Despite the warm-water rinse, 5 visible steps of silver in tanned gelatin remain on the support.

Since the number of visible steps retained in the test described in Section (B) above is equal to the number of steps produced in the conventional development cycle as described in Example 1, one can assume that no substantial speed loss is incurred by the incorporation of the cobalt hexammine acetate.

D. A repeat of the procedure described next above with an imbibition solution wherein the cobalt hexammine acetate has been replaced with an equal quantity by weight of cobalt hexammine chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, leads to the retention of only 4 visible steps of silver in tanned gelatin. This result suggests that the acetate salt of the complex is more effective than its chloride salt.

EXAMPLE 7

A. Control

A sample of the control coating of Example 6 is imbibed for 1 min. with an aqueous solution of citric acid having a pH of 5.5, dried, exposed as described in Example 1, and developed for 30 sec. in the following black-and-white developing solution:

Na_2SO_3	5.0	g.
hydroquinone	10.0	g.
KBr	0.5	g.
Na_2CO_3	30.0	g.
H_2O to 1 liter (pH adjusted to 11.8 with NaOH)		

Thereafter the sample is rinsed with water at a temperature of 38° C. (100° F.) for 2 min. and finally dried. The emulsion has been removed from its support during the warm-water rinse cycle.

B. When the procedure described in Section (A) above is repeated with a citric acid imbibition solution which contains, in addition, 5 g. of $[\text{Co}(\text{NH}_3)_6](\text{OAc})_3$ (about 110 mg./ft.²), the processed sample contains 4 visible steps of silver in imagewise-tanned gelatin.

EXAMPLE 8

A. Control (predeveloped silver - low-silver element)

A first sample of a single-layer, unhardened gelatinous silver bromide emulsion coating applied to a transparent support and containing 47.5 mg. of silver in 1222 mg. of gelatin/ft.² of coating is exposed as described in Example 1 and then processed in the following sequence:

The coating sample contains 10 visible steps of a silver image. Again, the emulsion has survived the room-temperature processing conditions by remaining attached to the support.

B. A second sample of the above coating is treated by

the procedure described in Section (B) of Example 6 (hydroquinone imbibition). The entire emulsion is removed from its support during the rinse cycle.

C. When the procedure set forth in Section (B) above is repeated in the manner described in Section (C) of Example 6, 14 visible steps in the form of predeveloped silver embedded in tanned gelatin are retained on the support.

The above-described results prove the effectiveness of the catalytically induced tanning of gelatin by the incorporation in a photographic element of both a developing agent (hydroquinone) and cobalt hexammine. The tanning efficiency is demonstrated by the presence of 14 visible steps in the test sample vs. only 10 visible steps in the control sample.

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

I claim:

1. A process of imagewise tanning a photographic element comprising at least one layer containing an unhardened hydrophilic colloid and at least one layer containing an imagewise distribution of a catalytic metal, said process comprising effecting contact of said imagewise distribution of metal with a liquid composition containing a cobalt (III) ion complex at a pH of at least 11, whereby said unhardened hydrophilic colloid is imagewise tanned.

2. A process according to claim 1 wherein said photographic element comprises an imagewise distribution of silver.

3. A process according to claim 1 wherein said hydrophilic colloid is a gelatin and said catalytic metal is a noble metal.

4. A process according to claim 1 wherein said cobalt (III) ion complex has a net charge of +3.

5. A process according to claim 1 wherein said cobalt (III) ion complex comprises at least three amino ligands.

6. A process according to claim 1 where said liquid composition has a pH of from about 11 to about 13.

7. A process according to claim 1 wherein said catalytic metal is a metal of Groups Ib, VIa or VIII.

8. A process according to claim 1 wherein said metal is silver and said cobalt (III) ion complex is a cobaltic hexammine complex.

9. A process for providing an imagewise distribution of a hardened hydrophilic colloid in a photographic element which comprises at least one layer containing an imagewise distribution of silver and at least one layer containing an unhardened hydrophilic colloid, said process comprising effecting contact of said photographic element with a solution containing a cobalt (III) ion complex wherein said solution has a pH of at least about 11.

10. A process according to claim 9 wherein said hydrophilic colloid is gelatin.

11. A process according to claim 9 wherein said cobalt (III) ion complex comprises at least three amino ligands.

12. A process of providing an imagewise distribution of tanned hydrophilic colloid in a photographic element containing an imagewise-exposed silver halide emulsion, at least one layer containing a cobalt (III) ion complex and at least one layer containing an unhard-

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ened hydrophilic colloid, said process comprising the steps of developing said photographic element with a silver halide developing agent to produce an imagewise distribution of silver therein and effecting contact of said photographic element with a liquid composition containing a cobalt (III) ion complex wherein said liquid has a pH of at least above 10, whereby said unhardened hydrophilic colloid is tanned imagewise.

13. A process according to claim 12 wherein said photographic element contains an incorporated silver halide developing agent and said development is carried out by contacting said photographic element with an alkaline solution.

14. A process according to claim 12 wherein said liquid has a pH of from about 11 to about 13.

15. A process according to claim 14 wherein said cobalt (III) ion complex contains at least three ammino ligands.

16. A process according to claim 14 wherein said photographic element is maintained in contact with said liquid for a time sufficient to produce at least an increase of 20° F. in melting point in portions of said unhardened hydrophilic colloid.

17. A process according to claim 16 wherein said element is washed after contact with said liquid to remove the unhardened hydrophilic colloid.

18. A process according to claim 12 wherein said liquid composition contains said cobalt (III) ion complex in a concentration of from 10 mg. to about 10 g./l. of solution based on cobalt.

19. A photographic element comprising a support having thereon at least one layer containing a silver halide emulsion and a hydrophilic colloid wherein said element contains at least 0.5% by weight of said hydrophilic colloid of a cobalt (III) ion complex based on cobalt.

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20. A photographic element according to claim 19 which contains at least one layer which comprises unhardened gelatin.

21. A photographic element according to claim 19 which contains a silver halide developing agent.

22. A photographic element according to claim 19 wherein said cobalt (III) ion complex contains at least three ammino ligands.

23. A photographic element according to claim 19 wherein said cobalt (III) ion complex is present in said element in a concentration of at least 1.0% by weight of unhardened hydrophilic colloid based on cobalt.

24. A process of providing an imagewise distribution of tanned hydrophilic colloid in a photographic element containing an imagewise-exposed photographic element and at least one layer containing an unhardened hydrophilic colloid, said process comprising the steps of forming an imagewise distribution of a catalytic noble metal in said element and effecting contact of said element with a liquid composition containing a cobalt (III) ion complex wherein said liquid has a pH of at least above 10 whereby said unhardened hydrophilic colloid is tanned imagewise.

25. A process according to claim 24 wherein said liquid has a pH of about 11 to about 13.

26. A process according to claim 25 wherein said unhardened hydrophilic colloid is gelatin and said cobalt (III) ion complex comprises at least three ammino ligands and is present in said element in a concentration of at least 0.5% by weight of said gelatin based on cobalt.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,856,524

Dated December 24, 1974

Inventor(s) Vernon Leon Bissonette

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

Column 1, line 13, "lightsensitive" should read ---light-sensitive---. Column 3, lines 46-47, "numbers" should read ---have---; line 47, "numers" should read ---numbers---. Column 5, line 58, "lithographi." should read ---lithographic---; penultimate line, "hydrphobic" should read ---hydrophobic---. Column 7, line 5, that part of formula reading "pyrazlidone" should read ---pyrazolidone---. Column 10, lines 13-14, "singlelayer" should read ---single-layer---; line 32, "deposit" should read ---deposit---; line 63, "380°" should read ---38°---. Column 11, line 54, that part of formula reading "(H₂)" should read ---(H₂O)---. Column 12, line 61, "examples" should read ---example---. Column 14, line 13, "its" should read ---it---. Column 15, line 59, "appplied" should read ---applied---; line 63, after "sequence:", the following table should be inserted:

---developer (developer of Example 1)	2 min.
wash	2 min.
fix (fix of Example 1)	2 min.
wash	5 min.
dry---	

Column 17, line 23, "hydrohilic" should read ---hydrophilic.

Signed and Sealed this

second Day of September 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks