

1

3,565,622

PROCESS USING COBALT (II) OR MANGANESE (II) AS A DEVELOPING AGENT

Joseph A. Sincius, Little Silver, N.J., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Continuation-in-part of application Ser. No. 432,005, Feb. 11, 1965. This application July 6, 1966, Ser. No. 563,035

Int. Cl. G03c 5/24

U.S. Cl. 96—63

6 Claims

ABSTRACT OF THE DISCLOSURE

A process for developing silver halide emulsion layers by incorporating therewith a salt of copper (I), cobalt (II), or manganese (II), exposing the element imagewise, reacting said salt with a nitrogen donor complexing agent, e.g., ammonia or an aliphatic amine of 1–6 carbons which may be formed from a compound which generates such an agent upon hydrolysis and/or by heat, e.g., salts of the amines, and urea or potassium cyanate in the presence of water to develop the exposed silver halide. When a copper salt is employed an aliphatic amine is used. The invention is useful with high speed negative emulsions, graphic arts emulsions, radiographic emulsions, and paper emulsions.

This application is a continuation-in-part of Ser. No. 432,005, filed Feb. 11, 1965, now abandoned.

This invention relates to photographic materials of the silver halide type. More particularly, this invention relates to silver halide materials of the developing-out type. In a more particular aspect, this invention relates to silver halide developing-out materials having in operative association therewith, stable, finely-dispersed inorganic compounds which when activated by suitable complexing agents will develop silver halide latent images. This invention also relates to a process for producing visible images in a silver halide photographic element utilizing, in finely-dispersed form, a compound of a polyvalent metal in its lower oxidation state having latent reducing properties for exposed silver halides.

Photographic materials of the silver halide type containing silver halide reducing agents in the silver halide emulsion layers or in contiguous layers are, of course, known. For example, the prior art teaches that conventional developers, i.e., hydroquinone, p-methylaminophenol, 1-phenyl-3-pyrazolidone, 1-phenyl-4,4-dimethyl-3-pyrazolidone, pyrogallol, p-phenylenediamine, etc., may be incorporated in silver halide photographic emulsions. After exposure of such emulsions, the visible image is obtained, either by subjecting the exposed element to alkaline vapors, e.g., ammonia, or by immersing the element in a liquid alkaline bath, e.g., sodium hydroxide, sodium carbonate, ammonium hydroxide, etc. It is also known to incorporate with the conventional developing agent so-called development promoter precursors which release alkaline substances on heating which, in turn, activate the developer. Even older in the art is the use in developer solutions of soluble inorganic developing agents, the most familiar of which is ferrous oxalate. Lower oxidation states of chromium, tungsten, molybdenum and vanadium have also been proposed as well as the ammoniacal solutions of cuprous salts.

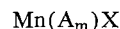
The presence of the above organic developing agents in the silver halide emulsion layer has the disadvantage of causing changes which may be undesirable in the physical and/or sensitometric characteristics of the layer. For example, the hydroxybenzene derivatives may cause un-

2

controlled hardening of the layer. All of the above inorganic developers in solution have the disadvantage of oxidizing readily in air, and produce weak images and fog. They are also quickly exhausted because the presence of oxidized metal ion diminishes the reduction potential.

The present invention comprises a process for developing exposed light sensitive silver halide elements by incorporating in a light-sensitive silver halide layer of a photographic element or a layer contiguous therewith a compound of copper (I) cobalt (II) or manganese (II), exposing the element to actinic radiation and contacting the exposed element with a nitrogen donor complexing agent to develop the exposed silver halide with the proviso that when the compound is of copper the complexing agent is an amine.

The preferred metal compounds of this invention are insoluble in water and thus form more stable coatings, are resistant to aerial oxidation and are not quickly dissipated in aqueous processing baths. Typical examples of the preferred compounds are cuprous thiocyanate, basic cobalt (II) carbonate, cobalt (II) oxalate, manganese (II) oxalate, and water insoluble complex salts of manganese (II) with the apparent composition:



where:

$m=2$ or 4

A =nitrogen donor ligand such as NH_3 or $(\text{CH}_2)_2$

$(\text{NH}_2)_2$

X =anion such as SO_3^- or CO_3^-

Simple soluble Mn (II) salts such as MnCl_2 can be used but are not preferred.

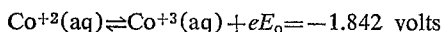
The preferred concentration ranges for the polyvalent metal compounds are from 10/1 to 1/10 silver to polyvalent metal on a molar ratio basis although wider limits are possible.

The above developing agents can be activated by: (1) nitrogen donor complexing agents which react directly with the metal compounds, and (2) compounds which generate nitrogen-donor complexing agents upon hydrolysis and/or increase in temperature which subsequently react with the metal compounds. Exemplary of the former group are ammonium hydroxide, ammonia vapor and aliphatic amines such as ethylenediamine, triethanolamine, butylamine, ethanolamine and hexylamine. The latter group is exemplified by compounds such as urea, potassium cyanate and salts of aliphatic amines such as those listed above. Compounds which generate ammonia or reactive amines on heating or decomposition are described in U.S. Pat. 2,410,644. The amount of the activator to be used can be empirically determined for each metal compound; however, in general, it is best to use an excess of the activator to form the active complex. Coordination bonds formed by nitrogen donation are discussed in "Chemistry of the Coordination Compounds" by Bailar, Reinhold Pub. Co., ACS monograph series No. 131 (1956), pp. 59 et seq.

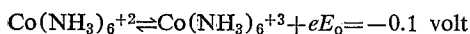
The mechanism of producing a visible image in the photographic silver halide layer of this invention is quite different from that of the prior art self-developing photographic elements. In this invention, the novel developing agents capable of forming a visible silver image from exposed silver halide are incapable of producing any undesirable side reactions in the light-sensitive system or of losing their effectiveness due to atmospheric oxidation. The developing agents are also characterized by being capable of effecting extremely rapid development of the latent silver halide image when activated by a nitrogen donor complexing agent.

3

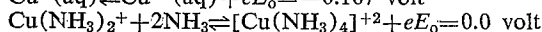
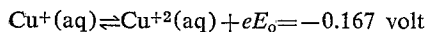
For example, the +2 state of cobalt is normally its preferred oxidation state as shown by the standard potential:



However, cobalt (III) amine complexes are so stable that in ammoniacal media



Copper exhibits the same effect:



Although the mechanism of development is not known, the importance of bridged-intermediates in electron transfer reactions is well known in the art. It is believed that complexes are formed with both the silver ion and the inorganic cations employed in this invention and thus furnish reacting species with similar ligand atmospheres with a lower energy barrier for electron transfer.

The process of producing a visible image by the use of the developing agents of this invention is quite versatile in its application. For example, the polyvalent metal compound not only may be dispersed in the silver halide emulsion and the silver halide layer developed after exposure by immersing in a suitable solution of a nitrogen donor complexing agent, the process may also be carried out by incorporating both the developing agent and a nitrogen donor generating agent in the silver halide emulsion. A visible image is then obtained by exposing the light-sensitive element and merely heating the layer and/or immersing the exposed element in a water bath depending on the most efficient method of producing the nitrogen donor complexing agent. The developing agent and/or the nitrogen donor generating agent may also be incorporated in a layer contiguous with the silver halide emulsion layer such as an undercoating or an anti-abrasion layer. This two-layer structure may be applied to a direct positive process when an unhardened silver halide emulsion is coated over a hardened undercoat containing an inorganic developing agent of this invention, e.g., cuprous thiocyanate. After exposure and processing in a nitrogen donor complexing solution, the silver halide layer is removed by washing in warm water, leaving a positive image of unconsumed developer in the hardened underlayer. This image may be intensified by an appropriate technique, e.g., treatment with silver nitrate solution to convert a cuprous thiocyanate image to a silver image. In a further adaptation of the process, the developing agents and/or the nitrogen donor generating compounds may be incorporated in a colloid carrier, e.g., gelatin coated on a separate support. In this case, the exposed, light-sensitive silver halide layer is dipped in either a nitrogen donor or a nitrogen donor generating solution if the compounds were not incorporated in said colloid carrier or in plain water if the compounds were incorporated in said colloid layer. After dipping, the element is pressed in intimate contact with the developer-containing element and then separated to give good dense images of silver in the silver halide film. All of the silver halide layers developed by the above process may be fixed in the conventional manner, but a particular advantage of this invention is that development and fixing or stabilization may be accomplished in a single solution bath, which combines the nitrogen donor complexing agent and fixers and/or stabilizers such as alkali thiosulfates and thiocyanates.

In a further version of the process, it is possible to make multiple copies of silver images. By imagewise exposing and developing but not fixing a silver halide emulsion containing cuprous thiocyanate, a preferred inorganic developing agent of this invention, it is possible to use this developed film to make other copies carrying silver images complementary to that in the developed film. This is done by using, for example, a silver halide developing-out paper which has been given a flash ex-

4

posure to fog the element. After developing the imagewise exposed element containing the cuprous thiocyanate by immersing in an ethylenediamine solution, the developed element is pressed, while still wet, in contact with the emulsion layer surface of the flash-exposed photographic paper. Upon separation of the two elements, a positive silver image having good density will be found on the developing-out photographic paper. Several sheets of flash-exposed photographic paper can have images formed thereon by pressing them successively in contact with the above developed and still wet image-carrying element containing the cuprous thiocyanate.

The activated manganous salts of this invention also exhibit a unique property. These salts when activated by an excess of a nitrogen donor complexing agent in a non-gaseous system (i.e., activated by ammonia vapors) will not immediately reduce the exposed silver halide. The reduction to form the silver image will occur only when the element is later contacted with an aqueous solution. This allows elements to be formed by mixing a manganous salt with the emulsion and then activating the salt with an excess of nitrogen donor agent. This element can be stored and when finally exposed to an image, it can be developed by merely washing with water.

The use of amines as complexing agents is advantageous due to their general low volatility. They form stronger complexes with copper, cobalt or manganese than that formed by ammonia. Also, the variety of amines permits better control of the developer and the use of amines results in higher solvent action and reduction potential permitting the use of silver bromide or chlorobromide with higher bromide content.

This invention will now be illustrated by the following examples.

EXAMPLE I

The following solutions were prepared:

Solution A—	Grams
Distilled water	660
5% (by weight) aqueous gum arabic	160
Ammonium thiocyanate	64
Sodium bisulfite	90
Solution B—	
Distilled water	800
Copper sulfate pentahydrate	200

Solution B was slowly added to solution A with constant stirring. A voluminous white precipitate formed. An additional 10 grams of solid sodium bisulfite was then added and the mixture stirred for ½ hour. The mixture was centrifuged, the supernatant liquid decanted, and the precipitate washed with 100 milliliters of distilled water. Centrifuging and washing were repeated three times. The precipitate was ball-milled with 160 grams of 5% aqueous gum arabic for 24 hours. This mixture was transferred into 540 grams of 8% aqueous gelatin solution and stirred 15 minutes at 120° F., yielding a cuprous thiocyanate-gelatin emulsion.

A gelatino silver bromochloride emulsion containing 30% silver bromide and 70% silver chloride was prepared and mixed with the above cuprous thiocyanate emulsion so that the molar ratio of silver halide to cuprous thiocyanate was 3/1. The two emulsions were thoroughly mixed by vigorous stirring at 120° F. for 15 minutes. Conventional hardeners and coating aids were added and the emulsion was coated on a polyethylene terephthalate film made according to Example I of Alles et al., U.S. Pat. 2,627,088, issued Feb. 3, 1953, and Example I of Alles, U.S. Pat. 2,779,684, issued Jan. 24, 1957. The element had a dry coating weight of cuprous thiocyanate and silver halide of approximately 100 mg./dm.². The element was exposed and developed by immersion for one minute in a 1% aqueous solution of ethylenediamine to produce a good silver image.

5 EXAMPLE II

Example I was repeated with three separate exposures by using a 5% aqueous solution of triethanolamine to develop one exposure, a 5% aqueous solution of n-butylamine to develop the second exposure and a 0.2 M hexylamine in 4/1 water ethanol solution to develop the third exposure. One minute immersion in each solution gave results similar to those in Example I.

EXAMPLE III

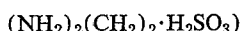
To a solution of 400 ml. water and 100 ml. of ethanol there was added 25 grams of hexylamine. The solution which had a pH of 11.75 was cooled in an ice bath and CO₂ was introduced until the pH was 7. A sheet of the light-sensitive film made according to Example I was immersed in the solution for 10 minutes and then dried. The treated film was given an overall fogging exposure to light and then given an imagewise heat treatment through a process negative by means of an infrared heat lamp (G.E. 250-watt, red filter envelope) to give a black, silver image in the heat irradiated areas.

EXAMPLE IV

A solution comprising 400 ml. of aqueous 0.5 M ethylenediamine were treated with gaseous CO₂ until the pH (initially 11.75) was steady at approximately 6.4. A sheet of light-sensitive film made according to Example I was exposed to a halftone process negative and then immersed in the above solution for two minutes. The film was then heated to 130° F. to form a black silver image.

EXAMPLE V

A solution of 150 ml. water and 50 ml. of ethanol containing 60 grams of ethylenediamine was made and SO₂ gas was passed into the solution until the initial pH of 13.15 fell to 6.0 and a white crystalline solid was precipitated. After settling, the supernatant liquid was decanted and the precipitate collected, washed with ethanol and dried. A 1 M aqueous solution was prepared of the resulting compound (assuming the formula:



and a sheet of the material made according to Example I was immersed in the solution for 15 seconds and then air dried. The film was exposed to light through a 65-line halftone process negative, and heated by contact with a hot metal plate (250° F.) for a few seconds. A black silver image rapidly became visible.

EXAMPLE VI

The following dispersion was prepared:

	Grams
Basic cobalt (II) carbonate (2CoCO ₃ ·3Co(OH) ₂ ·H ₂ O) -----	30
8% (weight) aqueous gelatin -----	180

The cobalt carbonate was added slowly to the gelatin solution at 120° F. with rapid stirring. The resulting composition was added to a gelatino silver bromochloride emulsion containing 30% silver bromide and 70% silver chloride so that the molar ratio of silver to cobalt was 3/1. The two emulsions were thoroughly mixed by vigorous stirring at 120° F. for 5 minutes. Conventional coating aids were added and the emulsion was coated to the film support described in Example I.

After drying in a conventional manner, the film was exposed to a 65-line halftone process negative. The latent image was developed to a dense black silver image by immersion for 2 minutes in a 6 M ammonium hydroxide solution. The image was stabilized by conventional photographic fixing in an aqueous solution of sodium thiosulfate followed by washing and drying.

6 EXAMPLE VII

The following solutions were prepared:

	Grams
(A) Potassium oxalate monohydrate in 150 ml. 5 water -----	38.8
(B) Cobalt (II) chloride hexahydrate in 100 ml. water -----	47.6

(B) was added to (A) with stirring. The precipitate was collected on a fritted glass funnel, washed with two 50 ml. portions of water and then ball-milled with 75 ml. of water for 12 hours. This suspension was dispersed in 100 grams of a 10% aqueous gelatin solution and then added to a gelatino silver bromide emulsion. The ratio of silver to cobalt was 3/2. The resulting mixture was coated on the film base described in Example I and dried. The film was exposed through the process negative described above and the latent image was developed by two minutes immersion in 6 M ammonium hydroxide and then 20 fixed, washed and dried in the conventional manner. A good, high-density, permanent black silver image was obtained.

EXAMPLE VIII

A solution was prepared by dissolving 29 grams of potassium oxalate monohydrate in 100 ml. of water. To the solution there was added 50 ml. of 3 M manganese (II) sulfate with constant stirring. Stirring was continued for 15 minutes, and then the solution was allowed to settle and the supernate was decanted. The manganese oxalate precipitate was washed four times with water and then ball-milled for 12 hours with 70 ml. of 5% aqueous gum arabic and then blended with 50 grams of 8% aqueous gelatin solution. The manganese oxalate emulsion was added to a gelatino silver bromochloride emulsion containing 30% silver bromide and 70% silver chloride so that the molar ratio of silver to manganese was 1/1. The resulting emulsion was coated on the film base described in Example I. After drying, the film was exposed through the process negative described above and developed to a black silver image by treatment for 90 seconds in 2 M ammonium hydroxide solution followed by fixing, washing and drying.

EXAMPLE IX

A sheet of film made according to Example VIII was exposed and then developed by immersion for 90 seconds in a 0.5 M solution of ethylene diamine to a satisfactory image.

EXAMPLE X

A sheet of film made according to Example III was exposed through a process negative and then subjected to ammonia vapor in equilibrium with concentrated ammonium hydroxide for five minutes. No image was visible. Subjecting the film to a spray of water produced a dense black image.

EXAMPLE XI

Example X was repeated except that the exposed film was subjected to ethylenediamine vapor at 77° F. before spraying with water. A satisfactory image was produced.

EXAMPLE XII

The vapor treatments of Example X and XI were repeated except that the film elements were subject to the vapor treatments before exposure. After exposure, the elements were subjected to water sprays which produced good, dense images immediately.

EXAMPLE XIII

The following solutions were prepared:

	Grams
(A) Photographic gelatin -----	8
Water -----	500
(B) 3 M AgNO ₃ -----	
(C) 1 M K ₂ C ₂ O ₄ -----	
75 (D) 1 M MnBr ₂ -----	

7

50 ml. of solution (B) were added to solution (A) at 95° F. with stirring. 76 ml. of solution (C) were added. After 10 minutes stirring, 95 ml. of solution (D) were added, and the mixture stirred for 20 minutes. The dispersed silver bromide and manganese oxalate grains were coagulated and washed, then redispersed in a solution of 50 grams photographic gelatin in 300 ml. water. This emulsion was used to prepare coatings as in Example VIII. Exposure and processing as in Example VIII yielded a similar image.

EXAMPLE XIV

The following solution was prepared:

Water—500 mls.

Ethylenediamine sulfite (prepared as in Example XI)—47 grams

50 ml. 3 M $MnCl_2$ were added and the mixture stirred for 5 mins. A white, finely-divided precipitate formed whose empirical composition is believed to be $Mn(en)_2SO_3$ (en=ethylenediamine). After filtering, a gelatin emulsion of this material was prepared by vigorously stirring with a solution of 8 g. gelatin in 200 ml. water for ½ hour at 95° F. The resulting composition was added to the gelatino-silver bromochloride emulsion containing 30% silver bromide and 70% silver chloride so that the molar ratio of silver to manganese was 2/1 and the emulsions mixed by vigorous stirring for 5 minutes at 95° F. Conventional coating aids were added and the emulsion was coated to the film support described in Example I. After drying, the film was exposed through the process negative described in Example I. Black silver images were developed by the following alternative treatments

(A) 0.5 M NH_4OH , 2 minutes

(B) 0.5 M ethylenediamine, 90 seconds

followed in either case by fixing, washing and drying.

EXAMPLE XV

A solution of ethylenediamine carbonate was prepared as follows:

120 grams ethylenediamine, 300 ml. water, and 100 ml. ethanol were blended and cooled in an ice bath. CO_2 gas was then passed into this solution until the initial pH of 13.5 decreased and was steady at 6.98. The resulting ethylenediamine carbonate solution was a light brown, syrupy liquid with a total volume of 460 ml.

75 ml. of the above solution were diluted with 150 ml. water and 30 grams $MnCl_2 \cdot 4H_2O$ dissolved in 200 ml. water were added. The mixture was stirred for 5 minutes. A voluminous white precipitate formed whose empirical composition is believed to be $Mn(en)_2CO_3$. This solid was separated by centrifuging and blended with 8 g. gelatin dissolved in 200 ml. water by stirring vigorously for 30 minutes at 95° F. This emulsion was blended with silver bromochloride and coated as described in Example XIV. The resultant coating was exposed and processed as in Example XIV to yield similar black silver images.

EXAMPLE XVI

The following solutions were prepared:

Solution A—	Grams
Distilled water	660
5% (by weight) aqueous gum arabic	160
Ammonium thiocyanate	64
Sodium bisulfite	90
Solution B—	
Distilled water	800
Copper sulfate pentahydrate	200

Solution B was slowly added to solution A with constant stirring. A voluminous white precipitate formed. An additional 10 grams of solid sodium bisulfite was then added and the mixture stirred for ½ hour. The mixture was centrifuged, the supernatant liquid decanted, and the precipitate washed with 100 milliliters of distilled water.

8

Centrifuging and washing were repeated three times. The precipitate was ball-milled with 160 grams of 5% aqueous gum arabic for 24 hours. This mixture was transferred into 540 grams of 8% aqueous gelatin solution and stirred 15 minutes at 120° F., yielding a cuprous thiocyanate-gelatin emulsion.

The following coating composition was prepared:

Cuprous thiocyanate-gelatin emulsion—88 grams

Water—175 grams

10 Gelatin—15 grams

1% aqueous chrome alum solution—10 mls.

This composition was coated at 95° F. on a polyethylene terephthalate film made according to Example I of Alles et al. U.S. Pat. 2,627,088 issued Feb. 3, 1953, and Example I of Alles U.S. Pat. 2,779,684 issued Jan. 24, 1957, to give a dry coating weight of 70 mg./dm.² based on cuprous thiocyanate.

A commercial lithographic type, gelatino silver chlorobromide film was exposed through a process negative for one second by a #2 photoflood at a distance of 24 inches. The exposed film was dipped into a 0.5 M 2-aminoethanol solution for 10 seconds. The wet film was brought into intimate contact with the surface of the cuprous thiocyanate layer by passing the juxtaposed films through rubber rollers under slight pressure. The films were separated at the end of two minutes. The silver halide film displayed a black silver image corresponding to the light struck areas.

EXAMPLE XVII

A gelatino silver bromochloride emulsion containing 30% silver bromide and 70% silver chloride was coated over the cuprous thiocyanate-gelatin layer of Example XVI so that the silver halide coating weight was approximately 50 mg./dm.². After drying in a conventional manner, the film was exposed as described in Example XVI. The exposed element was developed by immersion for two minutes in a 0.5 M 2-aminoethanol solution. A good, dense silver image was obtained which was made clear and permanent by conventional fixing, washing and drying.

EXAMPLE XVIII

The cuprous thiocyanate emulsion of Example XVI was added to the gelatino silver bromochloride emulsion of Example XVI so that the molar ratio of silver halide to cuprous thiocyanate was 3/1. The two emulsions were thoroughly mixed by vigorous stirring at 120° F. for 15 minutes. Conventional hardeners and coating aids were added and the emulsion was coated on the film base described in Example XVI to a dry coating weight of cuprous thiocyanate and silver halide of approximately 100 mg./dm.². The resulting light-sensitive photographic element was exposed through a process negative for one second by a 60-watt lamp placed at a distance of 24 inches and developed by immersion for 5 seconds in a 2 M 2-aminoethanol solution. The developed film was conventionally fixed, washed and dried to give a good high density silver image.

EXAMPLE XIX

An exposed film made in accordance with Example XVIII was developed and fixed by immersion for 90 seconds in the following solution:

1.0 M 2-aminoethanol
0.4 M cysteine at pH 11.8

A black silver image developed rapidly and the unexposed silver halide and unused cuprous thiocyanate were removed completely to yield a good, clear stable image.

Although the invention has been demonstrated with gelatino-silver bromochloride and bromiodide emulsions, it is by no means limited to these particular types. The process, developers and activators of this invention may be used with any emulsions, including silver bromide, sil-

ver chloride, silver bromiodide, silver chlorobromide, etc. They may be used with high-speed negative emulsions, graphic arts emulsions, radiographic emulsions and paper emulsions.

The emulsions may be optically and chemically sensitized by any of the known procedures. For example, sulfur sensitizers containing labile sulfur, e.g., allyl isothiocyanate, allyl diethyl thiourea and phenyl isothiocyanate; the polyoxyalkylene ethers of Blake et al. U.S. Pat. 2,400,432 and the polyglycols disclosed in Blake et al. U.S. Pat. 2,432,549 and the metal salts as taught by Baldisiefen, U.S. Pat. 2,540,086 may be used.

The emulsions may also contain known antifoggants, e.g., 6 - nitrobenzimidazole, benzotriazole, triazaindenes, etc., as well as the usual hardeners, i.e., chrome alum, formaldehyde, dimethylol urea, mucochloric acid, etc. Developed silver-covering power-increasing agents may be added such as those disclosed in Forsgad U.S. Pat. 3,043,697; Chambers U.S. Pat. 3,043,698; U.S. Pat. 3,069,267; U.S. Pat. 3,085,009; U.S. Pat. 3,085,010; U.S. Pat. 3,087,818 and Jennings U.S. Pat. 3,063,838. Other emulsion adjuvants that may be added comprise matting agents plasticizers, toners, optical brightening agents, coating aids, etc. In place of the gelatin used in the above examples, there may be employed other colloid carriers such as albumin, cellulose derivatives, synthetic polymers, e.g., polyvinyl alcohol and derivatives thereof such as the acetals. Also, certain polymers and copolymers from the acrylamides disclosed in Shacklett, U.S. Pat. 2,777,872; U.S. Pat. 2,830,972; U.S. Pat. 2,833,650 and U.S. Pat. 2,834,758 may be used. Any material conventionally used as a photographic support will serve as a support for the coatings of the instant invention.

This invention may also be used with emulsions intended for color photography; for example, emulsions containing color couplers or other color generating systems. It may also find utility in photographic materials utilized in the graphic arts field, e.g., lithographic films, gravure films, stripping films and silk screen films. It may also find utility in the cine field where rapid development is very important.

The presence of an insoluble inorganic developing agent does not affect the emulsion properties and may be introduced into the emulsion by a mild blending operation just prior to coating. It has the further advantage of eliminating the need for complex, unstable developing baths of the conventional type and also permits rapid image access. The invention also provides a convenient method of development adaptable to large scale continuous processing or to making an occasional print. The invention may also allow the design of unconventional systems having silver halide emulsions which utilize the development concept of this invention to yield images by high-speed print-out or thermal development procedures.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for forming images in a light-sensitive element having incorporated in a light-sensitive silver halide layer thereof or in a water-permeable layer contiguous therewith, a water-insoluble metal salt of cobalt (II), or manganese (II), in a concentration range from 10/1 to 1/10 silver to the water-insoluble metal salt on a molar

ratio basis, exposing the element to actinic radiation, and treating and reacting said metal salt in the exposed element with a nitrogen donor complexing agent selected from the group consisting of ammonia, ammonium hydroxide, and a saturated aliphatic amine of not more than 6 carbon atoms to develop the exposed silver halide.

2. A process according to claim 1, wherein said nitrogen donor complexing agent is generated by hydrolysis and/or heat from urea, potassium cyanate, or a salt of said amine.

3. A process as defined in claim 1, wherein water is present during the reacting, and the water-insoluble metal salt is selected from the group consisting of cobalt (II) carbonate, cobalt (II) oxalate, manganese (II) oxalate, manganese (II) ethylenediamine sulfite or manganese (II) ethylenediamine carbonate, and said nitrogen donor complexing agent is selected from the group consisting of ammonia, ammonium hydroxide, a saturated aliphatic amine of not more than 6 carbon atoms.

4. A process for forming a direct positive image in a photographic element having a support bearing an unhardened water-permeable colloid layer of silver halide adjacent to and above a hardened water-permeable colloid layer containing a water-insoluble metal salt of cobalt (II) or manganese (II) in a concentration range from 10/1 to 1/10 silver to the water-insoluble salt on a molar ratio basis, exposing said coated support to actinic radiation, immersing said exposed element in an aqueous solution containing a nitrogen donor complexing agent selected from the group consisting of ammonia, ammonium hydroxide, a saturated aliphatic amine of not more than 6 carbon atoms, to develop said exposed silver halide and washing said element to remove said silver halide layer and leave a positive image of unconsumed developing agent in the hardened colloid layer.

5. A process as defined in claim 4, where said positive image is intensified with an aqueous silver nitrate solution.

6. A photographic element having in a light-sensitive silver halide layer or a layer contiguous therewith a water-insoluble salt of cobalt (II) or manganese (II) in a molar ratio with respect to the silver of the silver halide of 10/1 to 1/10.

References Cited

UNITED STATES PATENTS

2,839,405 6/1958 Jones ----- 96—107

FOREIGN PATENTS

37,138 2/1927 Denmark ----- 96—66X

OTHER REFERENCES

Photographic Processing in Metal-Ion-Chelate System by G. M. Haist et al. in Photographic Engineering, vol. 7, Nos. 3 and 4, pp. 182—189.

NORMAN G. TORCHIN, Primary Examiner

R. E. FICHTER, Assistant Examiner

U.S. Cl. X.R.

96—64, 48