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3,843,363

**PHOTOGRAPHIC DEVELOPER WITH CUPROUS AMINE COMPLEX****Michael T. Lehman, Hartford, Conn., assignor to Itek Corporation, Lexington, Mass.****No Drawing. Continuation of abandoned application Ser. No. 840,827, July 10, 1969. This application Oct. 25, 1972, Ser. No. 300,630****Int. Cl. G03c 1/58, 5/24, 5/30, 5/32****U.S. Cl. 96—48 R****35 Claims****ABSTRACT OF THE DISCLOSURE**

This disclosure relates to a photographic developer composition comprising an alkaline solution of cuprous amine complex ions  $[\text{Cu}(\text{NH}_3)_2^+]$ , which may be used as one component in a system for physical development or amplification of metal images in conjunction with certain reducing agents which selectively deposit copper metal on latent metallic images to increase the density thereof. The compositions of this invention are useful for photographic media comprising photosensitive materials capable of producing physically developable images and are particularly effective with photographic media comprising a radiation-activatable photoconductor. Also included within the scope of the disclosure are processes for developing and amplifying photographic images.

This is a continuation of application Ser. No. 840,827, filed July 10, 1969 and now abandoned.

**BACKGROUND OF THE INVENTION****(A) Field of the Invention**

This invention relates to processes and compositions for developing and amplifying photographic images.

**(B) Description of the Prior Art**

The physical development or amplification of latent metallic images in the photographic arts has long been known. Metal amplification compositions, including those containing copper ion solutions as the source of intensification metal, have been described in the literature. In general, metal amplification systems are electroless plating baths from which the reduced metal is plated out rapidly and selectively on a latent metal image. To be effective, an amplification system must plate the metal on the metal image, i.e. the primary metal image, at a rate substantially faster than on the background of the image. It is obvious then that all electroless plating baths cannot be expected to function as physical developers or image amplification systems.

Amplification of photographic metal images has been described at great length with respect to systems based on silver ion which is most commonly used. The use of copper ions in photographic image intensification has been suggested but operable systems based on the copper ion have been difficult to perfect. One problem associated with copper ion systems has been the need for reducing agents which achieve the necessary selectivity of deposition of copper metal in the latent metal image at a rapid rate to ensure deposition of copper in gray to black form rather than the usual reddish-yellow tone which is characteristic of electrolytically deposited copper. A second problem associated with such systems is that the copper ions are usually in the cupric form even when cuprous salts are used due to aerial oxidation of cuprous ion to cupric ion. The cupric ion oxidizes a latent metallic silver image in the presence of halide ions thereby preventing the silver from acting as a catalyst for the deposition of copper. This results in a loss in selectivity of copper deposition and poor image resolution and con-

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trast. Attempts have been made to maintain the copper ions in cuprous form by complexing with various complexing agents. However, the majority of cuprous complex ions tried are not stable against aerial oxidation.

In commonly assigned U.S. Pat. No. 3,512,972 there is described a successful photographic amplification or intensifying system utilizing copper ions as the source of copper metal and ascorbic acid as a reducing agent. The use of said system gives good results in latent metal image intensification. Another system is described in commonly assigned U.S. Pat. No. 3,674,489. This system utilizes copper ions as the source of copper metal and a reducing agent selected from the group consisting of vanadous ion, titanous ion, and complexes of the vanadous, titanous or ferrous ion with a complexing organic carboxylic acid containing at least one amino nitrogen and at least two carboxylic groups, said carboxylic groups being separated from said amino nitrogen by at least one methylene or methine group. Preferred complexes are those formed with such complexing acids in which the amino nitrogen is a tertiary amino nitrogen.

The developer composition and amplifying system of this invention to be discussed below in detail are used with photographic media comprising photosensitive materials capable of producing physically developable images. Physical development occurs when the reduction of solvated metal ions and the deposition of atoms created are triggered by photographically produced, catalytic metal nuclei. This means that so called electroless plating, when used in selective deposition of metal upon catalytically latent metallic images is included within the physical development and some photographic systems comprising photosensitive materials capable of producing physically developable images may be found in Jonker et al., *Photographic Science and Engineering*, vol. 13, No. 1, January-February 1969, pp. 1-7.

Preferred photosensitive materials useful in the invention are the radiation-activatable photoconductors described in British specification 1,043,250. In this patent, the method generally requires the formation on the media of a latent reversible image corresponding to a pattern of activating light, which image can be rendered irreversible by treatment with a redox system which deposits substances in the radiation struck portions of the media, the deposited substance generally being the reduction product of the reducible component of the redox system. The extent of reduction can be controlled to produce an irreversible latent image which is visible or invisible but which can be intensified by exposure to additional amounts of the selected redox system. For example, when the reversible latent image is contacted with silver ions in the presence of a reducing agent for silver ions, e.g. hydroquinone or equivalent reducing agent, the irreversible image obtained is either fully or partly visible, or alternatively, invisible, depending upon the amount of silver ions used and the activity of the reducing agent, as recognized by those skilled in the art.

The major consideration in attempting to develop suitable intensifying systems with copper ion as the reducible component is to reduce the overall cost by replacement of expensive silver salt with relatively inexpensive copper salts, or at least reduce the requirements for silver salts in processing exposed photographic media of the type described.

**SUMMARY OF THE INVENTION**

There have now been discovered compositions comprising cuprous amine complex ions,  $[\text{Cu}(\text{NH}_3)_2^+]$ , preferably containing hydroxylamine, that may be used to rapidly develop latent photographic images, and in conjunction with certain reducing agents, may be used to

simultaneously develop and amplify latent photographic images. The reducing agent is one capable of reducing the cuprous amine complex ion to metallic copper and is preferably one selected from the group consisting of vanadous ion, titanous ion, and complexes of vanadous, titanous or ferrous ion with a complexing organic polybasic carboxylic acid, or an organic carboxylic acid containing at least one amino nitrogen and at least two carboxylic groups, said carboxyl groups being separated from said amino nitrogen by at least one methylene or methine group. The titanous citrate complex is the most preferred reducing agent.

The specified reducing agents provide excellent results in the amplification of latent metal images, i.e. primary metal images, of such metals as silver, gold, copper, tin, mercury or palladium. For the purpose of this disclosure the expression "latent metal image" is intended to embrace invisible metal images as well as weakly or faintly visible metal images, and is believed generally understood by those skilled in the art.

The solution comprising the cuprous amine complex ion is stable against aerial oxidation in the presence of hydroxylamine and will not convert to cupric ions upon exposure to air. Therefore, the amplifying systems of this invention avoid the problems of the prior art denoted above as they do not oxidize a latent metallic image thereby destroying the catalytic capability of the metal in the image areas. Consequently, copper deposits selectively in the metal image areas yields developed prints of excellent resolution and density. When the solution comprising the cuprous amine complex ion and hydroxylamine is used as a developer, it has been found to provide developed images of silver in substantially shorter time than many prior art developers.

Exemplary of the use of the compositions of this invention is in the physical development of a visible image on a radiation-activatable photoconductor where a latent metallic image is produced by exposure of the medium to an image pattern of activating radiation after which the medium is contacted with a solution of metal ions to form the primary metal image, e.g. silver ions. The latent metal image thus formed is developed and amplified with the present new systems. Amplification is accomplished, in general, by contacting the latent metal image with a solution comprising the cuprous amine complex ion and then with the reducing agent solution to obtain the amplified photographic image.

Where the primary metal image is copper metal, the primary image can be preformed or, alternatively, the primary image as well as the amplified image can be formed in one processing operation. For example, the photoexposed medium can be immersed in a suitable solution of the cuprous amine-complex ion and then contacted with the solution of reducing agent, thus giving an all copper image, this embodiment thus obviating the need for any silver ion in the production of visible images on the photographic media.

When using a silver halide developing out emulsion, the image may develop following exposure by contact with a solution comprising the cuprous amine complex ion which develops the exposed silver halide, and then optionally with the reducing agent solution to obtain the amplified photographic image.

Optimum results are obtained when the reducing agent is titanous citrate.

#### Description of the Preferred Embodiments

Image formation occurs in physical development systems by (1) exposure of the light sensitive material, (2) metallic latent image formation and (3) physical development of the metallic latent image. The metallic latent image is formed by various methods dependent upon the photosensitizing material used. It may be instantaneous photonucleation upon exposure such as in a silver halide

system. Alternatively, it may be formed by photoinactivation of uniformly dispersed nuclei such as in a system containing uniformly dispersed physically developable nuclei and a mixture of a light-sensitive organic azide with a thioether coupler, which upon exposure, causes nuclei to be inactivated. Finally, latent image formation may occur through nucleation by consecutive reactions as in the case of disproportionation of mercurous ions with a mercury latent image or by the reduction of metal ions such as  $\text{Cu}^{+2}$ ,  $\text{Ag}^{+}$ ,  $\text{Pd}^{+2}$ , or  $\text{Pt}^{+2}$  to produce the respective metal nuclei. Exemplary photosensitive materials for systems involving nucleation by consecutive reaction includes diazocyanides, leucocyanides of triphenylmethane dyes, potassium octacyanomolybdate, ferric salts of organic acids, 2,7-anthraquinone-diazosulfonate, methylene blue and radiation activatable photoconductors such as titanium dioxide. All of these systems are well known in the art.

The preferred photosensitive materials for purposes of the invention are the radiation activatable photoconductors. With these materials, the photoconductor is not limited to any group of compounds, but may include both organic and inorganic photosensitive materials. Preferred photoconductors useful in this invention are metal containing photoconductors. A preferred group of such materials are the inorganic materials such as compounds of a metal and a non-metallic element of Group VIA of the Periodic Table<sup>1</sup> such as metal oxides including zinc oxide, titanium dioxide, zirconium dioxide, germanium dioxide, indium trioxide, tin oxide, barium titanate; metal sulfides such as cadmium sulfide, zinc sulfide, and tin disulfide; and metal selenides such as cadmium selenide. Metal oxides are especially preferred photoconductors of this group. Titanium dioxide is a preferred metal oxide because of its unexpectedly good results. Titanium dioxide having an average particle size less than about 250 millimicrons and which has been treated in an oxidizing atmosphere at a temperature above about 200° C. is especially preferred, and more especially, that titanium dioxide produced by high temperature pyrolysis of titanium halide.

Also useful in this invention as photoconductors are certain fluorescent materials. Such materials include, for example, compounds such as silver activated zinc sulfide and zinc activated zinc oxide.

Organic photoconductors suitable for use in this invention are, for example, the imidazolidinones, the imidazolidinethiones, the tetraarylazacyclooctatetraenes, and thiazines, such as

- 1,3-diphenyl-4,5-bis(p-methoxyphenyl)imidazolidinone-2;
- 4,5-bis(para-methoxyphenyl)imidazolidinone-2;
- 4-phenyl-5-(para-dimethylaminophenyl)imidazolidinone-2;
- 4,5-bis(paramethoxyphenyl)imidazolidenthione-2;
- 3,4,7,8-tetraphenyl-1,3,5,6-tetraazacyclooctatetraene-2,3,6,8.

While the exact mechanism by which the media are activated is not known, it is believed that the exposure to activating light, e.g. ultraviolet light, causes the transference of electrons of the photoconductor from the valence band to the conduction band, or at least to some similar excited state whereby the electron is loosely held, thereby converting the photoconductor from an inactive to an active form. If the photoconductor in the active form is in the presence of an electron-accepting agent, a transfer of electrons will take place between the photoconductor and the electron-accepting agent and the latter will be reduced. Accordingly, a simple test to determine whether photoconductors have reducing properties is to mix the material in question with aqueous silver nitrate. In the absence of light, little, if any, reduction of silver ions should occur. At the same time as exposing the same

<sup>1</sup> Periodic Table from Lange's Handbook of Chemistry, 9th edition, pp. 56-57, 1956.

mixture to light, a control sample of an aqueous silver nitrate solution alone is similarly exposed, and if the mixture darkens faster than the control sample, the test material is a photoconductor with reducing properties.

It is evident that the gap between the valence and the conducting band of a compound determines the energy needed to make electron transitions and the light required to provide the needed energy is called "bandgap light," as employed herein. The higher the energy needed, the higher the frequency to which the photoconductor will respond. It is known in the art that electrons may be present in secondary levels within the bandgap due to impurities or defects in the structure of the photoconductor. With light of suitable energy, which in this case would be less than the bandgap, electrons from these levels could be raised to the conduction band. A typical example of a secondary level due to a defect in the structure would be an F-center (electrons trapped at negative ion vacancies in an alkali halide crystal). The bandgap of KCl is about 8.5 ev. (1460 Å.), but the secondary levels due to F-centers are about 2.4 ev. (5400 Å.) below the conduction band. Electrons could be raised to the conduction band with 5400 Å. light.

The photoconductors may be sensitized to visible and other wavelengths of light by foreign ion doping, addition of fluorescent materials, exposure to radiant energy to elevate the electrons to levels between the valence band and the conduction band and/or by means of sensitizing dyes. Bleachable dyes useful for sensitizing the photoconductors of this invention include, for example, the cyanine dyes, the dicarbocyanine dyes, the carbocyanine dyes, and the hemicyanine dyes such as disclosed in commonly assigned U.S. Pat. No. 3,666,464.

As is generally known, the activation of photoconductors, i.e. transference of electrons from valence bands to conduction bands, is not permanent but rather the activation decays primarily as a function of time. The decay is apparently due to the loss of electrons in the conduction bands, the electrons reverting to lower energy levels, many reverting to the original valence band and others to energy levels intermediate between the respective bands, i.e. secondary levels, or traps. After decay of the activated photoconductor, the medium retains little, if any, ability to reduce silver ions, or similar metal ion, due to the fact that there are few, if any, electrons in the conduction band. Accordingly, if the medium while activated is contacted with a redox system, reduction of the reducible component thereof occurs. If the reducible component, in the reduced form, is a particulate solid, the result obtained is a visible image corresponding to the pattern.

The foregoing theoretical explanation is offered to enable a better understanding of, and is believed to reasonably interpret, the photoconduction phenomenon of this invention. Of course, applicant is not necessarily bound by this explanation.

The photographic medium comprising the radiation activatable photoconductor or any of the other photosensitive materials above described can be coated onto an inert carrier sheet which is usually any suitable backing of sufficient strength and durability to satisfactorily serve as a reproduction carrier. The carrier sheet may be in any form, such as, for example, sheets, ribbons, rolls, etc. The sheet can be made of any of a variety of suitable material such as wood, rag content paper, pulp paper, plastics such as polyethylene terephthalate (Mylar) and cellulose acetate cloth, metallic foil and glass. The preferred form of the carrier sheet is a thin sheet which is flexible and durable.

It is also useful to use a binder agent to bind the photosensitive materials to the carrier sheet. In general, these binders are translucent or transparent so as not to interfere with transmission of light therethrough. Preferred binder materials are organic materials such as resins. Examples of suitable resins are butadiene-styrene copolymer, poly(alkyl acrylates) such as poly(methacrylates),

polyamides, polyvinyl acetate, polyvinyl alcohol, polyvinylpyrrolidone and gelatin.

Where a radiation activatable photoconductor is used, it should be conditioned in the dark before exposure. Such conditioning is generally conducted from one to twenty-four hours. After conditioning, the photoconductor is not exposed to light prior to its exposure to activating radiation for recording an image pattern.

The period of exposure will depend upon the intensity of the light source, the particular imaging material, particular photosensitive material, the type and amount of catalyst, if any, and like factors known to the art. In general, however, the exposure may vary from a microsecond up to several minutes.

In those systems where it is necessary to form a latent metal image by chemical reduction of metallic ions, the image is formed by contacting the activated medium with a redox system composed of an oxidizing agent optionally containing a reducing agent. The oxidizing agent is usually silver ions, but also include such metal ions as mercury, copper, gold, tin or palladium ions and thus is the image-forming component of the image-forming material. The reducing agent of the redox system can be the cuprous amine complex ion solution of the invention or may be any of the known reducing agents for the oxidizing agent which are compatible with the present media and systems. For example, the reducing agents include organic compounds such as oxalates, formates, substituted and unsubstituted hydroxylamine, substituted and unsubstituted hydrazine, ascorbic acid, aminophenols, diamines and dihydric phenols. Specific suitable reducing agents include hydroquinone, o- and p-aminophenol, p-methylaminophenol, p-hydroxyphenylglycine, o- and p-phenylenediamine and 1-phenyl-3-pyrazolidone. The formation of the latent image is a function of the concentration of oxidizing agent, i.e. metal ion, and, if used, the activity of the reducing agent. The more facile method of controlling the extent of latent metal image is by controlling the quantity of metal ion in the medium prior to reaction with the reducing agent. Such considerations are well within the skill of the art and should not require excessive explanation herein. It should suffice for the purpose of this disclosure to indicate that the procedure for preparing the latent metal images is accomplished by controlling the amount of metal ion in the photographic medium by exposing to extremely dilute solutions of the metal ion or controlling the length of time of immersion of the medium in a solution of metal ion of higher concentration. Although either procedure can be used with equal effectiveness, it is preferred to utilize dilute solutions of the metal ion, particularly where the metal is silver, in view of economic considerations. As is obvious to any one in the art, the metal ion can be provided in the form of a soluble compound of the metal which does not adversely affect the desired effect. For example, silver ion is provided by dissolving silver nitrate in water or methanol.

The exposed photographic medium once sensitized with the oxidizing agent, i.e. metal ion, can then be treated with the reducing agent, e.g. in solution which is generally stabilized to permit longer shelf-life. The most commonly used stabilizer is sodium sulfite although many other stabilizers are available and known to those skilled in photographic processing. This treatment is by the standard methods and does not require any special method beyond those normally exposed in routine photographic processing. Optimum conditions for this step are easily determinable and are dependent on the selected reducing agent and the specific metal ion. The solution comprising cuprous amine complex ions is the preferred reducing agent since it decreases the number of processing steps of eliminating the requirement for a separate reducing agent.

Before proceeding with image intensification, it may be desirable, but not essential, to fix the media to remove traces of metal ion which would be reduced in the sub-

sequent processing steps. If the initial metal ion solution is sufficiently dilute, the fixing step is not always necessary. When significant amounts of the metal ion are present in the media, however, they may be removed by any of the art-recognized methods. For example, when the metal ion is silver, the preferred metal at present, a solubilizing agent can be used. Usually, the most facile method entails the use of agents which form soluble complexes with silver ion, such as thiosulfate or thiocyanate ion, the former being preferred under most circumstances. In lieu of a separate fixing step, the solubilizing agent, e.g. thiosulfate ion, can be incorporated into the subsequent treatment solution, e.g. the cuprous amine complex ion-containing solution, or even in the solution of the reducing agent, or in both solutions, as desired.

The image intensifying systems of the present invention comprise an alkaline solution of cuprous amine complex ion,  $[\text{Cu}(\text{NH}_3)_2]^+$ , and a solution of the indicated reducing agent therefor.

The solution comprising the cuprous amine complex ion is formed by dissolving either a cuprous or cupric salt in a solution containing an excess of hydroxylamine. Where a cuprous salt is used, the amount of hydroxylamine in solution should be sufficient to prevent aerial oxidation of the cuprous ion to the cupric ion and preferably should be used in an amount of at least two moles of hydroxylamine per mole of cuprous salt. Where a cupric salt is used to form the solution, a greater excess of hydroxylamine should be used, i.e. at least 3 moles of hydroxylamine per mole of cupric salt, to compensate for the reduction of cupric ion to cuprous ion. A suitable source of the hydroxylamine is hydroxyl ammonium sulfate  $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ .

The source of the cuprous ions for formation of the cuprous amine complex ion solution may be a cupric salt which is reduced in situ by excess hydroxylamine. Any of a variety of soluble salt can be employed. Suitable compounds include various cupric salts such as the nitrate, sulfate, acetate, chloride, and the like. Cuprous salts may also be used for formation of the complex ions, as many cuprous salts not soluble in water are solubilized in the presence of the hydroxylamine. Cuprous chloride is most preferred as the starting material in the formation of these solutions.

In order for the cuprous amine complex ion to be stable against aerial oxidation and reduction to elemental copper by the hydroxylamine, it is necessary that the solution be alkaline and preferably have a pH in excess of 7.5. Most preferred are solutions having a pH ranging between about 7.8 and 9.2. Therefore, it is frequently necessary to add a source of alkalinity to the solution. Ammonium hydroxide,  $(\text{NH}_4\text{OH})$ , is a preferred source of alkalinity as it forms the  $\text{NH}_4^+ - \text{NH}_3$  buffer. The amount of ammonium hydroxide may vary dependent upon desired pH.

As will be fully appreciated, the concentration of the copper ion in solution is not critical. A minimum of routine experimentation will indicate the optimum concentration for copper ion for any given system. Usually the concentration will be found in the range of about 0.05 M to about 1.0 M, and preferably about 0.1 M to about 0.4 M, although other concentrations can be used without appreciable benefits, and possibly with some difficulty, particularly with more concentrated solutions.

The solution of reducing agent is prepared by dissolving the reducing agent in a suitable solvent, which, for practical purposes, is normally an aqueous solvent system, and usually water to which may be added other compatible solvents such as lower alkanols. For most purposes, water suffices as solvent and is preferred. The addition of other solvents compatible with the present system is generally avoided but tolerable in practical limits as should be obvious to one skilled in the art. More conveniently, the reducing agent, when a complex compound, can be formed in solution by addition of a common sol-

uble salt of the metal ion thereof and the complexing agent, preferably in the form of its salt.

The reducing agent must be one capable of reducing the cuprous amine complex ion to metallic copper in the presence of the catalytic metallic latent image. Though many prior art reducing agents may be used, the preferred reducing agent is selected from the group consisting of vanadous ion, titanous ion, and complexes of vanadous, titanous or ferrous ions with a complexing organic carboxylic acid having at least two carboxyl groups, or a complexing organic carboxylic acid containing at least one amino nitrogen and at least two carboxyl groups, said carboxyl groups being separated from said amino nitrogen by at least one methylene or methine group. Preferred complexes are citric acid and those formed with such complexing acids in which the amino nitrogen is a tertiary amino nitrogen, e.g. ethylenediaminetetraacetic acid and nitrilotriacetic acid, e.g. ferrous ethylenediaminetetraacetic acid, (FeEDTA), titanous citrate, and titanous nitrilotriacetic acid (TiNTA), which at present appear to give best results. The most preferred reducing agent is titanous citrate.

Other complexing agents falling within the scope of the present invention include the following: N-hydroxyethyl-diaminetriacetic acid, diethylenetriaminepentaacetic acid, N-hydroxyethylaminodiacetic acid, N,N'-ethylenediaminediacetic acid, 1,2-diaminocyclohexanetetraacetic acid.

Additional compounds useful as complexing agents are hydroxyalkylaminoacetic acids described in U.S. Pat. No. 2,996,408. Such compounds may contain substituents which do not adversely affect the complexing properties such as hydrocarbons or substituted hydrocarbon radicals, e.g., lower alkyl groups such as methyl and ethyl in the ethylene radical. The ethylene radical can be replaced with other alkylene radicals such as propylene, butylene and the like without altering the complexing properties. Other complexing agents suitable for purposes of the present invention will be apparent to those skilled in the art.

The concentration of the reducing agent should be sufficient to accomplish the desired reduction of the cuprous amine complex ion to copper metal. For any given system, the optimum concentration can be readily determined by a minimum of experimentation. While a wide range of concentrations can be employed, in general, the optimum concentration of reducing agent is in the range from 0.05 M to 0.5 M, and preferably about 0.1 M. As should be obvious to those skilled in the art, the concentration of the reducing agent is not critical, except as a matter of efficiency of operation and the time requirements of any processing sequence. The aforementioned preferred range of concentration appears to give the most desirable results from the view point of effective image amplification in relatively short periods of time. For example, when amplifying a latent silver image with the solution comprising the cuprous amine complex ion, the aforementioned preferred concentration results in full amplification within about 5 to 10 seconds or less. Other concentrations are operable with suitable alteration in operating time.

The solution of reducing agent and cuprous amine complex ion, respectively, may contain other agents to assist in image intensification and improve formation of an image. The solution can contain a solubilizing agent for the oxidizing agent, i.e., metal ions, e.g. silver ions, of the initial redox system. The solubilizing agent is preferably thiosulfate ion which gives best results, although the lesser efficient thiocyanate ion can be employed. Where the reducing agent is readily oxidized, particularly under atmospheric conditions, a preservative, i.e. anti-oxidant can be employed. Soluble sulfites or bisulfites, e.g. sodium sulfite or bisulfite, can be added to the reducing agent solution. Vanadous ion when used as a reducing agent is particularly susceptible to oxidation under ambient conditions

and requires stabilization. One method of stabilization is protecting these reducing agents from contact with atmospheric oxygen by blanketing with a non-reactive gas such as nitrogen or argon.

In general, the intensification system of this invention comprises a two solution system containing cuprous amine complex ion and reducing agent in the respective solutions as previously described. The process of fully developing a photo-exposed medium comprising a radiation-activatable photoconductor can be in a three solution system as follows: (1) oxidizing agent, e.g. silver ion solution, (2) cuprous amine complex ion solution, and (3) reducing agent for cuprous amine complex ion. The intensification system of this invention is distinguishable from that of the prior art by the exclusion of a reducing agent for the oxidizing agent as a separate solution to be used after solution one and before solution two above. The intensification system is also well suited for automated processing, for example, in automated photographic development apparatus, or in photoduplicating apparatus which utilizes copy media as herein described for multiple copying. The intensification system permits the use of a developing system composed of only three treatment stations, i.e. baths, in the automated processor which has additionally the very desirable advantage of being based on only slight silver requirements, the visible images being predominantly copper. For example, the silver bath can be of a concentration of at little as 0.001 M silver ion and even lower. If copper intensification is not used, the normal requirements of silver ion is at a concentration of about 0.2 M to obtain a black image. The economic advantage of replacing silver in the image formation becomes more apparent when it is realized that one pound of silver nitrate will make about 700 gallons of 0.001 M silver nitrate, but only 3.5 gallons of 0.2 M solution.

The overall processing time is also an outstanding advantage of the present intensification system, processing times of about 20 seconds being quite practical with the aforementioned three solution development system.

In another embodiment of the invention, where the visible metal image is all copper, a simple development system is provided by the present intensification systems, since the cuprous amine complex ion solution forms the latent metal image and then intensifies the image to obtain an all copper image. For the formation of the latent copper image, it is not necessary to pretreat the photo-exposed medium with an oxygen-scavenger i.e. a compound which reacts with oxygen as in the prior art. This is because the excess hydroxylamine and the cuprous amine complex ion solution prevents absorption of oxygen on the surface of the photoconductor which would tend to re-oxidize copper of a latent metal image as it forms.

The solutions comprising the cuprous amine complex ion of this invention may also be used to intensify images formed on photographic media comprising silver halide emulsions. The process would be the same as that described above except that the system would be a two solution system as the oxidizing agent may be eliminated. In addition, the solution comprising the cuprous amine complex ion may also be used alone as a chemical developer to develop photographic media comprising a silver halide emulsion. For either intensification or development, concentrations of solutions would be substantially as described above.

In the above described intensification procedures, the quality of the intensified image can be controlled as to the blackness of the copper deposit. Urea and thiourea compounds can be added to either the cuprous amine complex ion solution or preferably the reducing agent solution, preferably at a concentration ranging up to  $10^{-2}$  M. With thiourea or its derivatives, e.g. ethylene thiourea, the copper deposit is blue-black in color. Urea tends to favor a reddish tint to the black deposit, but favorably affects the uniformity of the copper deposits. Combinations of urea

and thiourea give the advantages of each and, in proper ratios, the optimum combined benefits are obtained. In a ratio of about two moles of urea to about one mole of thiourea, optimum results are obtained with the preferred systems herein before described.

In the foregoing description, and in the following examples, the preferred order of use of the cuprous amine complex ion solution and the reducing agent is the sequence indicated. However, it is possible to first immerse the latent metallic image-bearing medium in the reducing agent, followed by the cuprous amine complex ion solution. However, with this reverse order, the results obtained may not always be optimum, nor easily reproducible, for which reason though operable, it is not preferred.

The following examples are intended to further illustrate the present invention.

#### EXAMPLE 1

A sheet of paper coated with titanium dioxide (as described in British specification 1,043,250) having a particle size of about 30 millimicrons is exposed to a photographic step tablet having a  $\Delta D$  of 0.15 for 0.001 second on an EG&G Mark 6 Sensitometer having a xenon flash source providing daylight quality radiation to give an exposure of 2,000 meter candle seconds. Following exposure, the sheet is processed through a machine processor. In the machine processor, the sheet is contacted with a 0.050 M silver nitrate solution which is simultaneously applied and squeezed off the paper by one pair of rollers. Next, a solution comprising the cuprous amine complex ion is applied by one pair of rollers and squeezed off by another pair of rollers. The formulation of the cuprous amine complex ion solution is as follows:

0.10 M CuCl  
0.20 M  $\text{NH}_2\text{OH} \cdot \frac{1}{2} \text{H}_2\text{SO}_4$   
0.50 M  $\text{NH}_4\text{OH}$   
pH 9.0

The sheet was then immersed into a titanous citrate reducing solution which is squeezed from the paper by one pair of rollers. The titanous citrate solution is formed from 0.10 M titanium chloride, 0.30 M potassium citrate and 0.0025 M thiourea, and possesses a pH of 4.7. Contact time with each of the aforementioned solutions is as follows:

|                                          | Seconds |
|------------------------------------------|---------|
| Silver nitrate solution -----            | 0.43    |
| Cuprous amine complex ion solution ----- | 1.1     |
| Titanium citrate solution -----          | 2.3     |

Following development, the sheet is washed in water and dried in air. The developed image has thirteen steps, the  $D_{\text{max}}$  is 1.2, and the fog density is about 0.10.

#### EXAMPLE 2

The procedure of Example 1 is repeated twice using the slowest and fastest machine speeds. The following processing times were applied at the slowest machine speed:

|                                          | Seconds |
|------------------------------------------|---------|
| Silver nitrate solution -----            | 2.4     |
| Cuprous amine complex ion solution ----- | 6.1     |
| Titanous citrate complex solution -----  | 12.8    |

At the fastest machine speed, contact time with the various solutions is as follows:

|                                          | Seconds |
|------------------------------------------|---------|
| Silver nitrate solution -----            | 0.23    |
| Cuprous amine complex ion solution ----- | 0.59    |
| Titanous citrate complex solution -----  | 1.23    |

At both speeds, copper images were obtained with the number of steps being 13 and 11, respectively.

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The following three examples illustrate the use of the cuprous amine complex ion solution for the development of photographic media comprising silver halide emulsions.

## EXAMPLE 3

Eastman Kodak spectroscopic film, type 649-0 was exposed for 0.001 second on an EG&G sensitometer and developed for ½ minute in a cuprous amine complex ion solution having the following formulation:

0.10 M CuCl  
0.20 M  $\text{NH}_2\text{OH} \cdot \frac{1}{2}\text{H}_2\text{SO}_4$   
0.50 M  $\text{NH}_4\text{OH}$   
pH 9.0.

The film was then fixed for one minute in a standard fixer, washed with water and dried to yield a visible image of good density and contrast. The developer was stable toward aerial oxidation and could be reused.

The procedure may be repeated with development time in the cuprous amine complex ion solution varying between 1 and 2 minutes.

## EXAMPLE 4

The procedure of Example 3 is repeated with substitution of the following composition:

0.10 M  $\text{Cu}(\text{NO}_3)_2$   
0.30 M  $\text{NH}_2\text{OH} \cdot \frac{1}{2}\text{H}_2\text{SO}_4$   
0.50 M  $\text{NH}_4\text{OH}$   
0.20 M NaOH  
pH 9.0.

## EXAMPLE 5

The procedure of Example 3 may be repeated with substitution of the following developer composition:

0.10 M  $\text{Cu}(\text{NO}_3)_2$   
0.30 M  $\text{NH}_2\text{OH} \cdot \frac{1}{2}\text{H}_2\text{SO}_4$   
0.63 M  $\text{NH}_4\text{OH}$   
pH 8.0.

## EXAMPLE 6

For purposes of comparison, the procedure of Example 3 is repeated with the elimination of cuprous chloride from the developer composition. The composition employed had the formulation as follows:

0.10 M  $\text{NH}_4\text{Cl}$   
0.20 M  $\text{NH}_2\text{OH} \cdot \frac{1}{2}\text{H}_2\text{SO}_4$   
0.40 M  $\text{NH}_4\text{OH}$   
0.025 M  $\text{H}_2\text{SO}_4$   
pH 9.0.

Use of this formulation failed to produce a visible image in six minutes. This shows that the active reducing agent for the silver halide film in Examples 3, 4, and 5 was the cuprous amine complex ion.

What is claimed is:

1. In a process for amplifying a metal image on a photographic medium comprising the steps of contacting said medium with a solution of copper ions and then contacting the medium with a reducing agent for said copper ions, the improvement wherein the solution of copper ions comprises an alkaline solution of cuprous amine complex ions and hydroxylamine and wherein the reducing agent is one capable of reducing said cuprous amine complex ions to metallic copper and is selected from the group consisting of vanadous ion, titanous ion, and complexes of vanadous, titanous or ferrous ion with a complexing organic carboxylic acid having at least two carboxyl groups or a complexing organic carboxylic acid containing at least one amino nitrogen and at least two carboxyl groups where said carboxyl groups are separated from said amino nitrogen by at least one methylene or methine group, said solution having a pH of at least 7.5.

2. The process of claim 1 wherein the concentration of copper ions is between about 0.05 M and about 1.0 M.

3. The process of claim 2 where the photographic

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medium comprises a photosensitive material capable of producing physically developable images.

4. The process of claim 3 where the photosensitive material is a radiation activatable photoconductor.

5. The process of claim 3 where the photographic medium comprises a photosensitive silver halide emulsion.

6. The process of claim 1 where the complexing acid is selected from the group of citric acid, ethylenediamine-tetraacetic acid and nitrilotriacetic acid.

7. The process of claim 1 where the reducing agent comprises an aqueous solution of titanous citrate.

8. The process of claim 1 where the reducing agent comprises a complex of titanous ion with ethylenediamine-tetraacetic acid or nitrilotriacetic acid.

9. The process of claim 3 where the solution comprising the cuprous amine complex ions has a pH varying between 7.8 and 9.2.

10. The process of claim 3 where the solution comprising cuprous amino complex ions is buffered by hydroxylamine and ammonium hydroxide.

11. The process of claim 3 where the solution comprising cuprous amine complex ions is formed from a source of hydroxylamine and a cupric salt.

12. The process of claim 3 where the solution comprising cuprous amine complex ions is formed from hydroxylamine and a cuprous salt.

13. The process of claim 1 where the ratio of hydroxylamine to cuprous salt exceeds 2 to 1.

14. The process of claim 2 where the metal of said latent metal image is selected from the group of silver, gold, copper, palladium and tin.

15. In a process for producing a visible image on an image-wise exposed photographic medium comprising a radiation-activatable photoconductor including the step of contacting said medium with a solution of copper ions and then contacting the medium with a reducing agent for said copper ions, the improvement wherein the solution of copper ions comprises an alkaline solution of cuprous amine complex ions and hydroxylamine and wherein the reducing agent is one capable of reducing said cuprous amine complex ions to metallic copper and is selected from the group consisting of vanadous ion, titanous ion, and complexes of vanadous, titanous or ferrous ion with a complexing organic carboxylic acid having at least two carboxyl groups or a complexing organic carboxylic acid containing at least one amino nitrogen and at least two carboxyl groups where said carboxyl groups are separated from said amino nitrogen by at least one methylene or methine group, said solution having a pH of at least 7.5.

16. The process of claim 15 wherein the concentration of copper ion is between about 0.05 M and about 1.0 M.

17. The process of claim 15 where the photographic medium comprises titanium dioxide.

18. The process of claim 15 where the reducing agent comprises titanous citrate.

19. The process of claim 15 where the solution comprising cuprous amine complex ions and hydroxylamine has a pH of about 7.8 to 9.2.

20. The process of claim 15 where the solution comprising the cuprous amine complex ions is buffered by hydroxylamine and ammonium hydroxide.

21. The process of claim 15 where the solution comprising the cuprous amine complex ions is formed from hydroxylamine and a cupric salt.

22. The process of claim 15 where the solution comprising the cuprous amine complex ions is formed from hydroxylamine and a cuprous salt.

23. The process of claim 22 where the ratio of the cuprous salt to the hydroxylamine is at least 1 to 2.

24. The process of claim 15 where thiourea is present during the reduction of the cuprous amine complex ions.

25. In a process for developing a latent metallic photographic image, the improvement comprising contact of the latent photographic image with a developer comprising an alkaline solution of cuprous amine complex ions

and hydroxylamine, and wherein the developer has a pH of at least 7.5.

26. The process of claim 25 wherein the concentration of copper ions is between about 0.05 M and about 1.0 M.

27. The process of claim 25 where the pH of the solution comprising cuprous amine complex ions ranges between about 7.8 and 9.2.

28. The process of claim 25 where the solution comprising the cuprous amine complex ions is formed from a cupric salt and hydroxylamine.

29. The process of claim 25 where the solution comprising the cuprous amine complex ions is formed from a cuprous salt and hydroxylamine.

30. The process of claim 25 where the solution comprising cuprous amine complex ions is formed from a cuprous salt, hydroxylamine and ammonium hydroxide.

31. The process of claim 29 where ratio of cuprous salt to hydroxylamine is at least 1 to 2.

32. A composition for developing a photographic image comprising an alkaline solution of cuprous amine complex ions and hydroxylamine, and wherein the composition has a pH of at least 7.5.

33. The composition of claim 32 wherein the concen-

tration of copper ions is between about 0.05 M and about 1.0 M.

34. The composition of claim 32 having a pH of from about 7.8 to 9.2.

35. The composition of claim 32 formed a cuprous salt, hydroxylamine and ammonium hydroxide where the ratio of the cuprous salt hydroxylamine is at least 1 to 2.

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U.S. Cl. X.R.

96—48 PD, 49, 60 R, 66 R