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PHOTOGRAPHIC DEVELOPER SYSTEMS

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ABSTRACT OF THE DISCLOSURE

This disclosure relates to an improved photographic process, developer solution, and developed copy medium. The process comprises contacting a copy medium comprising an image-pattern of a free metal with a developer solution comprising ascorbic acid and cupric ion to selectively deposit metallic cooper in the image areas of the copy medium. In a preferred system the copy medium is exposed and contacted with a reducible metal ion to form a latent metal image in the exposed portions of the copy medium, and then contacted with a developer comprising ascorbic acid and capric ion. The preferred system contains an acid acceptor such as an amine.

The present invention relates to data storage systems and methods, and relates in particular to systems and methods for image reproduction.

It is known from commonly owned copeding applications Ser. No. 199,211 filed May 14, 1962, of E. Berman et al., now abandoned, and Ser. No. 445,797 filed Apr 5, 1965 of Ronald Francis, now U.S. Patent No. 3,445,230 that certain photo-sensitive materials, including pigments such as titanium dioxide and metal carbonyls such as chromium, tungsten, and molybdenum carbonyls, can be rendered reactive with reducible metal ions by exposure to activating radiation. The reaction of the exposed material with metal ions causes formation of free metal, which is deposited as a finely divided precipitate.

The phenomenon can be used for image reproduction. For example, when the light-sensitive materials, incorporated in a copy medium, are exposed to an image pattern of radiation and then developed by contact of the medium with a reducible metal ion, a latent image comprising free metal is formed in the copy medium.

It is further known that latent metal images of this type can be amplified or intensified by bringing the latent images into contact with silver ion and a redox system, usually an organic redox system, such as hydroquinone, metol, or phenidone, for example. When metal is already present in the latent image on the copy medium, additional metal is precipitated by reaction of silver ion with the reducing components of the redox system. Analogous amplification or intensification systems have heretofore been used in the art for the development of images in silver halide photography, for example. A disadvantage of this prior art image intensification process is its dependence on the use of silver, a material which is becoming increasingly more rare and more expensive.

According to the present invention, it has been discovered that image intensification or amplification can be effected employing systems using cupric ion as the redicible metal ion in the image intensifying step. In particular, cupric ion has been employed according to the present invention to amplify latent images comprising

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free metals, particularly images of copper and silver.

Compositions suitable for the non-electrolytic deposition of copper are known in the prior art, for example mixtures of Rochelle salts, copper ion, and formaldehyde. However, such compositions give a uniform deposition of copper and if employed in an attempt to develop an image according to the present invention, they deposit copper indiscriminately over both image areas and background areas, without preferential deposition.

The developing compositions of the present invention comprise cupric ion in combination with ascorbic acid and, suitably, an acid acceptor. It is known in the prior art that ascorbic acid reduces cupric ion to copper, and the reaction has been used in analytic chemistry. However, the autocatalytic nature of the reaction, critically resulting in selective deposition of copper where metal is already present, has heretofore not been recognized in the art. This selective autocatalytic feature brings about the preferential deposition of copper metal in those areas of an exposed and developed data processing medium in which a latent image of deposited metal already exists, resulting in amplification of the latent image without a corresponding intensification of the background.

Cupric ion and ascorbic acid react with the formation of dehydro-ascorbic acid and free copper according to the equation:

$$Cu^{++}+C_6H_8O_6 \rightleftarrows C_6H_6O_6+2H^{+}+Cu$$

The equilibrium of this reaction can be displaced by the presence of an acid acceptor neutralizing hydrogen ions formed in the reaction. Accordingly, in the preferred compositions of the present invention, an acid acceptor is present.

As acid acceptors in the system of the invention, any basic material not precipitating copper hydroxides can be employed. In general, inorganic hydroxides are not suitable, but ammonium hydroxide can be employed, apparently because formation of copper ammonia complexes discourages the precipitation of copper hydroxides. Amine acceptor materials are, however, the preferred reagents. Amines of the widest variety can be employed, including primary, secondary, and tertiary aliphatic, cycloaliphatic, and aromatic amines, including isocyclic and heterocyclic compounds. The amines need not be hydrocarbon materials, but include such substituted amines as triethanol amine, and urea. Cycloaliphatic amines such as N-methyl cyclohexyl amine can be employed, as can heterocyclic amines such as pyrrole, imidazole, quinoline, morpholine, and hexamethylenetetramine. Since the principal function of the amine or NH_4OH acid acceptor is to neutralize hydrogen ions, the chemical structure of the acid acceptor is immaterial providing only, as mentioned earlier, that the material is not one precipitating copper hydroxides. What is critical to the present invention is the well-known property of amines to accept or neutralize hydrogen ions.

In the present specification and claims, the term "nitrogenous acid acceptor" is used to define amine materials of the type discribed and ammonium hydroxide as the sole inorganic acid acceptor.

In general, in preparing the image intensifying composition of the present invention, ascorbic acid and cupric ion can be present in widely varied proportions. While it is preferred to have substantially equimolar quantities of the materials present in view of the reaction between the substances, images will be formed if according to the invention either of the components is in a ration of 100:1 to the other. Suitably, the components are present in a 10:1 or 1:10 ratio to avoid waste. If an acid acceptor is present, substantially equimolar quantities of the acceptor and ascorbic acid are preferred, but the acid acceptor can be used in amounts as slight as 1/10 mol percent of the acid employed. Large amounts of acid acceptor tend to cause precipitation of copper hydroxides, and are preferably avoided.

With these concentration ranges for the reagents in the amplifying compositions, the optical densities of amplified images produced according to the present invention will vary from about 0.1 to greated than 1, measured by diffuse reflectance.

In general, the time required for development of a latent image by amplification is between about 15 seconds and about 5 minutes when an acid acceptor is present in the solutions. If no acceptor is present in the solutions, the time of development may vary from between about 2 minutes to about 20 minutes. Still longer development times can be employed, but there is in general no observable improvement in the image after the period of time indicated.

As mentioned earlier, the copper-containing amplifying compositions and the techniques of the present invention can be used to amplify latent metal images, particularly those of silver or copper. The latter metals are of principal commercial importance in the photographic arts. However, the systems of the present invention can be used to amplify images comprising other metals, particularly of metals at least as noble as copper, such as images of palladium, platinum, gold, etc.

Latent silver images are formed, for example, by irradiation of a copy medium comprising a readiation sensitive substance such as titanium dioxide or a metal carbonyl, as disclosed in the aforementioned U.S. patent applications, with subsequent contact of the exposed medium with a solution of silver ion. Metallic silver is deposited on the medium to form a latent image. Contact of the latent silver image with the copper ion-ascorbic acid compositions of the present invention will cause metallic copper to be deposited on the medium in image areas where silver is already present.

The copper ion-ascorbic acid compositions of the present invention can also advantageously be employed to intensify latent images of copper. On contact of cupric ion with irradiated TiO_2, for example, cuprous ion is formed. On heating, the cuprous ion disproportionates with formation of metallic copper. Latent images of metallic copper can also be formed if copper ion is present in contact with a photosensitive pigment such as titanium dioxide at the time of exposure to activating radiation. The resultant latent copper images can then subsequently be amplified with the compositions of the present invention.

For example, a copy medium having a titanium dioxide coating thereon can be contacted with a solution of cupric

ion and exposed to light, whereupon a latent image of copper metal is formed in the light struck areas. The copy medium, still having residual cupric ion thereon, is then suitably simply contacted with a mixture of ascorbic acid and an acid acceptor, additional copper metal is deposited in the image areas where the latent image of copper metal already exists, and the latent image is made visible.

A better understanding of the present invention and of its many advantages will be had by referring to the following specific examples given by way of illustration.

EXAMPLES 1–17

For each of Examples 1–17, a primary silver image was prepared as follows. Titanium dioxide dispersed in a commercial acrylate resin binder ("Rhoplex") commonly employed in the photosensitive-paper coating art was used to coat paper stock to form a copy medium. After drying, the coated paper was exposed to an image pattern of radiation from a 6 watt black light "Raymaster" fluorescent bulb for 30 seconds. The irradiated sample was then immersed in a saturated solution of methanolic silver nitrate for 10 seconds, washed in a 50:50 mixture of methanol and water for one minute, fixed in a sodium thiosulfate fixer buffered with sodium sulfite and sodium bisulfite for 15 minutes, washed in tap water for 30 minutes, and then dried.

TABLE I.—EXAMPLES 1-17

Ascorbic acid		$Cu(NO_3)_2$						Image Characteristics	
Vol. (ml.)	Conc. (M)	Vol. (ml.)	Conc. (M)	Base	Vol. (ml.)	Conc. (M)	Dev. time, sec.	Visual appearance	Optical density
10	1	10	1	Triethanolamine (in CH_3OH)	10	0.75	60	Black	1.12
10	1	10	1	Urea	15	1	180	Grey	0.60
10	0.1	10	1	Hexamethylenetetramine	10	0.1	150	Black	0.88
10	1	10	0.1	do	10	0.1	150	do	0.80
10	1	10	0.1	Triethanolamine	10	0.1	150	Violet-black	0.63
10	0.1	10	0.1	do	10	0.1	150	do	0.86
10	0.1	10	0.1	NH_4OH	2	1.5	120	Dark-grey	0.78
10	0.5	10	0.35	Imidazole (in CH_3OH)	5	0.35	90	Grey	0.67
10	0.5	10	0.5	Pyrrole (in CH_3OH)	10	0.5	600	Purple	0.32
10	1	10	1	Quinoline (in CH_3OH)	10	0.5	240	do	0.62
10	0.6	10	0.5	Dodecylamine (in CH_3OH)	3	0.5	30	Violet	0.90
10	1	10	1	Aniline (in CH_3OH)	10	1	20	Black	0.99
15	1	10	1	do	5	1	60	do	1.10
10	0.2	25	0.1	1,1,3,3 tetramethyl guanidine (in CH_3OH).	10	0.2	120	Grey	0.78
10	0.5	10	0.5	Morpholine	5	1	30	Purple	0.62
15	0.35	15	0.35	N-methylcyclohexylamine (in CH_3OH).	2	1	120	Grey	0.62
10	0.1	10	0.01	Hexamethylene tetramine	10	0.1	150	do	0.25

The resultant primary latent silver image was amplified by immersion of the copy medium into a variety of aqueous solutions containing copper ion, ascorbic acid, and an acid acceptor. These experiments are summarized in accompanying Table I.

Alternatively, free silver latent images can be formed by exposing a copy medium comprising tungsten carbonyl to an image pattern of ultraviolet light and then contacting the medium with a solution of silver ion, as in copending application (CMS 32527).

Contact of the exposed copy medium with solutions of ions of gold, palladium, platinum, etc., rather than silver ion, results in the formation of latent images comprising these free metals respectively.

EXAMPLE 18

A silver halide emulsion-coated film (Kodak 649) was exposed for 30 seconds to a step-wedge and fixed to remove all non-photolyzed silver halide. The invisible latent image was then amplified by immersion in a mixture comprising 50 ml. of 1 M aqueous ascorbic acid, 50 ml. of 1 M aqueous $Cu(NO_3)_2$, and 50 ml. of 0.75 M triethanol amine in 50:50 H_2O-methanol. After 60 seconds, 15 steps were visible. The maximum optical density was about 1.33.

EXAMPLE 19

The paper copy medium of Examples 1–17, coated with titanium dioxide in an acrylate resin binder, was soaked for 5 minutes in a 5% aqueous solution of cupric nitrate, and then dried. The dry paper was exposed to a

6 watt black light "Raymaster" fluorescent bulb for 60 seconds, then immersed for 150 seconds in a mixture comprising 10 ml. of 1 M aqueous ascorbic acid, 10 ml. of 1 M aqueous $Cu(NO_3)_2$, and 10 ml. of 0.75 M triethanol amine in 50:50 H_2O—CH_3OH. A black image having an optical density of 0.92 resulted.

In an alternative method, the paper can first be exposed and then contacted with a cupric ion solution. On heating to about 75° C., the cuprous ion formed by reaction of the cupric ion and activated TiO_2 disproportionates to cupric ion and copper. The latent copper image can be amplified with the solution disclosed herein.

EXAMPLE 20

Paper treated with cupric nitrate as in Example 19 was exposed after drying, and was then immersed for amplification in a mixture comprising 10 ml. of 1 M aqueous ascorbic acid and 10 ml. of 0.75 M triethanol amine solution for a period of 180 seconds. A bluish-black image having an optical density of 0.95 was produced. In this case, the cupric ion reacting was ascorbic acid for image intensification of the latent copper image was supplied by the residual copper ion in the coating.

EXAMPLE 21

A primary silver image prepared as in Examples 1–17 was immersed for amplification in a solution comprising 25% water and 75% methanol. The concentration of $Cu(NO_3)_2$ in said aqueous-methanol solution was 0.25 M and the concentration of ascorbic acid in said solution was also 0.25 M. After immersion for about 180 seconds, a purple image was obtained which had an optical density of about 1.01.

In formulating image intensification solutions comprising cupric ion and ascorbic acid in combination with an acid acceptor, the cupric ion and ascorbic acid are preferable first combined and the acid acceptor added subsequently since if the acid acceptor is added directly to the cupric ion, precipitation of copper hydroxides may result. Apparently, if ascorbic acid is added first to the copper ion, complexes may be formed between the acid and copper ion which tend to discourage formation of copper hydroxides.

Prints produced by the present process are suitably dried soon after their production to discourage air oxidation of deposited copper in the presence of moisture.

The copper salts used to supply cupric ion are not critical, nor are the solvents employed in preparing the compositions of the invention. The solvents should not cause formation of copper hydroxides, and should be miscible with the acid acceptor desired. In general, aqueous solutions, or solutions in lower alcohols are employed, as are mixtures of water and a lower alcohol such as methanol.

The chemical deposition of copper for amplification of images in a copy medium according to the present invention must be distinguished from prior art processes using the electrical deposition or electroplating of copper to render metal latent images visible. No passage of electric current is required or used in the present invention, and the copy media employed are not limited to those having conductive carriers to which electrical contact can be made. Insulating carriers such as of ordinary paper, glass, or cloth or wood are acceptable in the present invention.

Although specific embodiments have been shown and described herein, it will be understood that they are illustrative and are not to be construed as limiting on the scope and spirit of the invention.

What is claimed is:

1. The method of amplifying a metallic image of a metal at least as noble as copper, which method comprises contacting a physically developable copy medium comprising said metallic image with ascorbic acid and cupric ion to deposit selectively metallic copper in image areas of said copy medium where metal is already present.

2. The method as in claim **1** wherein a nitrogenous acid acceptor is additionally present with said ascorbic acid and said cupric ion.

3. The method as in claim **1** wherein said metallic image comprises metal selected from the group consisting of copper and silver.

4. The method of amplifying a latent metallic image in a copy medium which comprises contacting a copy medium comprising a latent metallic image with a developer comprising ascorbic acid and cupric ion to deposit selectively metallic copper in areas containing the latent image.

5. A process as in claim **4** wherein the latent metallic image is produced by exposing a photosensitive medium comprising a photoconductor and contacting said medium with image-forming materials comprising a solution of metal ions of a metal at least as noble as copper.

6. A process as in claim **4** wherein the latent metallic image is produced by exposing a copy medium comprising photosensitive silver halide.

7. The method as in claim **4** wherein said latent metallic image comprises a metal at least as noble as copper.

8. The method as in claim **7** wherein said medium is contacted with cupric ion ascorbic acid and an acid acceptor which acid acceptor does not precipitate copper hydroxides.

9. The method as in claim **7** wherein a copy medium having cupric ion thereon is contacted with a solution of ascorbic acid and of an acid acceptor which acid acceptor does not precipitate copper hydroxides.

10. The method as in claim **7** wherein said latent metallic image comprises metallic silver.

11. The method as in claim **7** wherein said latent metallic image comprises metallic copper.

12. In the method of image reproduction which comprises exposing a copy medium to activating radiation, said copy medium comprising a photosensitive material rendered capable, by exposure to said radiation, of reducing silver ion to metallic silver on contact, and contacting said exposed medium to silver ion prior to, at the time of, or subsequent to the exposure step to form a latent image of metallic silver in said copy medium, the improvement wherein said latent silver image is amplified and made visible by contact of said medium with ascorbic acid and cupric ion.

13. The method of producing a visible image in a copy medium comprising titanium dioxide and cupric ion, which method comprises exposing said medium to form a latent image of metallic copper in said copy medium, and then amplifying and making said latent image visible by contacting said medium with ascorbic acid and cupric ion.

14. A developed copy medium having a visible image therein, said medium comprising a carrier and an image formed therein by a first metallic latent silver image and a second, heavier, visible overlying metallic copper image.

15. A copy medium as in claim **14** wherein said carrier is electrically insulating.

16. A developed photosenitive copy medium comprising a carrier and a visible image comprising a first latent image of a metal more noble than metallic copper and a second, heavier, visible overlying metallic copper image.

17. A copy medium as in claim **16** wherein the carrier is electrically conductive.

18. A copy medium as in claim **16** wherein the copy medium comprises at least one member selected from the group consisting of silver halide and a photoconductor.

19. A copy medium as in claim **16** wherein the copy medium comprises a photosensitive titanium dioxide.

20. A composition for the amplification of images formed in a copy medium by the presence therein of a metal, which composition comprises a solution of cupric ion, an acid acceptor, and ascorbic acid in a common solvent and wherein the acid acceptor is at least one member of the group consisting of ammonium hydroxide and an organic amine.

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