United States Patent [19]

McKee et al.

[11] **3,790,380**

[45] **Feb. 5, 1974**

[54] **IMAGE RECORDING MEDIUM AND PROCESS**

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[22] Filed: **May 28, 1969**

[21] Appl. No.: **828,572**

[52] **U.S. Cl.** ..... **96/48 PD**, 96/67, 117/34, 117/42

[51] **Int. Cl.** **G03c 5/24**

[58] **Field of Search** ..... 96/48, 48 PD, 66, 67, 27; 117/34, 211, 42; 346/107, 108, 110

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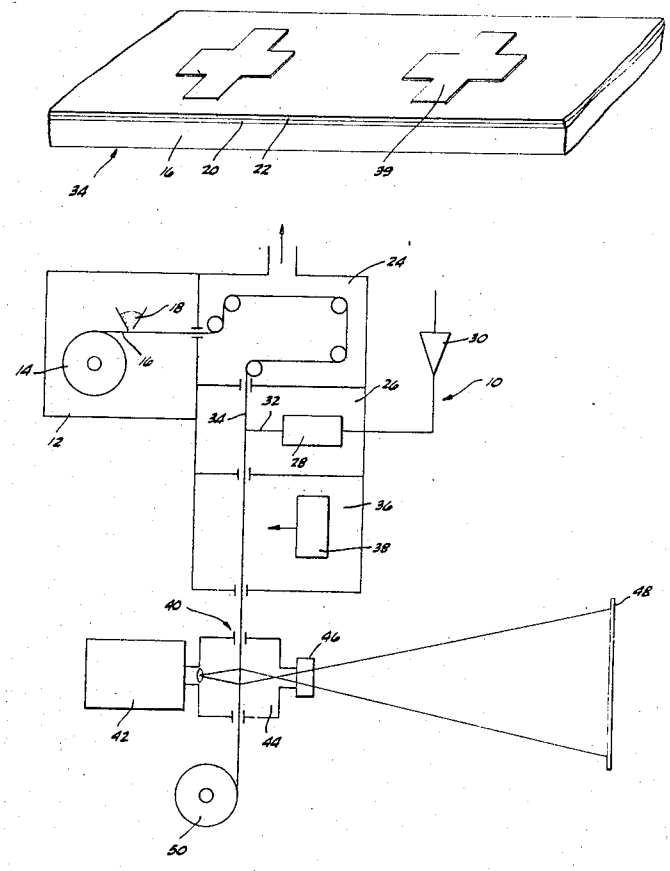
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[57] **ABSTRACT**

An electron and/or photon sensitive soluble copper salt in solution is coated upon a substrate, with subsequent evaporation of its solvent. For substrates which resist wetting by the copper salt solution, a wetting agent or film former is employed to obtain an even copper salt coating. For cases where the medium is to be electron exposed, resistivity of the medium is maintained at a sufficiently low level by an additional coating of adequately low resistivity applied beneath the cooper salt layer. After electron or photon exposure, the latent image is developed by exposing the latent image to metal vapor. Thereupon a stable and visible image is formed. The optical density of the image is proportional to the exposure. When the substrate is transparent, this image can be employed in projection.

6 Claims, 2 Drawing Figures



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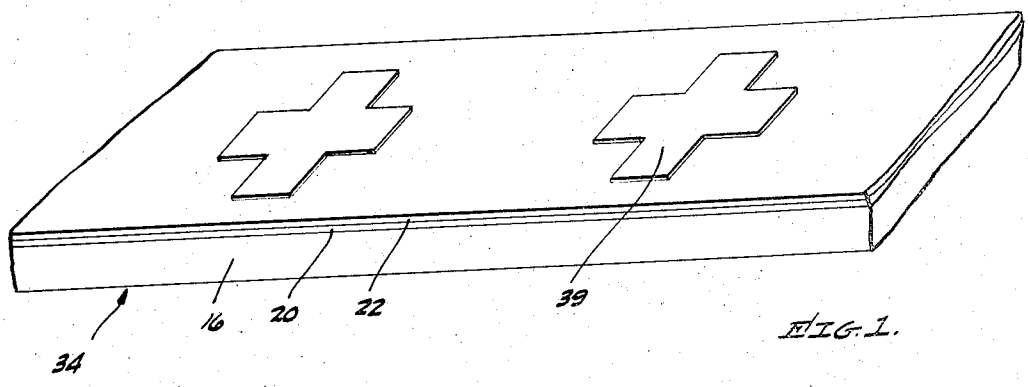


FIG. 1.

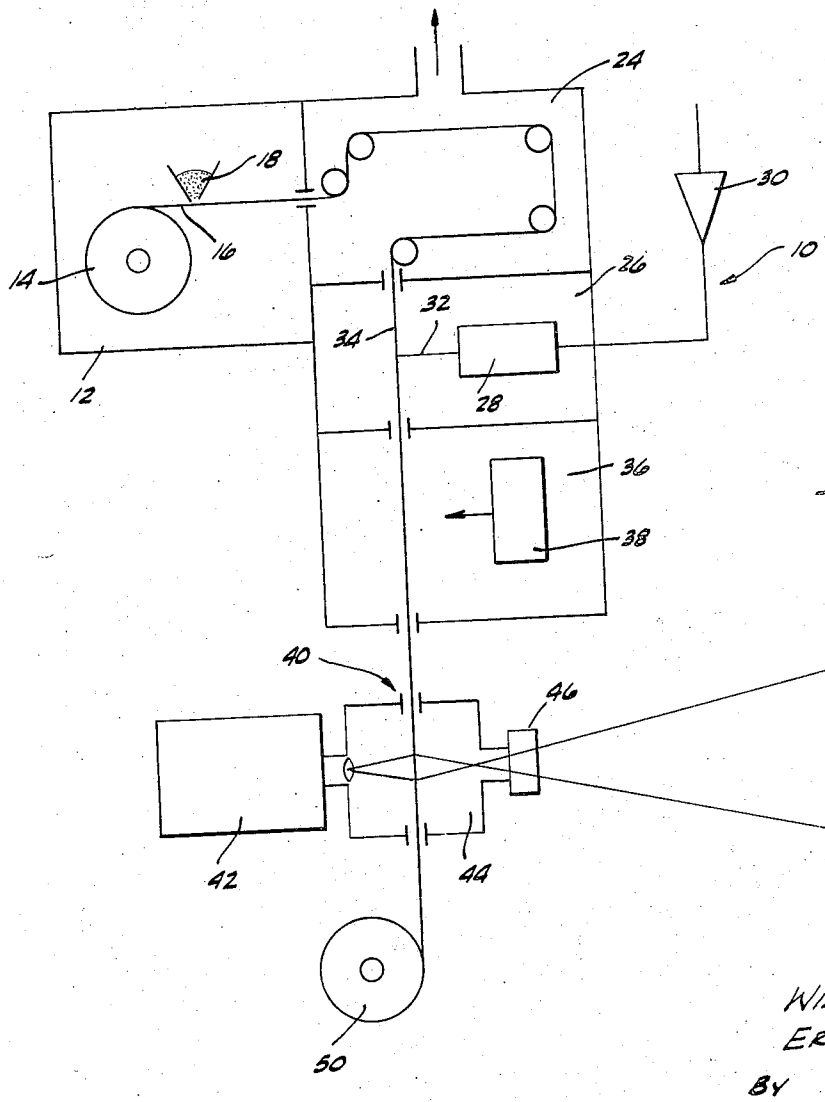


FIG. 2.

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IMAGE RECORDING MEDIUM AND PROCESS

BACKGROUND

This invention is directed to image recording, and particularly to the recording and near real time projection of images on transparent substrates.

In image recording, silver halide recording is well-known. Silver halide emulsions can be formulated to be particularly sensitive to electron beam recording, and thus such emulsions are useful to perform recording and projection steps. However, silver halide emulsions require wet development which prevent them from being satisfactory for situations in which projection is required in near real time.

A medium which is capable of near real time projection is that in which a film is employed, the surface of which is heat deformable in a controlled manner by the electric charge deposited on the film by an electron beam. These are often called thermoplastic films. However, such films require schlieren optics, which consume at least 50 percent of the projector output. This inefficiency leads to careful design to prevent film overheating, and leads to lesser screen illumination.

SUMMARY

In order to aid in the understanding of this invention, it can be stated in essentially summary form that it is directed to an image recording medium and process. The medium employs a soluble sensitive copper salt deposited on a substrate from solution, which deposit layer is sensitive to photon and/or electron exposure. After exposure, the latent image created by the exposure is developed by the imagewise deposition of metal from vapor. The imagewise deposition of metal produces a visible image. When the substrate is transparent, the image can be used for projection. The optical density of the image in transmission is substantially proportional to the exposure so that continuous tone images are possible.

Accordingly, it is an object of this invention to provide an image recording medium and process wherein an image can be produced by irradiating a deposited soluble sensitive copper salt layer, followed by metal vapor development. It is another object to provide an image recording medium which has a substantially transparent substrate and has an image recording copper salt layer deposited thereon, which layer is substantially transparent until a visible image is developed thereon, so that the medium can be employed in projection. It is a further object to provide an image recording medium which is stable and has a long life in ordinary atmospheres so long as the light level is minimized, until it is exposed and developed, and thereafter has a long life in an open atmosphere. It is a further object to provide an image recording medium which comprises the deposition of the copper salt from a copper salt solution on a substrate, and where the substrate is hydrophobic, includes the employment of a wetting agent or a film former. It is still another object to provide an image recording medium on a conductive coating where the image recording medium is to be employed in electron beam recording so that the electron beam charge can be dissipated, and wherein the conductive layer is substantially transparent so as not to hinder the projectability of the developed image. It is still another object to employ copper compounds which are stable in an atmospheric environment, and which are soluble so that they can be deposited upon a substrate from solution. It is another object to select a copper salt from those which are soluble in water and those which are soluble in organic solvents, and to select copper salts which are stable in atmospheric environments. It is still another object to employ a copper salt with a film former wherein the copper complexes directly with the film-forming polymer.

Other objects and advantages of this invention will become apparent from the study of the following portion of the specification, the claims and the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic perspective view of the image recording medium of this invention.

FIG. 2 is a schematic sectional view illustrating the employment of the medium, and the process of this invention.

DESCRIPTION

Referring to FIG. 2, shown therein is a schematic of recording and projection device **10** which employs the medium and process of this invention. Light-tight chamber **12** contains a roll **14** of substrate **16** which is to be coated at coater **18.**

The preferred use of the image recording medium is for projection, and thus the substrate **16** is substantially transparent. For convenience in handling, it is preferable that the substrate be flexible so that it can be rolled. However, if flexibility is not required, glass is a satisfactory substrate. In the preferred embodiment of a flexible substrate, any of the conventional types of transparent films are satisfactory. Clear Cronar film, a polyester synthetic composition material, made by E.I. DuPont de Nemours, of Wilmington, Del., is preferred, because it is conveniently available and is vacuum stable. In some cases, as will become clear hereinafter, a substrate which is hydrophyllic, such as a polyester film with a gelatin-modified surface, known to the trade as subbed, is desirable. Other substrate, such as cellulose acetate and Nesa coated glass, are also useful in particular circumstances, as is hereinafter described.

The sensitive layer is sensitive to both ultraviolet photons and to electrons. When the medium is employed for photon exposure, there is no requirement that electrons be conducted away. However, for electron exposure, the charge resulting from the electron beam must be conducted away. This can be accomplished either by a suitable substrate or a suitable sensitive coating, or can be accomplished by the application of a substantially transparent conductive coating **20.** The electrical resistivity of the finished medium should be less than 1 megohm per square, so that the character of the substrate **16** and the sensitive coating determine the amount of conductive coating **20** required for electron beam exposure applications. Examples of conductive coatings **20** which have the highest light transmission are vacuum-deposited copper iodide, bismuthoxide-gold and, to a lesser extent, vacuum-deposited aluminum and chromium. In order to decrease the amount of conductive coating **20** required, the conductivity of the sensitive coating may itself be increased by the addition of antistatic compounds, such as Stearamidopropyl dimethyl, B-hydroxy ethyl ammonium nitrate (Catanac SM, American Cyanamide).

Substrate **16**, with or without conductive coating **20**, as required, is supplied to coater **18**. Coater **18** applies the sensitive coating layer **22**. The sensitive layer is a soluble copper salt. The copper salt has the requirement that it be soluble either in water or in organic solvent; that it be stable in atmospheric oxygen and moisture; and that it be photon and/or electron sensitive. Organic solvents include acetone, toluene and alcohol. Water soluble copper salts include copper bromide, copper chloride, copper sulfate, copper formate, copper acetate, copper proprionate, copper lactate and copper salts of 2-hydroxyisobutyric acid, glycolic acid, 2-hydroxylauric acid and glyceric acid. Included in the class of organic solvent soluble copper salts are copper salts of long-chain, fatty acids and complex organic acids consisting of oleic, linoleic, napthenic, stearic, undecylenic and behenic acids; and coordination compounds consisting of copper acetylacetonate, Bis (ethyl acetoacetato) copper, Bis (1 phenyl 1, 3-butanediono), and copper dimethyldithiocarbamate.

Whether or not a wetting agent or a polymeric film-forming material is employed in the coater **18** for coating on the substrate **16** depends on whether or not the copper solution wets the substrate, including conductive coating **20**, if there is one. In other words, if the coating solution does not smoothly coat the substrate, a film-forming material or wetting agent must be added. When the substrate is hydrophyllic, such as a gelatin modified polyester film, either water or organic solvent dissolved copper salts will smoothly deposit. However, hydrophobic substrates, such as non gelatine modified polyester or glass, require the addition of a film former or a wetting agent. Water soluble polymeric film-forming materials, such as polyvinyl alcohol, hydroxy propylmethyl cellulose, carboxymethyl cellulose, polyethyleneimine, and organic solvent solubles, such as the styrene-butadiene copolymers and acrylic type polymers are suitable. Such film-forming polymers improve the spreading and coating of copper salt in solution on the substrate and serve to protect the deposited copper salt from abrasion.

After coating, the coated substrate goes to drying chamber **24** wherein the solvent is removed from the coated layer. Drying can be accomplished either by forced hot air, or by evacuation, as illustrated in FIG. **2**. After drying, the recording medium is complete and it can be stored, provided it is maintained at a low light level. Shelf life of the medium is at least in the order of months. On the other hand, if desired, the medium may be immediately used.

The medium is illustrated as passing directly into exposure chamber **26**. The copper salts listed are sensitive to photon exposure at about 3,000 A. or less Angstroms wavelength, in the ultraviolet portion of the spectrum. Here it may be either exposed to photons or electrons. In the drawing, scanning electron gun **28**, which receives its signals from signal source **30**, which provides signals in accordance with the desired image, directs a modulated electron beam **32** onto the sensitive material so that the image recording medium **34** is exposed. When only horizontal deflection is provided to the electron beam, the image recording medium can be advanced at a constant rate to record such information as that normally contained in video signals. On the other hand, when both vertical and horizontal deflection are provided, the image recording medium **34** can be advanced in stepwise fashion to expose one frame at a time. The earlier method is preferred, and suitable conventional means for proper rate of advance of the medium can be provided. Of course, scan speed and frame rates must be consistent with sensitivity of the medium so that adequate exposure occurs.

Exposure causes a latent image to be formed upon the sensitive material of the image recording medium **34**. After exposure, the image recording medium **34** is moved to development chamber **36** for development of the latent image. Development is accomplished by exposing the latent image to a source **38** of metal vapor. A suitable metal for development of the latent image into a visible image having lesser transparency than the unexposed parts is zinc, which is preferred. However, mercury and cadmium are also believed suitable development metals. Development is caused by suitable vaporization of the metal, as in a boat, to produce a low pressure of metal vapor, which then deposits metal selectively in an imagewise fashion in thicknesses proportioned to the amount of exposure. Such an image is indicated at **39** in FIG. **1**. For development of a fully exposed image, and using zinc as the development metal, a zinc flux is desired to produce a zinc layer having an optical density of about one, corresponding to a thickness of about 300–500 A. in the fully developed densest areas. Such development produces a permanent image so that exposure to light is not deleterious.

The copper compounds used in this invention must have certain characteristics and properties to produce the image formation process. The principal function is to provide a source of copper ions which can be reduced by ultraviolet light or electrons to form metallic atoms which further combine to form the stable nuclei which comprise the latent image. These nuclei act as sites for further condensation of metal atoms from the metal vapor of the metal used as the image developer; for example, zinc. Each electron striking the sensitive surface will produce a nucleation site upon which will condense, as an average, 10^4 to 10^6 metal atoms. In order to produce images capable of projection, the compound should be soluble in its carrier solution and binder, so that it can be deposited in either a film of such minute thickness that it is transparent or as crystals of such small size that they are transparent. The carrier solution may be water, for water soluble copper compounds, or an organic solvent appropriate to the solubility of the compound.

After development, the developed image-recording medium can be stored for later examination, or can be immediately passed to a suitable reading device. FIG. **2** illustrates the film going directly to projector **40**. Projector **40** includes light source **42**, which includes proper condensing optics, projector housing **44** which includes proper image-recording medium, incremental advance and shutter mechanism, as well as projection lens **46**. In addition, screen **48** is provided for viewing. The projector **40** is a conventional transparency projector.

After projection, the image-recording medium can be rolled up onto storage roll **50**, or may be otherwise kept for later inspection or otherwise disposed of.

In view of the fact that the development metals usually deposit upon the exposed areas, a negative picture would conventionally result. Thus, signal source **30** is preferably arranged so that electron beam **32** causes maximum exposure in the areas where it is desired that

the final projected image be dark. This can be conventionally electronically accomplished.

Examples of specific image recording media, and the manner in which they were created, exposed, developed and its resultant optical properties are as follows:

EXAMPLE I

Fifty mg of cupric acetyl acetonate were dissolved in 100 ml acetone. Several samples of Cronar, a polyester film made by DuPont, in the form of 1½ inch long sections of 35 mm transparent leader were dipped briefly into the solution and the acetone was allowed to evaporate. An invisible layer of the cupric acetyl acetonate remained on the surface. Electrical resistance of the surface was of the order of a megohm per square, but was adequate to permit a surface conduction of the applied electrons. In a vacuum chamber maintained at 10^{-5} to 10^{-6} torr, latent images were produced in the layer of copper compound by exposure to an intensely modulated electron beam with a current of approximately 4×10^{-7} amps at 10kV. The electrons were deposited in a checkerboard pattern with alternating ⅛ inch squares of exposed and unexposed surface. Varying the duration of the exposure time produced different electron dosages for each sample. For development of a visible image from the latent image, the samples were placed in another vacuum chamber which was then evacuated to 50 – 100 torr. The temperature of an electrically heated zinc evaporation boat was raised to 450° – 500° C in 5 – 10 seconds and quickly cooled. The small amount of zinc vapor produced during this time was absorbed selectively by the electron exposed areas while the unexposed areas remained uncoated and transparent. A visible checkerboard image was obtained. Difference in the optical densities of the exposed and unexposed areas was readily apparent, making optical projection possible. Transmission optical densities were measured on one sample which had received an electron dosage of 6.1×10^{-6} coulombs/cm^2. The density difference between the exposed and unexposed areas ranged from 1.3 to 1.4.

EXAMPLE II

1.25 gms of polyvinyl alcohol type 51–05–DuPont were dissolved in 100 ml boiling water. To the cooled solution was added 0.25 gms of cupric formate. Samples of 35 mm Cronar film leader were cut to approximately 1½ inch × 1½ inch, dipped into this solution and allowed to dry overnight. The resistance was high, but surface conductivity was enough to allow the charge to bleed off. A checkerboard test pattern was applied, as in Example I, and similarly zinc developed. The checkerboard image developed showed a low background and a differential density between background and image of 1.3 to 1.7 with an electron exposure of approximately 2.4×10^{-6} coulombs/cm^2.

EXAMPLE III

The same solution as in Example II was dipcoated onto electrically conductive glass and dried overnight in the dark. This glass is coated with a conductive transparent coating of tin oxide available from Corning Glass Works, Corning, N.Y., and is sometimes referred to as Nesa glass. Surface conductivity of such glass ranges from 30–100 ohms/square. Exposure of the dipcoated samples with electrons to produce a checkerboard pattern, as in Example I, with 3.2×10^{-6} coulombs at 10kV, and subsequently developed with zinc vapor, as in Example I, produced a measured differential optical density of 2.1 to 2.8. Exposure to 8.5×10^{-7} coulombs of electrons and zinc vapor development in a similar manner produced differential densities of 1.9 to 2.2.

EXAMPLE IV

The same solution as in Example II was applied to Cronar film which had been coated with a transparent, conductive layer of codeposited gold-bismuth having a surface resistance of 15–10 ohms/square. In this case, electron exposure and development, as in Example I, with 2.2 to 10^{-6} coulombs/cm^2 gave a differential density of 2.7. Exposure to 1×10^{-6} coulombs/cm^2 gave a differential density of 2.0. Exposure to 0.7×10^{-6} coulombs/cm^2 gave a differential density of 1.1. Exposure to 0.3×10^{-6} coulombs/cm^2 gave 0.7 density.

EXAMPLE V

The same solution as in Example II was applied to a Cronar film, which had been coated with a transparent, conductive cuprous iodide coating having a resistance of about 2,500 ohms/square. Electron exposure to 3.8×10^{-6} coulombs/cm^2 and development, as in Example I, produced a differential density of 2.3.

EXAMPLE VI

One gram of hydroxyl propyl methyl cellulose and 0.5 gram of cupric formate were dissolved in 100 ml H_2O. This solution was dipcoated on clear Cronar without application of conductive subcoating. Exposure to 5×10^{-6} coulombs/cm^2 at 10kV and development, as in Example I, produced a maximum density differential of 0.9. Surface resistance was very high, but sufficient to permit electrons to leak away from the exposed areas to ground.

EXAMPLE VII

0.119 gms of bis (ethyl) acetoacetato copper were dissolved in 100 ml. of toluene containing 0.3 gms of 30 percent by weight of Goodyear Tire and Rubber Co. Pliolite S–7 (a polystyrene budadiene copolymer). This solution was coated by immersion of 35 mm perforated polyster film with trade name "Cronar." After evaporation of solvent, exposure of the film to light in total quantity of about 18×10^6 ergs/cm^2 from a low pressure mercury arc (maximum output at 2,537A.) during a period of 3 minutes through a metal mask with imagewise openings produced a latent image which could be developed to a visible image by exposure to zinc vapor, as in Example I. Maximum density differential between exposed and unexposed areas was 1.0. The exposed areas were clear while the unexposed areas became dark. This represents a positive image.

EXAMPLE VIII

0.049 gms of copper acetyl acetonate was dissolved in 100 ml of toluene containing 0.3 gms of Rohm and Haas Acroyloid B–72 solution (an acrylic type polymer). The solution was coated on film, as in Example VII, and similarly exposed and developed with zinc vapor, as in Example I. In this case, a negative image was produced. The exposed areas were dark and visible while the unexposed areas remained clear. The differential densities were not measured.

This invention having been described in its preferred embodiment, it is clear that it is susceptible to numerous modifications and embodiments within the ability of those skilled in the art and without the exercise of the inventive faculty. Accordingly, the scope of this invention is defined by the scope of the following claims.

What is claimed is:

1. An image-recording medium, said image-recording medium comprising:

a transparent substrate;

the active ingredient of said medium consisting essentially of a radiation sensitive, liquid-soluble, transparent precipitated crystalline copper salt on said substrate to form a transparent uncoated, reducing-agent-free, electron-sensitive layer on said substrate, said copper salt being unchanged in transparency upon exposure and being reducible by electron impingement to produce copper atoms which combine to form stable nuclei which comprise a latent image, said substrate and said sensitive layer having a resistivity less than 1 megohm per square.

2. The image-recording medium of claim **1** wherein said copper salt is a water-soluble salt of copper in the valence 2 state selected from the group consisting of cupric bromide, cupric chloride, cupric sulfate, cupric formate, cupric acetate, cupric proprionate, cupric lactate and copper salts of 2-hydroxyisobutyric acid, glycolic acid, 2-hydroxylauric acid, and glyceric acid.

3. The image-recording medium of claim **1** wherein said copper salt is an organic solvent soluble salt of copper in the valence 2 state selected from the group consisting of copper salts of long-chain, fatty acids and complex organic acids consisting of oleic, linoleic, napthenic, stearic, undecylenic and behenic acids; and coordination compounds consisting of copper acetylacetonate, Bis (ethyl acetoacetato) copper, Bis (1 phenyl 1, 3-butanediono), and copper dimethyldithiocarbamate.

4. The image-recording medium of claim **3** wherein a conductive layer is positioned between the substrate and the sensitive layer, said conductive layer being substantially visually transparent and providing resistivity of said medium below about 1 megohm per square.

5. The process of recording an image, said process comprising the steps of:

providing a transparent substrate;

dissolving essentially only a soluble copper salt which is sensitive to electron and photon radiation exposure in a liquid solvent to form a liquid solution consisting essentially of solvent and copper salt;

coating the substrate with the liquid solution of radiation sensitive soluble copper salt;

evaporating the solvent to provide a transparent deposited layer, the active ingredient consisting essentially of radiation sensitive copper salt on the substrate;

imagewise exposing by electron or photon impingement the image-sensitive copper salt layer to provide a latent image configured in accordance with the exposure;

developing the latent image by directing an elemental metal vapor flux of a metal which is less noble than copper at the latent image-carrying copper salt layer in subatmospheric pressure so that the elemental metal deposits as a solid in accordance with the latent image on the sensitive copper salt layer to produce a visible image.

6. The process of claim **5** further including the succeeding step of:

projecting light onto the metal-developed, image-carrying substrate so that light passes through the substrate where no development metal has been image-wise deposited to project an image configured in accordance with the exposure step.

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