

[54] **X-RAY SENSITIVE ELEMENTS AND
PROCESS OF FORMING AN IMAGE
THEREFROM**

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96/1.5

3,620,721 11/1971 Edegem 250/315 A

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[57] **ABSTRACT**

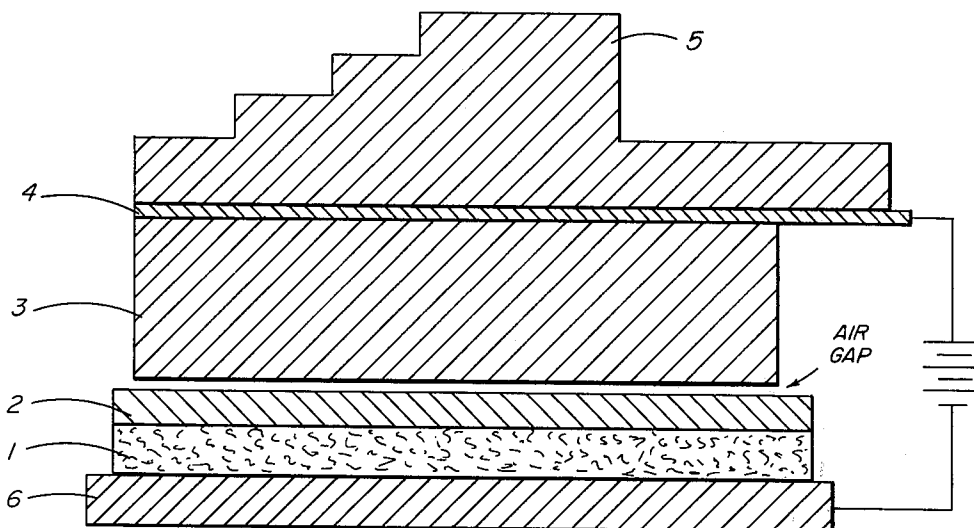
Elements containing layers which form active sites for reduction of metal ions when subjected to an electric field and layers containing inorganic photoconductors can be subjected to imagewise x-radiation and an electric field to form metal nuclei which may be developed to an image by physical development. The process is characterized by images of high contrast and high Dmax.

[56] **References Cited**

UNITED STATES PATENTS

2,825,814 3/1958 Walkup 250/315 A

42 Claims, 1 Drawing Figure



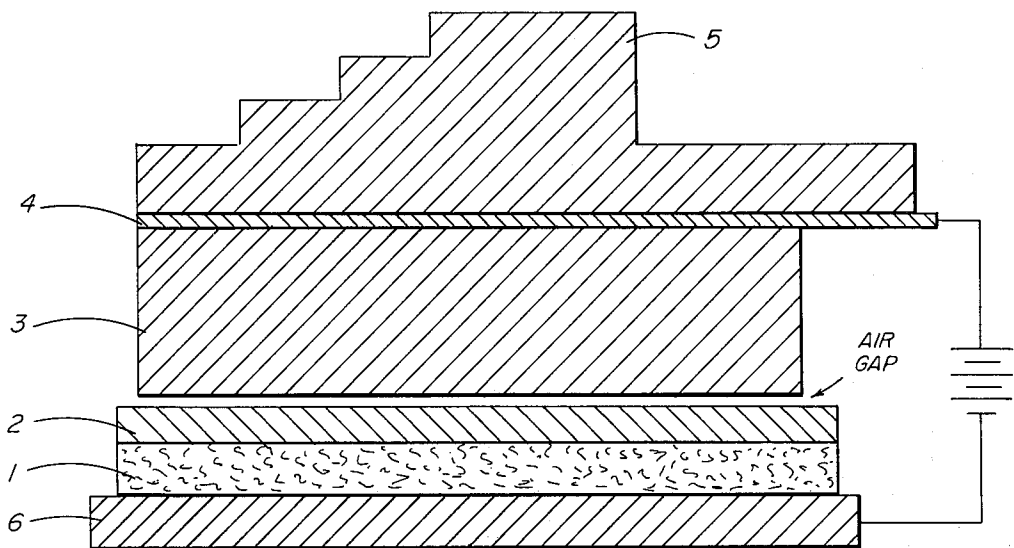


FIG. 1

X-RAY SENSITIVE ELEMENTS AND PROCESS OF FORMING AN IMAGE THEREFROM

This invention relates to elements and a process for producing visible images from an x-ray exposed image.

The process of forming a visible image by exposure to x-radiation is quite valuable for medical and industrial applications. Although the primary use is in diagnosis of human disease, x-radiation can also be used as a means of detection of mechanical flaws in machinery and equipment for industrial purposes. The major requirements for elements to be treated by x-radiation for these purposes are that the intensity and length of time of exposure be as low as possible and the resulting image be of high contrast and high Dmax. For industrial applications the speed is of less importance than the contrast and Dmax.

The process of xeroradiography such as described in U.S. Pat. Nos. 3,577,272 and 3,453,141, employs a xeroradiographic element comprising a support material bearing a coating of a normally insulating material whose electrical resistance varies with the amount of incident x-radiation it receives during an imagewise exposure. The element, commonly termed a photoconductive element, is first given a uniform surface charge. It is then exposed to a pattern of x-radiation which has the effect of differentially reducing the potential of this surface charge in accordance with the relative energy contained in various parts of the radiation pattern. The differential surface charge or electrostatic latent image remaining on the xeroradiographic element is then made visible by contacting the surface with a suitable electroscopic marking material. Such marking material or toner, whether contained in an insulating liquid or on a dry carrier, can be deposited on the exposed surface in accordance with either the charge pattern or in the absence of charge pattern as desired. Deposited marking material can then be either permanently fixed to the surface of the sensitive element by known means such as heat, pressure, solvent vapor, or the like, or transferred to a second element to which it can similarly be fixed. Likewise, the electrostatic latent image can be transferred to a second element and developed there.

The above process is, however, not always useful for medical applications or industrial applications requiring extremely high contrast and Dmax. The xeroradiography process produces images having only acceptable contrast and Dmax so that the detail required may not be sufficient to be useful. Further, the xeroradiography method generally results in a problem known as "fringe toning". Fringe toning is the phenomenon of differential Dmax in image areas. Thus, the Dmax may be high at the edges or fringes of the image and low around the center of the image.

A further problem involved with the use of x-radiation in xeroradiography is xeroradiographic undercutting caused by the ionization of air in the dark space between the dark slide and the surface of the radiographic plate. The x-rays create positive and negative air ions in the dark spaces with the negative ions being attracted preferentially to the image discontinuities of the surface. This results in a neutralization of surface charges and a narrowing of the unexposed areas of the electrostatic image. Substantial damage to the resulting image occurs. The problem is further described in Schaffert R.M., *Electrophotography*, New

York, Focal, 1965 (pages 105-106) and Dessauer and Clark, *Xeroradiography and Related Processes*, New York, Focal, 1965, (pages 500-501).

A still further problem involving the use of electrical radiographic processes is the dark decay inherent in such a process. The photoconductor cannot hold the charge for as long as is necessary for the x-ray exposure and this results in a substantial loss of contrast and Dmax. Therefore, if prolonged exposure times are required a substantial loss of image results.

It is, therefore, an object of this invention to provide an element capable of being exposed to x-radiation at high speed and being developed to an image of high Dmax and contrast with no loss of image due to dark decay and fringe toning.

It is another object of this invention to provide novel x-ray sensitive elements which can result in negative or positive images.

It is a further object of this invention to provide a novel process for producing images of high contrast and Dmax using the elements of this invention.

It is a still further object of this invention to provide a novel process for producing negative or positive images at high speed using the elements of this invention.

These and other objects of the invention are accomplished with an x-ray sensitive element comprising a support (1) coated with a layer (2) which comprises pigments which form active sites for reduction of metal ions when subjected to an electric field and a binder, wherein the pigment to binder weight ratio is from 2:1 to 10:1, and a layer (3) thereover comprising an inorganic photoconductor including atoms having an atomic number of 48 or higher with a conductive topcoat (4), wherein an air gap of up to 20 microns separates the layers (2) and (3).

An advantage of these elements is that the contrast and Dmax obtained are exceptionally good for exposures in the x-ray region. An additional advantage of these elements is that the contrast and Dmax are not deleteriously affected by dark decay and the images obtained from these elements having uniform Dmax properties. Further, the undercutting problem encountered in the xeroradiographic method is not encountered using the elements of this invention. Actually the ions formed by the x-rays aid in the ionization of the air gap and produce better image resolution.

Also in accordance with this invention a process is provided wherein an x-ray pattern is projected onto an element comprising a support 1 coated with a layer 2 which forms active sites for reduction of metal ions when subjected to an electric field and a layer 3 thereover comprising an inorganic photoconductor including atoms having an atomic number of 48 or higher and preferably a binder therefor with a conductive topcoat 4, wherein an air gap of up to 20 microns separates the layer forming actinic sites for the reduction of metal ions 2 and the layer comprising the inorganic photoconductor 3, and applying an electric field across said element to form metal nuclei and separating the layers 1 and 2 from layers 3 and 4 and physically developing the metal nuclei on layer 2 to form an image. The image obtained can be either negative or positive depending upon the particular process used.

In the drawing, the FIGURE is a horizontal section through an element and shows the process of exposing and applying potential to said element to create sites for physical development.

In accordance with this invention, the figure of the drawing represents an element comprising layer 1 which is a support, preferably baryta coated paper, and a pigmented layer 2 preferably a TiO_2 containing layer which is sandwiched with a photoconductive layer 3 and conductive support 4. The air gap depicted between layers 2 and 3 is greatly enlarged since the photoconductive layer 3 generally rests on layer 2. The process comprises exposing x-rays to a test object 5 while either simultaneously or later applying a potential between the conductive layer 4 and a grounded platen 6 adjacent to the support layer 1.

The support 1, on which the layer forming active sites for reduction of metal ions when subjected to an electrical field is coated, may be any electrically conducting or semiconducting support material, such as paper or conventional film supports, e.g., cellulose acetate, cellulose nitrate, poly(styrene), poly(ethylene terephthalate), poly(vinyl acetal), polycarbonates and related films containing an evaporated or chemically deposited metal layer such as nickel-coated supports. Further examples of supports to which conductive coatings can be added which are useful herein are described in *Product Licensing Index*, Vol. 92, December 1971, Publication 9232, page 108. The layer 1 should have an electrical resistivity of less than about 10^{10} ohm-cm.

Layer 2 comprises a material which forms active sites for reduction of metal ions when subjected to an electric field. This electrically activatable amplifier forms activatable sites which may be physically developed to an image. The preferred pigments having the above properties are TiO_2 , WO_3 , MoO_3 and lead iodide with rutile TiO_2 being especially preferred.

The pigments generally have particle sizes in the range of from about $0.25\ \mu\text{m}$ to about $3.0\ \mu\text{m}$. As the reaction involves surface effects, the surface-to-volume ratio increases as the particle size decreases. Therefore, it is preferable to use pigments having lower particle sizes.

Binders for use in preparing layer 2 include any hydrophobic binders such as styrene-butadiene copolymers; polyolefins; soya-alkyd resins; poly(vinyl chloride); poly(vinylidenechloride); vinylidene chloride-acrylonitrile copolymers; poly(vinyl acetate); vinyl acetate - vinyl chloride copolymers; poly(vinyl acetals), such as poly(vinyl butyral); polyacrylic and methacrylic esters, such as poly(methylmethacrylate); poly(n-butylmethacrylate); poly(isobutyl methacrylate), etc.; polystyrene; nitrated polystyrene; poly α -methylstyrene; isobutylene polymers; polyesters, such as poly(ethylenealkaryloxyalkylene terephthalate); phenolformaldehyde resins; polyamides; polycarbonates; polythiocarbonates; poly(ethyleneglycol-cobishydroxyethoxyphenyl propane terephthalate) copolymers of vinyl haloparalates and vinyl acetate such as poly(vinyl-m-bromobenzoate-co-vinylacetate) and the like. Useful binders are insulating filmforming resins having an electrical resistivity greater than 10^{10} ohm-cm.

Solvents of choice for preparing coating compositions of layer 2 can include a number of solvents such as benzene, toluene, acetone, methyl iso-butyl ketone, methylene chloride, and the like, or mixtures of the above.

In preparing layer 2, useful results are obtained when the pigment and binder are present in an amount from

about 30 to about 60 % by weight of the solvent solution. The pigment to binder ratio is dependent on particle size and the particular pigment or binder used, but may range from about 2:1 to 10:1. In the preferred embodiment herein, the pigment to binder ratio is from about 3:1 to about 5:1.

The pigmented layer 2 can be applied to the support 1 by any conventional coating process such as dip coating, curtain coating, etc. A description of various methods of coating can be found in *Product Licensing Index*, Vol. 92, December 1971, Publication 9232, page 109. The coating thickness of layer 2 may vary widely, but the preferred dry thickness is from about $4\ \mu\text{m}$ to about $15\ \mu\text{m}$. The thickness should be enough so as to give covering power to the support without being excessively thick. As the process takes place in the surface of the layer and the physical developer does not penetrate deeply into layer 2, a heavy thickness is not needed.

If desired, an overcoat may be used over layer 2 in order to protect layer 2 from smearing or oxidation. Any overcoat layer which does not affect the electrical transmission from layer 3 to layer 2 may be used. Generally a thin layer of a water-penetratable colloid such as gelatin, polyvinyl alcohol, ethyl cellulose and the like can be used. Gelatin is most effective, e.g., 2 to $5\ \mu\text{m}$ thickness.

The element is preferably prepared by applying a coating of layer 3 onto a conductive topcoat 4 and sandwiching these layers with support 1 coated with layer 2.

Suitable conductive topcoat materials 4 on which the photoconductive layers 3 can be coated include any of a wide variety of electrically conducting supports, for example, paper (at a relative humidity above 20 percent); aluminum-paper laminates; metal foil such as aluminum foil, zinc foil, etc.; metal plates, such as aluminum, copper, zinc, brass, and galvanized plates; vapor deposited metal layers, such as silver, nickel or aluminum and the like on paper and resin film supports. Such conducting layers both with and without insulating barrier layers are described in U.S. Pat. No. 3,245,833. Likewise, a suitable conducting coating can be prepared from the sodium salt of a carboxyester lactone maleic anhydride and a vinyl acetate polymer. Such kinds of conducting layers and method for their optimum preparation and use are disclosed in U.S. Pat. Nos. 3,007,901 and 3,267,807.

Preferably, layer 4 is more electrically conductive than is layer 3. Preferred layer 4 materials have an electrical resistivity of less than about 10^4 ohm-cm.

The layer containing the inorganic photoconductor 3 is generally prepared by milling a dispersion of the photoconductive material with a binder and coating the layer 3 onto the layer 4.

Preferred binders for use in preparing the present photoconductive layers are film-forming hydrophobic polymeric binders having fairly high dielectric strength which are good electrically insulating film-forming vehicles. Materials of this type comprise styrene-butadiene copolymers; polyolefins; soya-alkyd resins; poly(vinyl chloride); poly(vinylidenechloride); vinylidene chloride-acrylonitrile copolymers; poly(vinyl acetate); vinyl acetate-vinyl chloride copolymers; poly(vinyl acetals), such as poly(vinyl butyral); polyacrylic and methacrylic esters, such as poly(methylmethacrylate), poly(n-butylmethacrylate), poly(isobutyl metha-

crylate), etc.; polystyrene; nitrated polystyrene; polymethylstyrene, isobutylene polymers; polyesters, such as poly(ethylenealkaryloxyalkylene terephthalate); phenolformaldehyde resins; ketone resins; polyamides; polycarbonates; polythiocarbonates; poly(ethyleneglycol-co-bishydroxyethoxyphenyl propane terephthalate) copolymers of vinyl haloarylates and vinyl acetate, such as poly(vinyl-m-bromobenzoate-co-vinylacetate), etc. Suitable resins of the type contemplated for use in the photoconductive layers of the invention are sold under such tradenames as Vitel PE-101, Cymac, Pliolite S-5, Piccopale 100, Saran F-220, Lexan 105 and Lexan 145. Other types of binders which can be used in the photoconductive layers of the invention include such materials as paraffin, mineral waxes, etc.

Solvents of choice for preparing coating compositions of the present invention can include a number of solvents such as benzene, toluene, acetone, 2-butanone, chlorinated hydrocarbons, e.g., methylene chloride, ethylene chloride, etc., ethers, e.g., tetrahydrofuran, or mixtures of these solvents, etc.

The inorganic photoconductor used must contain metallic atoms having an atomic number of 48 or higher such as PbO, CdS, Bi₂O₃, CdSe, Se, Sb₂S₃ and the like such as described in U.S. Pat. No. 2,825,814. The preferred inorganic photoconductor is tetragonal lead monoxide as described in U.S. Pat. No. 3,577,272.

In preparing the coating composition, useful results are obtained where the photoconductor substance is present in an amount equal to at least about 30 weight percent of the coating composition. The upper limit in the amount of photoconductor substance present can be widely varied in accordance with usual practice. More generally, from 1.5 to 12.5 parts by weight of photoconductor for each part by weight of binder in the final composition is used. A preferred weight range in the final coated and dry composition is 1.5 to about 7.5 parts by weight of photoconductor for each part by weight of binder.

If desired, the layer 3 can be prepared without a binder by hot-pressing such as by a process described in U.S. application Ser. No. 439,653, filed Feb. 4, 1974 by Weiss et al.

Coating thicknesses of the photoconductive composition on a support can vary widely. More generally, a coating in the range of about 0.005 inch to about 0.10 inch before drying is useful for the practice of this invention. The preferred range of coating thickness is in the range from about 15 μ m to about 200 μ m after drying although useful results can be obtained outside of this range.

The layer 3 can be applied to the layer 2 in a variety of ways as long as an air gap exists between the two layers. Thus, a solvent cast coating of layer 3 onto layer 2 is not an acceptable method of application. Generally, the layer 3 is merely sandwiched with layer 2 in a contiguous face-to-face relationship. Although layer 2 and layer 3 are in face-to-face relationship an air gap exists between the two layers owing to the roughness of the surfaces. In some cases it may be desirable to fasten layer 2 to layer 3 at the edges at a specified distance if a more substantial gap is preferred. Spaces of defined thickness can be built into the surface of either layer 2 or layer 3 such as by adding glass beads or polymeric beads to either or both of said layers. Other methods of forming the air gap between the layers are well known in the art.

The thickness of the air gap is generally determined by the roughness of the layers 2 and 3. Generally, an air gap of up to about 20 microns is satisfactory. The preferred air gap is from about 0.1 micron to about 10 microns.

The element is exposed imagewise to x-radiation and preferably simultaneously a potential is applied between the layer 1 and the layer 4. Alternatively, the exposure can take place prior to the application of the electric field.

The x-ray pattern is projected onto the element by irradiating through an object to be photographed and the electric charge is applied to form an electric field pattern corresponding to the x-ray pattern. Typical sources of x-radiation emit a wavelength from about 0.1 angstrom to about 100 angstroms. The period of exposure to x-radiation can vary from seconds to minutes dependant upon the particular use in either medical or industrial radiography.

The electric charge is generally applied with the application of a potential difference between the conductive layer 4 and a plate contiguous to layer 1 so that an electric field image is placed on layer 2 due to selective potential across the air gap between layers 2 and 3 in the x-ray exposed areas. The charge may be applied in any conventional manner, such as described in U.S. Pat. Nos. 2,825,814 and 3,598,579. A potential of from about 600 volts to 4,000 volts applied for from about 5 to about 60 seconds is generally sufficient to achieve the desired results.

After exposure and charging, the portion of the element comprising layers 1 and 2 can be removed from the portion of the element comprising layers 3 and 4 and the image developed on layer 2. The portion of the element comprising layers 3 and 4 is reusable in this process.

In some instances such as when the activatable layer 2 comprises WO₃ or MoO₃ pigments, nucleating sites are formed directly which upon the application of a physical developer form a visible image. In other cases, such as when the activatable layer 2 comprises TiO₂ or BaTiO₃, treatment with a nucleating agent (a material which is an oxidizing agent containing a reducible metal ion) may be necessary prior to the use of the physical developer. Examples of nucleating agents useful herein include metal ions such as Ag⁺, Hg⁺², Pb⁺⁴, Au⁺³, Pt⁺⁴, Ni⁺², Sn⁺², Pb⁺², Cu⁺¹ and Cu⁺². The preferred nucleating agent is silver nitrate.

The nucleating agent generally comprises from about a 0.05 to about a 5% by weight solution in a solvent such as water or alcohol and water, or the like. In a preferred embodiment, the nucleating agent is in a concentration of 2% by weight in water. The layer 2 can be treated with the nucleating agent by merely immersing the layer 2 in a bath of the nucleating agent for a period of from about 10 to about 60 seconds.

The image on layer 2 is physically developed in any conventional physical development bath. The physical development bath generally contains metal ions in salt form and a reducing agent for the metal ions. Typical physical developer solutions are well-known (see Hornsby, *Basic Photographic Chemistry*, (1956) 66, and Mees and James, ed., *The Theory of the Photographic Process*, 3rd edition (1966), 329-331, and U.S. Pat. No. 3,650,748 by Yudelsohn et al. issued Mar. 21, 1972) and contain the metallic ions such as silver, copper, iron, nickel or cobalt necessary to form a visible

image at and in the vicinity of the nucleating centers.

The preferred metal salts employed as the source of metal for physical development are water-soluble salts such as silver nitrate, silver acetate, cupric salts such as copper chloride, copper nitrate, copper sulfate, copper formate, copper acetate and the like, and nickel salts such as nickel chloride, nickel bromide, nickel sulfate, nickel nitrate, nickel formate and the like.

Typical reducing agents used in the physical developer include, for example, polyhydroxy-substituted aryl compounds such as hydroquinones, catechols, and pyrogallols; ascorbic acid derivatives; aminophenols; p-phenylenediamines; and the like developing agents used in the photographic art. Particular examples of reducing agents for physical developer solutions are 2-methyl-3-chlorohydroquinone, bromohydroquinone, catechol, 5-phenylcatechol, pyrogallol monomethyl ether (1-methoxy-2,3-dihydroxybenzene), 5-methylpyrogallol monomethyl ether, isoascorbic acid, N-methyl-p-aminophenol, dimethyl-p-phenylenediamine, 4-amino-N,N-di(n-propyl)aniline and 6-amino-1-ethyl-1,2,3,4-tetrahydroquinoline. Particularly useful reducing agents are ferrous-ferric salts containing silver nitrate. Borane reducing agents such as amineboranes, borohydride and the like may also be used.

The preferred physical development baths include the Copper Enthone developer baths (a trademark of Enthone Corp.) containing copper sulfate, formaldehyde, Rochelle salt and nickel sulfate and physical developers prepared from ferrous ammonium sulfate, ferrous nitrate, citric acid, and silver nitrate.

The physical developer solutions, in addition to the metal salt and reducing agent, can comprise a complexing agent for the metal salt such as Rochelle salt or other ligands such as ethylene diamine tetraacetic acid for the metal salt, and can include a variety of other materials to facilitate maintenance and operation of the developer and to improve the quality of the developed image, such as acids and bases to adjust pH, buffers, preservatives, thickening agents, brightening agents and the like. The rate of development can be increased, and hence the time of development decreased, by adding to the developer solution a surfactant such as an alkaline metal salt of a sulfonated fatty acid, e.g., dodecyl sodium sulfonate.

The proportions in which the various components of the physical developer are present in the developer solution can vary over a wide range. Suitable concentrations of reducible heavy metal salt can range from about 0.01 mole to about 1.0 mole of metal salt per liter of solution. The upper limit of concentration is dependent upon the solubility of the particular metal salt employed. Preferably, the solution is about 0.1 molar to about 0.4 molar with respect to the heavy metal salt. The relative proportions of metal salt and complexing agent are dependent upon the particular heavy metal salt or salts and the particular complexing agent or agents which are employed. As a general rule, sufficient complexing agent should be incorporated to "tie up" the reducible heavy metal ions which are in solution and to lessen the tendency of these metal ions to be reduced prior to use of the developer solution. Depending upon the particular heavy metal salt and the particular complexing agent which is employed, the amount of complexing agent present typically can vary from about 0.2 mole to about 10 moles of complexing

agent per mole of metal salt present. Typically, the reducing agent can be present in amounts from about 0.01 mole to about 5 moles of reducing agent per mole of metal salt present in the solution. In order to permit the developer solution to be utilized for its maximum life, at least one equivalent of reducing agent should be present in the solution for each equivalent of reducible heavy metal salt.

The physical developers are operative over a wide range of pH. However, since the borane reducing agents undergo an acid-catalyzed hydrolytic reaction which reduces their stability during storage, it is preferred that the physical developers be maintained at a moderately alkaline pH of about 8 to 11, and preferably of about 8.5 to 9.5. Nevertheless, the physical developers can be used under acidic conditions as low as pH 3 in such conditions are advantageous for the particular photographic process in which they are used. The physical developer solution can be brought to the desired pH by addition of an appropriate amount of a suitable base, for example, ammonium hydroxide or sodium hydroxide, and can be maintained at the desired pH by addition of a suitable buffering system, for example, sodium carbonate and sodium bicarbonate. Other materials which can be used to adjust the pH to the desired range and buffers which will maintain the pH in that range can be readily determined by those skilled in the art.

The process outlined above may yield a positive or negative image depending on the nature of the photosensitive complex used and the development process.

Development of an image according to the invention can be carried out under ambient conditions of temperature and pressure, such as at a temperature of about 20° to about 30°C at atmospheric pressure.

As described above, a negative image is developed when the layer 3 is made the negative terminal of the circuit. If a direct positive image is desired, layer 2 can be fogged prior to exposure and charging by pre-flashing uniformly with Tungsten or UV light such as to a Photoflood for 1 to 60 seconds at a distance of 6 to about 18 inches and the layer 3 can be made the positive terminal. Thus, the x-ray exposure deactivates the exposed sites and the sites in the unexposed areas can be developed.

Alternatively, a positive image can be obtained by pre-activating the layer 2 prior to exposure and charging by uniformly charging with negative electricity and then following with imagewise x-ray exposure and applying a potential with layer 3 being made the positive terminal to deactivate the sites in the exposed areas.

In a preferred embodiment of this invention, a "gain" mechanism can be used to produce increased speed. This is accomplished by the use of specific inorganic photoconductors such as PbO which are persistent photoconductors. These photoconductors remain more conducting for long periods of time in the areas struck by radiant energy after the radiant energy is removed. Therefore, less exposure to x-radiation is required.

The invention is further illustrated by the following examples which include preferred embodiments thereof.

EXAMPLE 1

The following materials were added to a ball mill containing 30 three-eighth inch o.d. agate balls:

11.6 grams of a 34.5% solution of 70/30 styrenebutadiene copolymer in toluene (Pliolite S-7)

20.0 grams of TiO_2 (rutile)

35.2 grams of toluene

The materials were milled for 24 hours and coated at 0.005 inch wet thickness on baryta-coated paper support. The coating was air dried at room temperature for 4 hours. A 0.003 inch wet thickness overcoat of 40% gelatin in water containing 0.2% formalin was coated on top of the TiO_2 layer, chill set and forced air dried in a dark cabinet for 24 hours.

The layer of TiO_2 was sandwiched with a 100 μm thick layer of PbO in a styrene-butadiene binder coated on a conducting support as described in Example 2 of U.S. Pat. No. 3,577,272. A potential of 3 KV was established across the sandwich with the PbO layer being made the negative terminal of the circuit and a platen being made the positive terminal, simultaneously with the application of 1 mm aluminum filtered 60 KVP (3mA) (60 kilovolt peak having a rating of 3 milliamps) x-rays through a test object for 30 seconds.

The TiO_2 layer on paper support was then removed from the sandwich, bathed in 2% AgNO_3 solution in water for 10 seconds, and then immersed in a physical developer bath containing 0.4 M ferrous ammonium sulfate, 0.16 M ferric nitrate, 0.18 M citric acid and 0.1 M AgNO_3 for 30 seconds. A high contrast negative image of the test object having a reflective maximum density of 1.2 resulted.

The above element and process was compared to the same process using the same element with the exception that only the TiO_2 layer on the support was exposed to x-rays and treated. The photoconductive layer was not sandwiched with the TiO_2 layer. No image resulted after treatment in the nucleating agent and in the physical developer bath.

EXAMPLE 2

The TiO_2 coated layer on paper support of Example 1 was pre-flashed uniformly under a photoflood for 5 seconds at a distance of 8 inches. The pre-flashed layer was sandwiched with the photoconductor of Example 1. A potential of 3 KV was applied across the sandwich with the PbO layer being the positive terminal of the circuit, simultaneously with exposure of 1 mm aluminum filtered, 60 KVP x-rays (3mA) through the same test object of Example 1 for 30 seconds. The TiO_2 layer on paper support was removed from the sandwich and developed as described in Example 1. A direct positive image of the test object resulted having a maximum reflective density of 1.05.

EXAMPLE 3

The following materials were added to a ball mill jar containing 30 three-eighth inch o.d. agate balls:

23.3 grams of a 30% solution in toluene of an 85/15 styrene-butadiene copolymer (Pliolite S-5)

21.0 grams of TiO_2 (anatase)

18.2 grams of toluene

The materials were ball milled for 24 hours and coated on a paper support as described in Example 1. A gelatin overcoat was applied as described in Example 1 and the photoconductive coated support of Example 1 was sandwiched to the TiO_2 layer. Negative and positive x-ray images having contrast maximum density

were obtained when the processes of Examples 1 and 2 were followed using the layers of Example 3.

EXAMPLE 4

The following materials were added to a ball mill jar containing 30 three-eighth inch o.d. agate balls:

12.0 gram of Pliolite S-7

20.0 grams of BaTiO_3

36.0 grams of toluene

The materials were milled in a ball mill for 24 hours and coated on a paper support as described in Example 1.

The BaTiO_3 layer on paper support was sandwiched with the PbO photoconductive layer on conductive support as described in Example 1 and exposed to x-ray exposure through a mask as in Example 1, simultaneously with the application of a potential of -2.5 KV on the PbO layer for 30 seconds.

The BaTiO_3 layer on paper support was removed from the sandwich and immersed in a 2% AgNO_3 solution in water for 20 seconds and physically developed in the physical developer bath of Example 1 for 40 seconds. A negative reproduction of the test object resulted.

EXAMPLE 5

The BaTiO_3 coating on paper support of Example 4 was uniformly pre-exposed to a UV-21 Mineralite lamp for 20 seconds at a distance of 8 inches. The layer was sandwiched with the photoconductive layer coated on a conductive support described in Example 1 and +3KV was applied to the PbO and across the sandwich, simultaneously with 1mm aluminum filtered 60 KVP x-ray exposure through a test object for 40 seconds.

The BaTiO_3 layer on paper support was removed from the sandwich and bathed in 2% AgNO_3 solution in water for 30 seconds and then immersed in the physical developer of Example 1 for 40 seconds. A direct positive reproduction of the test object resulted.

This example was repeated except that the PbO layer on a conductive support was not sandwiched with the BaTiO_3 layer during x-ray exposure. No image resulted after physical development without the PbO layer.

EXAMPLE 6

The following materials were added to a ball mill jar containing 30 three-eighth inch agate balls:

5.7 grams of Pliolite S-7

10.0 grams of WO_3

11.0 grams of toluene

The mixture was ball-milled for 24 hours on a ball mill and coated on paper support as in Example 1. No gelatin overcoat was used.

The WO_3 layer on paper support was sandwiched with PbO on a conductive support as described in Example 1. A 3 KV potential was applied across the sandwich with the PbO layer being the negative terminal of the circuit, simultaneously with the exposure from 1 mm aluminum filtered 60 KVP (3mA) x-rays through a test object for 30 seconds.

The WO_3 layer on paper support was removed from the sandwich at which time a visible printout image was discernible. The layer was then developed directly in the physical developer of Example 1 without pre-nucleation. A high density ($D_r = 1.15$) negative image of the test pattern resulted.

EXAMPLE 7

The following materials were added in a ball mill jar containing 30 three-eighth inch o.d. agate balls:

- 11.6 grams of Pliolite S-7
- 20.0 grams of TiO_2 (Titanox RA-50)
- 35.2 grams of toluene

The mixture was milled for 24 hours on a ball mill and coated onto a paper support as in Example 1. No gelatin overcoat was used.

The TiO_2 layer on paper support was sandwiched with a 100 μm thick layer of CdS powder dispersed in a 70/30 styrene-butadiene binder at a pigment-to-binder ratio of 4/1. The CdS powder had been doped with 15 parts per million copper and 100 parts per million antimony by a thermal activation process comprising firing the pre-doped powder at 700°C for 1 hour in a nitrogen and iodine atmosphere. The layer was coated on a conductive support of 0.4D nickel-coated poly(ethylene terephthalate) by knife coating.

A potential of 2KV was established across the sandwich with the CdS layer being made the negative terminal of the circuit, simultaneously with the application of 1 mm aluminum filtered 80 KVP x-rays through a test object for 60 seconds. The TiO_2 layer on paper support was then removed from the sandwich, bathed in a 2% AgNO_3 solution for 15 seconds and immersed in the physical developer bath of Example 1 for 20 seconds. A negative image of the test object resulted.

Although the invention has been described in considerable detail with reference to certain preferred embodiments thereof, it will be understood that variations and modifications can be effected without departing from the spirit and scope of the invention as described hereinabove.

I claim:

1. A process for forming an image of an x-ray pattern comprising (a) projecting an x-ray pattern onto an element comprising a support (1) coated with a layer (2) which forms active sites for reduction of metal ions when subjected to an electric field and a layer (3) thereover comprising an inorganic photoconductor including atoms having an atomic number of 48 or higher with a conductive topcoat (4), wherein an air gap of up to about 20 microns separates the layer forming actinic sites for the reduction of metal ions (2) and the layer comprising the inorganic photoconductor (3), and (b) applying an electric field across said element to form metal nuclei, (c) separating layers (1) and (2) from layers (3) and (4) and (d) physically developing the metal nuclei on layer (2) to form an image.

2. The process of claim 1 wherein the support (1) is baryta paper.

3. The process of claim 1 wherein the binder in Layer (2) is an insulating film-forming resin having a resistivity of greater than 10^{10} ohm-cm.

4. The process of claim 1 wherein layer (1) has an electrical resistivity of less than 10^{10} ohm-cm.

5. The process of claim 1 wherein layer (4) is more electrically conductive than layer (3).

6. The process of claim 1 wherein the air gap between layers (2) and (3) is from about 0.1 to about 10 microns.

7. The process of claim 1 wherein the element is treated with a nucleating agent prior to physical development.

8. The process of claim 1 wherein the x-ray exposure and the electric field are simultaneously applied.

9. The process of claim 1 wherein the physical developer is a ferrous-ferri-silver nitrate developer.

10. The process of claim 1 wherein the element is subjected to from 600 volts to 4000 volts.

11. The process of claim 1 wherein layer (2) comprises a pigment in a binder therefor wherein the pigment to binder ratio is from 2:1 to 10:1.

12. The process of claim 11 wherein the binder is styrene-butadiene copolymer.

13. A process of forming an image of an x-ray pattern comprising (a) projecting an x-ray pattern onto an element comprising a support (1) coated with a layer (2) comprising a member selected from the group consisting of TiO_2 , WO_3 , MoO_3 , BaTiO_3 and lead iodide, and a layer (3) thereover comprising an inorganic photoconductor having an atomic number of 48 or higher with a conductive topcoat (4) wherein an air gap of up to about 20 microns separates the layers (2) and (3) and (b) applying an electric field across said element to form metal nuclei, (c) separating layers (1) and (2) from layers (3) and (4) and (d) physically developing the metal nuclei on layer (2) to form an image.

14. The process of claim 13 wherein layer (2) comprises a binder and wherein the pigment to binder weight ratio of layer (2) is from 2:1 to 10:1.

15. The process of claim 13 wherein the binder of layer (2) is an insulating film-forming resin having an electrical resistivity greater than 10^{10} ohm-cm.

16. The process of claim 13 wherein the binder is styrene-butadiene copolymer.

17. The process of claim 13 wherein the air gap between layers (2) and (3) is from 0.1 to 10 microns.

18. The process of claim 13 wherein the x-ray exposure and electric field are simultaneously applied.

19. A process for forming an image of an x-ray pattern comprising (a) projecting an x-ray pattern onto an element comprising a support (1) coated with a layer (2) comprising a member selected from the group consisting of TiO_2 , WO_3 , MoO_3 , BaTiO_2 and lead iodide, and a layer (3) comprising a member selected from the group consisting of PbO , CdS, Bi_2O_3 , CdSe, Se, Sb_2S_3 , and SnO_2 with a conductive topcoat (4) wherein an air gap of up to about 20 microns separates the layers (2) and (3), and (b) applying an electric field across said element to form metal nuclei, (c) separating layers (1) and (2) from layers (3) and (4) and (d) physically developing the metal nuclei on layer (2) to form an image.

20. The process of claim 19 wherein the layer (2) comprises a binder and the pigment to binder weight ratio in layer (2) is from 2:1 to 10:1.

21. The process of claim 19 wherein the binder is styrene-butadiene copolymer.

22. The process of claim 19 wherein layer (1) has an electrical resistivity of less than about 10^{10} ohm-cm.

23. The process of claim 19 wherein the air gap between layers (2) and (3) is from 0.1 to 10 microns.

24. The process of claim 19 wherein x-ray exposure and the electric field are simultaneously applied.

25. A process of forming an image of an x-ray pattern comprising (a) projecting an x-ray pattern onto an element comprising a support (1) coated with a layer (2) comprising TiO_2 in a binder therefor and a layer (3) thereon comprising an inorganic photoconductor having an atomic number of 48 or higher with a conductive

topcoat (4) wherein an air gap of up to about 20 microns separates the layers (2) and (3) and (b) applying an electric field across said element, (c) separating layers (1) and (2) from layers (3) and (4), (d) treating said layer (2) with a nucleating agent to form metal nuclei and (e) physically developing the metal nuclei on layer (2) to form an image.

26. A process for forming an image of an x-ray pattern comprising (a) projecting an x-ray pattern onto an element comprising a support (1) coated with a layer (2) comprising BaTiO₃ in a binder therefor and a layer (3) thereon comprising an inorganic photoconductor having an atomic number of 48 or higher and a binder therefor with a conductive topcoat (4) wherein an air gap of up to about 20 microns separates the layers (2) and (3) and (b) applying an electric field across said element, (c) separating layers (1) and (2) from layers (3) and (4), (d) treating said layer (2) with a nucleating agent to form metal nuclei and (e) physically developing the metal nuclei on layer (2) to form an image.

27. A process for forming an image of an x-ray pattern comprising (a) projecting an x-ray pattern onto an element comprising a support (1) coated with a layer (2) comprising WO₃ in a binder therefor and a layer (3) thereon comprising an inorganic photoconductor having an atomic number of 48 or higher and a binder therefor with a conductive topcoat (4) wherein an air gap of up to about 20 microns separates the layers (2) and (3), (b) applying an electric field across said element to form metal nuclei, (c) separating layer (1) and (2) from layers (3) and (4), and (e) physically developing the metal nuclei on layer (2) to form an image.

28. A process for forming an image of an x-ray pattern comprising (a) projecting an x-ray pattern onto an element comprising a support (1) coated with a layer (2) comprising MoO₃ in a binder therefor and a layer (3) thereon comprising an inorganic photoconductor having an atomic number of 48 or higher and a binder therefor with a conductive topcoat (4) wherein an air gap of up to about 20 microns separates the layers (2) and (3), (b) applying an electric field across said element to form metal nuclei, (c) separating layers (1) and (2) from layers (3) and (4), and (d) physically developing the metal nuclei on layer (2) to form an image.

29. A process for forming a positive image of an x-ray pattern comprising (a) preparing a support (1) coated with a layer (2) which forms active sites for reduction of metal ions when subjected to an electric field, (b) pre-flashing the layer (2) uniformly with light, (c) preparing an element comprising the support (1) coated with the preflashed layer (2) and a layer (3) thereover comprising an inorganic photoconductor including atoms having an atomic number of 48 or higher with a conductive topcoat (4) wherein an air gap of up to about 20 microns separates the layer forming actinic sites for the reduction of metal ions (2) and the layer comprising the inorganic photoconductor (3) and (d) applying an electric field across said element to form metal nuclei and (e) separating layers (1) and (2) from layers (3) and (4) and (f) physically developing the metal nuclei on layer (2) to form a positive image.

30. The process of claim 29 wherein layer (2) comprises a member selected from the group consisting of

TiO₂, WO₃, MoO₃, BaTiO₃ and lead iodide and layer (3) comprises a member selected from the group consisting of PbO, CdS, Bi₂O₃, CdSe, Se, Sb₂S₃ and SnO₂.

31. A process for forming a positive image of an x-ray pattern comprising (a) preparing a support (1) coated with a layer (2) which forms active sites for reduction of metal ions when subjected to an electric field, (b) preactivating layer (2) uniformly with negative electrical charge, (c) preparing an element comprising the support (1) coated with the preactivated layer (2) and a layer (3) thereover comprising an inorganic photoconductor including atoms having an atomic number of 48 or higher with a conductive topcoat (4) wherein an air gap of up to about 20 microns separates the layer forming actinic sites for the reduction of metal ions (2) and a layer comprising the inorganic photoconductor (3) and (3) applying an electric field across said element wherein layer (3) is made a positive terminal to form metal nuclei and (e) separating layers (1) and (2) from layers (3) and (4) and (f) physically developing the metal nuclei on layer (2) to form a positive image.

32. The process of claim 31 wherein layer (2) comprises a member selected from the group consisting of TiO₂, WO₃, MoO₃, BaTiO₃ and lead iodide and layer (3) comprises a member selected from the group consisting of PbO, CdS, Ti₂O₃, CdSe, Se, Sb₂S₃ and SnO₂.

33. An x-ray sensitive element comprising a support (1) coated with a layer (2) which comprises pigments which form active sites for reduction of metal ions when subjected to an electric field in a binder wherein the pigment to binder weight ratio is from 2:1 to 10:1 and a layer (3) thereover comprising an inorganic photoconductor containing a metallic atom having an atomic number of 48 or higher with a conductive topcoat (4) wherein an air gap of up to about 20 microns separates the layers (2) and (3).

34. The element of claim 33 wherein the layer (2) comprises a member selected from the group consisting of TiO₂, WO₃, MoO₃, BaTiO₃ and lead iodide.

35. The element of claim 34 wherein layer (3) comprises a member selected from the group consisting of PbO, CdS, Bi₂O₃, CdSe, Se, Sb₂S₃ and SnO₂.

36. The element of claim 35 wherein layer (3) comprises a binder for the inorganic photoconductor.

37. The element of claim 33 wherein the binder for layer (2) is a styrene-butadiene copolymer.

38. The element of claim 33 wherein layer (1) has an electrical resistivity of less than about 10¹⁰ ohm-cm.

39. The element of claim 33 wherein layer (4) is more electrically conductive than layer (3).

40. The element of claim 33 wherein the air gap between layers (2) and (3) is from about 0.1 to about 10 microns.

41. The element of claim 33 wherein the pigment to binder ratio of layer (2) is from 2:1 to 5:1.

42. An x-ray sensitive element comprising a support (1) coated with a layer (2) which comprises TiO₂ pigments in a binder wherein the pigment to binder weight ratio is from 2:1 to 10:1 and a layer (3) thereover comprising PbO with a conductive topcoat (4) wherein an air gap of up to about 20 microns separates the layers (2) and (3).

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