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METHOD OF MAKING X-RAY SENSITIVE ELECTRORADIOGRAPHIC ELEMENTS

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ABSTRACT OF THE DISCLOSURE

Electroradiographic elements containing, as a photoconductor, tetragonal lead monoxide prepared by heating orthorhombic lead monoxide in water and subjecting the material to a post heat treatment are sensitive to X-radiation and useful in electroradiography.

This invention relates to electroradiography, and in particular to photoconductive compositions and elements.

The process of xeroradiography 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 image-wise 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.

Various photoconductive insulating materials have been employed in the manufacture of xeroradiographic elements. For example, inorganic materials such as amorphous selenium, cadmium sulfide, zinc sulfide and sulfur, and organic materials such as anthracene and stilbene coated on a suitable support are sensitive to X-rays.

Another material which has been found to be sensitive to X-radiation is orthorhombic lead monoxide. One of the problems encountered in using any of these materials is their exposure-speed characteristics. Most of these photoconductors are too slow for medical applications. Selenium and orthorhombic lead monoxide have adequate speeds for exposures of such areas as the limbs, hips, shoulders, cervical spine and ribs but are not fast enough for heavier parts such as the abdomen, pelvis and lumbar spine. Because of the slow speeds involved in the exposures of the members of this latter group, these photoconductors are unsuitable since, in order to obtain acceptable reproductions, the member would have to be subjected to X-rays for an undesirably long period.

It is, therefore, an object of this invention to provide a novel class of photoconductors having high X-ray sensitivity when electrically charged.

It is another object to provide novel photoconductor-containing compositions which exhibit high electrical speeds when exposed to X-radiation.

It is also an object to provide novel X-ray sensitive photoconductor-containing compositions which can be positively and negatively charged.

It is another object to provide novel electroradiographic elements having high speed characteristics when subjected to X-radiation.

It is a further object of this invention to provide a novel electroradiographic process for producing images using the elements of this invention.

These and other objects of this invention are accomplished with electroradiographic elements having coated thereon X-ray sensitive photoconductive compositions containing, as the photoconductor, particulate tetragonal lead monoxide prepared by heating particulate orthorhombic lead monoxide in water and thereafter subjecting the resulting tetragonal lead monoxide to a heat treatment. The particulate tetragonal lead monoxide prepared in this manner has excellent photoconducting properties when used as a photoconductor in xeroradiographic elements. The elements have high speeds when subjected to X-radiation, i.e., electromagnetic radiation having a wavelength of from about 0.1 to about 100 angstroms. Higher speeds are obtainable with these elements than those containing other forms of lead monoxide as the photoconductor, e.g., orthorhombic lead monoxide. Also, when compared to elements containing tetragonal lead monoxide prepared by other processes, the speeds obtained are much greater for exposures in the X-ray region.

An additional advantage of these materials over other forms of lead monoxide is that there is little or no residual charge after exposure to X-radiation in the exposed regions whereas other materials have a residual charge of 100 volts or more. As a result the latent images produced are easily toned or transferred without the need for additional biasing. A further advantage of the tetragonal lead monoxide elements of this invention is their improved dark decay characteristics as compared to elements containing other forms of lead monoxide.

Also, in accordance with this invention, a process is provided wherein an electrostatic charge pattern is formed on a photoconductive element by exposing the element to a pattern of X-radiation, the photoconductor contained in the photoconductive layer being red tetragonal lead monoxide.

The tetragonal lead monoxide useful in this invention is prepared by heating a suspension of particulate orthorhombic lead monoxide in water (preferably distilled or deionized) for a period sufficient to convert at least 80% of the orthorhombic to the tetragonal form. While useful speeds are attainable from 80% conversion, higher speeds are achieved with higher conversions. The time for the conversion ranges from about 15 minutes to about 3 hours. The conversion can be carried out by heating the slurry generally from about 50° C. to about 200° C. and preferably from 80° C. to 125° C. The conversion pressure generally ranges from about 0.1 atmosphere to about 50 atmospheres and is preferably atmospheric pressure. The weight ratio of water to orthorhombic lead monoxide used for the conversion ranges from about 0.1 part of water for each part of orthorhombic lead monoxide to about 10.0 parts of water to each part of orthorhombic lead monoxide. The conversion should be carried out in the absence of impurities such as the silicate ion since its presence inhibits the conversion.

After the conversion is completed, the solids are removed and washed with distilled water and optionally additional wash liquids such as ethyl alcohol, trichlorotrifluoroethane, etc. The resulting particulate red tetragonal lead monoxide is then dried at a temperature from about 50° C. to about 150° C. to remove residual wash liquids. The dried particulate material is subjected to a post heat treatment in an inert atmosphere (i.e., an atmosphere not reactive with tetragonal lead monoxide) such

as nitrogen, argon, helium, neon, etc., at a temperature from about 350° C. to about 500° C. for a period sufficient to remove residual impurities. The period for such treatment is generally 30 minutes or more. The average particle size (diameter) of the final red tetragonal lead monoxide ranges from about 0.25 microns to about 10 microns.

Electroradiographic elements can be prepared with the novel tetragonal lead monoxide of the invention by blending a dispersion of the photoconductive material with a binder and coating the photoconductor-containing material on a suitable conducting support.

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 methacrylate), 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 tradnames 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.

In preparing the coating composition useful results are obtained where the photoconductor substance is present in an amount equal to at least about 1 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 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 composition is 1.5 to about 7.5 parts by weight of photoconductor for each part by weight of binder.

Coating thicknesses of the photoconductive composition on a support can vary widely. More generally, a coating in the range of about 0.001 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 0.002 inch to about 0.02 inch before drying although useful results can be obtained outside of this range.

Suitable supporting materials for coating the photoconductive layers of the present invention can 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. An especially useful conducting support can be prepared by coating a resin film support material such as poly(ethylene terephthalate), cellulose acetate etc. with a layer containing a semiconductor dispersed in a resin. Such conducting layers both with and without insulating barrier layers are described in U.S. Pat. 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 methods for their optimum preparation and use are disclosed in U.S. 3,007,901 and 3,267,807.

The elements of the present invention can be employed in a xeroradiographic process. In a process of this type the electroradiographic element is given a blanket electrostatic charge by placing the same under a corona discharge which serves to give a uniform charge to the surface of the photoconductive layer. This charge is retained by the layer owing to the substantial insulating property of the layer, that is, the low conductivity of the layer in the absence of X-radiation. The electrostatic charge formed on the surface of the photoconducting layer is then selectively dissipated from the surface of the layer by exposure to a pattern of X-rays which is to be reproduced so that the X-rays discharge the irradiated areas by photoconduction. By exposure of the surface in this manner, a charged pattern is created by virtue of the fact that the X-rays cause the charge to be conducted away in proportion to the intensity of the irradiation in a particular area. The charge pattern remaining after exposure is then developed, i.e., rendered visible, by treatment with a medium comprising electrostatically attractable particles having optical density. The developing electrostatically attractable particles can be in the form of a dust, e.g., powder, pigment in a resinous carrier, i.e., toner, or a liquid developer may be used in which the developing particles are carried in an electrically insulating liquid carrier. Methods of development of this type are widely known and have been disclosed in U.S. Pat. 2,397,691 and in Australian Pat. 212,315, for example. In processes of electroradiographic reproduction such as in xeroradiography, by selecting a developing particle which has as one of its components, a low-melting resin, it is possible to treat the developed photoconductive material with heat and cause the powder to adhere permanently to the surface of the photoconductive layer. In other cases, a transfer of the image formed on the photoconductive layer can be made to a second support such as paper, which would then become the final print. Techniques of the type indicated are well known in the art and have been described in U.S. Pat. 2,297,691 and 2,551,582 and in "RCA Review," vol. 15 (1954), pages 469-484, for example.

Additionally, the electrostatic charge comprising the latent image which is produced on the surface of the photoconductive element after exposure can be transferred to a receiving sheet and developed there. The charging and exposing of the photoconductive element and the transfer of the latent image can occur simultaneously as described in Walkup U.S. Pat. 2,825,814.

The electroradiographic materials described herein are particularly responsive to X-radiation, i.e., radiation having a wavelength from about 0.1 angstrom to about 100 angstroms and are useful in various types of xeroradiographic systems.

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

EXAMPLE I

500 grams of particulate yellow orthorhombic lead monoxide designated as Evans fumed litharge (Evans Lead Corp.) having a diameter ranging from 0.25 to 10 microns, is added to 500 cc. of boiling distilled water. The mixture is allowed to boil for 30 minutes. After filtering, the solids are washed once with distilled water, twice with ethyl alcohol and twice with Freon 113 (trichlorotrifluoroethane). After drying at 110° C. for 30 minutes, the solids are fired in a quartz boat in a furnace at 400° C. for one hour in nitrogen. X-ray diffraction indicates that all of the yellow orthorhombic lead

monoxide is converted to the particulate red tetragonal form having a particle size ranging from 0.25 to 10 microns in diameter by the above procedure.

EXAMPLE II

A coating composition is prepared from the tetragonal lead monoxide of Example I by milling the following composition for 24 hours with agate balls:

(a) 30 grams tetragonal lead monoxide,
(b) 20 grams Pliolite S–7 (trademark of Goodyear Tire and Rubber Co. for a 70:30 styrene-butadiene copolymer) and
(c) 86.7 grams toluene.

The resulting composition is coated at 0.010 inch wet-thickness on an aluminum foil paper laminate directly on the aluminum. The coating block is maintained at a temperature of 90° F. until dry. The electroradiographic element is charged under a negative corona source until the surface potential, as measured by an electrometer probe, reaches about 450 volts. The potential of the surface is measured just prior to exposure (V_0) and immediately after exposure (V) to a 240 mr. source (generated by 50 kv. at 20 ma. in 2 seconds). The exposure causes a reduction of the surface potential. The speed of the element is expressed as the change in the surface potential divided by the surface potential immediately prior to exposure multiplied by 100 i.e.,

$$\text{Speed} = \frac{(V_0 - V)}{V_0} 100$$

The above element has a negative speed of 75.

EXAMPLE III

A portion of particulate yellow orthorhombic lead monoxide of the same type used in Example I, is converted to the red tetragonal state by the following treatment:

About 50 parts by weight of the orthorhombic lead monoxide are boiled for one hour in 148 parts by weight of a 12 molal aqueous solution of sodium hydroxide. The resulting dark red tetragonal crystals are separated by repeated decantation and washing with distilled water followed by washing with absolute methanol. An electroradiographic member is prepared and tested from this material using the procedure described in Example II. It is found to have a negative speed of 9.

EXAMPLE IV

Particulate yellow orthorhombic lead monoxide obtained from the Evans Lead Corp. having a diameter ranging from 0.25 to 10 microns is heat treated at 300° C. for one hour in air. Electroradiographic elements are prepared from this material and tested in the manner described in Example II, using instead a positive charging polarity. These elements are found to have a positive speed of 4.5.

In comparing the results of Examples II through IV, it is seen that only the red tetragonal lead monoxide prepared by boiling the yellow orthorhombic gives unexpectedly high speeds when exposed to a source of X rays.

EXAMPLE V

Coating dopes are prepared in the manner described in Example II using the materials set forth therein. The red tetragonal lead monoxide used is prepared by the method described in Example I. In a darkened room, the surface of the element so prepared is charged to a potential of about —450 volts under a corona charger. The element is then exposed to a pattern of X-rays from a 240 mr. source. The resulting electrostatic latent image is developed in the usual manner by cascading over the surface of the layer a mixture of negatively charged black thermoplastic toner particles on glass beads functioning as carriers for the toner particles. A good reproduction of the pattern is obtained. Similar results are obtained using a liquid developer.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A process for preparing an electroradiographic element useful in xeroradiography comprising the steps of:
   (a) heating particulate orthorhombic lead monoxide in water for a period sufficient to convert at least 80% of said orthorhombic lead monoxide to tetragonal lead monoxide,
   (b) separating the resulting particulate tetragonal lead monoxide,
   (c) heating the said separated tetragonal lead monoxide at a temperature of about 350° C. to about 500° C. in an atmosphere inert to tetragonal lead monoxide,
   (d) mixing the particulate tetragonal lead monoxide with an insulating binder, and
   (e) coating the resultant mixture on a conducting support.

2. The process of claim 1 wherein the insulating binder is a copolymer of butadiene and styrene.

3. The process of claim 1 wherein the inert atmosphere comprised nitrogen.

4. The process of claim 1 wherein the weight ratio of tetragonal lead monoxide to binder is at least 1:1.

5. The process of claim 1 wherein the water is distilled water.

6. The process of claim 1 wherein the weight ratio of water to orthorhombic lead monoxide used in (a) is 0.1 parts to about 10.0 parts of water for each part of orthorhombic lead monoxide.

7. The process of claim 1 wherein the particulate orthorhombic lead monoxide of (a) is converted to particulate tetragonal lead monoxide by heating in distilled water at a temperature of about 50° C. to about 200° C.

8. The process of claim 1 wherein the separated particulate tetragonal lead monoxide is heated at a temperature of about 350° C. to about 500° C. in an inert atmosphere for at least 30 minutes.

9. The process of claim 1 wherein the separated particulate tetragonal lead monoxide is heated at a temperature of about 350° C. to about 500° C. in a nitrogen atmosphere for a period sufficient to remove impurities.

10. A process for preparing an electroradiographic element useful in xeroradiography comprising the steps of:
   (a) heating particulate orthorhombic lead monoxide in distilled water free of silicate ions at a temperature of 80° C. to 125° C. for at least 15 minutes to form particulate tetragonal lead monoxide solid,
   (b) separating the resulting particulate tetragonal lead monoxide,
   (c) heating the said separated tetragonal lead monoxide at a temperature of about 350° C. to about 500° C. in a nitrogen atmosphere for at least 30 minutes,
   (d) mixing the particulate tetragonal lead monoxide with a styrene-butadiene copolymeric binder, and
   (e) coating the resultant mixture on a conducting support.

References Cited

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