May 12, 1970 B. ROSENBERG 3,511,651

PERSISTENT INTERNAL POLARIZATION IMAGING SYSTEM WITH ELECTROPHORETIC DEVELOPMENT

Filed Aug. 22, 1966

FIG I

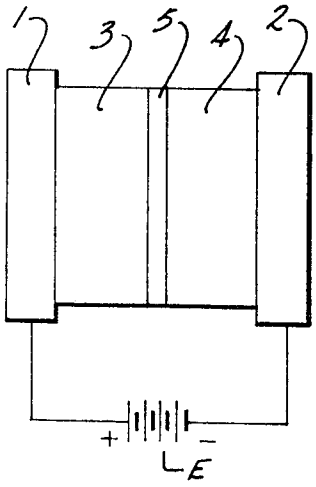


FIG IIA

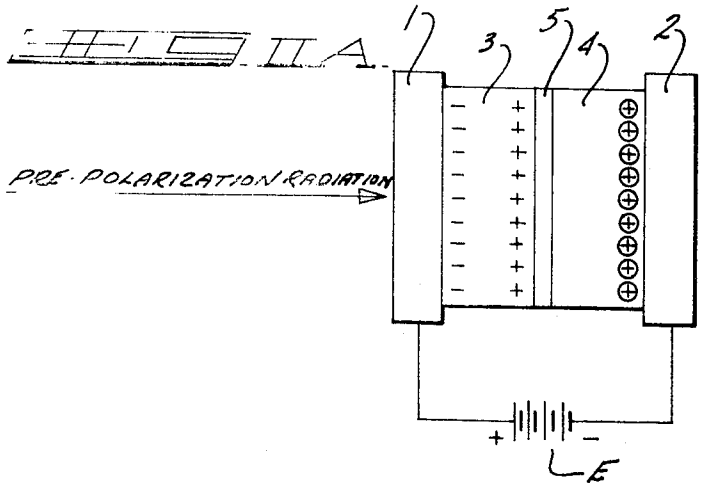
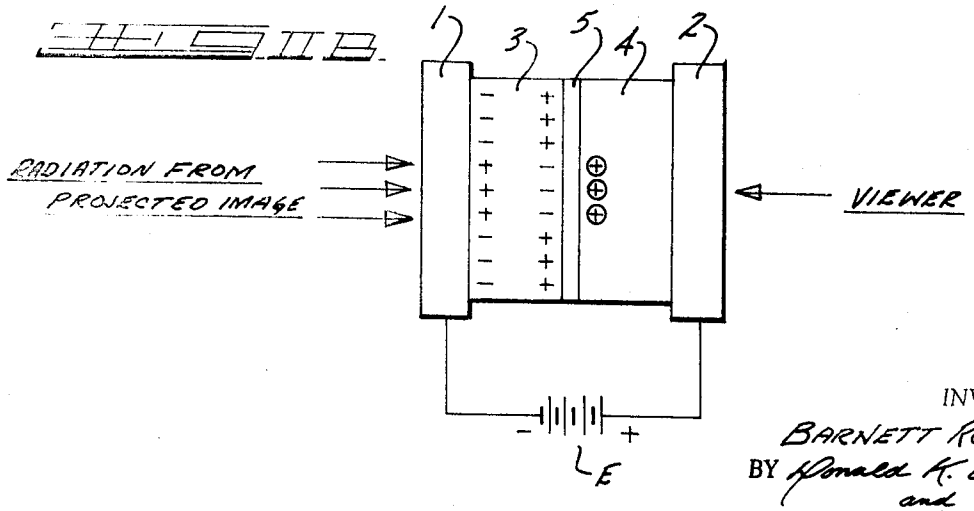


FIG IIB



INVENTOR.
BARNETT ROSENBERG
BY Ronald K. Spedding
and
W. A. Schaich
ATTORNEYS

United States Patent Office 3,511,651
Patented May 12, 1970

3,511,651

PERSISTENT INTERNAL POLARIZATION IMAGING SYSTEM WITH ELECTROPHORETIC DEVELOPMENT

Barnett Rosenberg, Lansing, Mich., assignor to Owens-Illinois, Inc., a corporation of Ohio

Filed Aug. 22, 1966, Ser. No. 574,212
Int. Cl. G03g 13/22; B01k 5/00; B01d 13/02
U.S. Cl. 96—1.5 5 Claims

ABSTRACT OF THE DISCLOSURE

A five layer system is employed to produce visible images. The system is composed of a conductive transparent electrode, a photoconductive layer, an opaque layer, a layer of liquid toner, and a second electrode. The system forms images on the opaque layer by electrophoretic deposition of toner particles in image configuration. The system may be erased and reused.

This invention relates to a novel method and apparatus for practicing electrophotography. More particularly, this invention relates to a method and apparatus utilizing photoconductive insulating materials and the principles of persistent internal polarization for reproducing, storing, and/or viewing an image.

Persistent internal polarization (abbreviated herein as PIP) involves the separation of positive and negative charges in a photoconductive insulating material by simultaneous irradiation and the application of an electric field. The charges are subsequently trapped and remain fixed or "frozen" in the photoconductor for a finite time to form an internal polarization field. This process and the theory thereof are well known in the art. See, for example, Electrophotography by R. M. Schaffert, The Focal Press, London and New York (1965), pages 59–77, and Persistent Internal Polarization by Kallmann and Rosenberg, The Physical Review, vol. 97, No. 5 (Mar. 15, 1955), pages 1596–1610, both of which are incorporated herein by reference.

In accordance with this invention there is provided a novel image panel system whereby an optical image is projected on a surface for a short period of time so as to impress the image information. The information is then stored for a given period of time during which it is continuously visible in any suitable light condition including high ambient light intensity.

Additional advantages of this invention include the capability of quick erasure, rapid preparation of a new image, and reuseability for an indefinite number of images.

For a further understanding of this invention, including additional advantages thereof, reference is made to the drawing and the figures thereon.

In FIG. 1, there is schematically shown a novel image panel comprising a photoconductor cell 3 and a confined chamber 4 containing a liquid electrophoretic developer which comprises charged particles dispersed in a liquid. An opaque layer 5 is interposed between the cell 3 and chamber 4 which may conveniently form one wall of the chamber 4. The opaque layer 5 may also serve as a support base for the cell 3.

The photoconductor cell 3, opaque layer 5, and chamber 4 are suitably sandwiched between two transparent electrodes 1 and 2 connected to a D.C. (direct current) energizing source E. By way of illustration in FIG. I, electrode 1 has been designated the positive electrode and electrode 2 negative.

FIGS. IIA and IIB schematically illustrate the operation of this invention utilizing the embodiment of FIG. I.

As shown in FIG. IIA, an electric field is established

across the photoconductive PIP cell or layer 3 by connecting electrode 1 to the positive terminal of D.C. source E and electrode 2 to the negative terminal. Simultaneously, the PIP layer 3 is irradiated with a prepolarizing radiation through conductive transparent electrode 1.

The simultaneous application of the electrode field and flooding with the prepolarization radiation causes the photoconductive material layer 3 to develop PIP; that is, an internal persistent polarization field is established with negative charges being internally trapped within the photoconductive material in the direction of the positive electrode 1 and positive charges being internally trapped in the direction of the negative electrode 2. By the way of illustration the segregation of the charges is schematically exaggerated in FIGS. IIA and IIB.

Simultaneously the charged toner particles supended in the carrier fluid within chamber 4 are attracted in the direction of the electrode of opposite polarity. As shown in FIG. IIA, the toner particles are positively charged and are thus attracted in the direction of negative electrode 2.

In FIG. IIB, the electric field across the PIP photoconductive layer 3 is reversed (e.g. conveniently by means of a reversing switch which is not shown) and the layer simultaneously irradiated with radiation projected from the image through conductive transparent electrode 1.

As illustrated in FIG. IIB, the internal polarization field within the PIP layer is reversed in that portion exposed to the image radiation such that positive charges are established within the PIP layer in the direction of negative electrode 1 and negative charges in the direction of positive electrode 2, the charges corresponding to the projected image. That portion of the internal polarization field which is not exposed to the image radiation is not reversed but remains the same as in FIG. IIA.

Simultaneously in FIG. IIB, the charged toner particles in chamber 4 are repelled by positive electrode 2 and a suitable portion thereof are attracted in the direction of the opaque insulating layer 5 by the negative charges within the PIP layer adjacent to the opposite side of the opaque layer 5. The charged toner particles attracted toward the opaque insualting layer 5 form a true picture of the image which may be stored and/or viewed through transparent electrode 2.

The length of time of the persistence of the image is determined by the persistence of the polarization. Depending upon the PIP material, such polarization may typically persist for hours, days, or even years in some instances.

For rapid erasure of the image picture, the PIP layer is irradiated with radiation of any appropriate wave length preferably while under the influence of an electric field. Such erasure of the preceding image information may conveniently serve as the pre-polarization of the PIP layer for the projection of subsequent image information.

Although not illustrated in FIG. IIB, it is contemplated that a camera or other suitable means may be used to permanently record the image picture before the erasure thereof.

Likewise, it is contemplated using a filter, shutter arrangement, or like means in conjunction with transparent electrode 1 to control the amount of radiation and also to prevent undesired radiation from penetrating to the PIP cell 3 and affecting the charge distribution thereof. The opaque layer 5 suitably serves to prevent radiation from penetrating to the PIP cell 3 from the opposite side thereof.

It is further contemplated using an electrode 2 which is transparent to light in the visible range for convenience in viewing the image picture formed by the charged tone particles in chamber 4. However, a filter or shutter arrangement is not required for electrode 2 since as noted hereinbefore the opaque layer 5 serves to prevent radi-

ation through electrode 2 from penetrating to PIP cell 3.

Typically, the opaque layer 5 is a thin film of plastic of any suitable color. It may be positioned onto the surface of the PIP layer. In the practice of this invention, it appears that the presence of this thin plastic film enhances the appearance of the visible image of toner particles.

Any suitable commercially available plastic film may be used. Best results, however, are obtained with plastics having high electrical resistance with an opacifier added which does not significantly change the electrical resistance of the plastic. In addition the plastic must be chemically resistant to the toner and carrier fluid in chamber 4 if the layer 5 forms one wall of the chamber. Although it may in some instances be desirable for the plastic film 5 to be opaque to all forms of radiation, it is generally necessary only that it be opaque with respect to light in the visible range.

The prepolarization radiation and the image radiation may be of any appropriate wave length so long as electrode 1 is transparent thereto. Typical radiation contemplated herein includes not by way of limitation radiation in the visible, X-ray and infra-red ranges. The prepolarization radiation and the image radiation may be of substantially the same or of different wave lengths.

In accordance with one embodiment of this invention, it is contemplated using an electrode 1 which is transparent to *both* the prepolarizing and image radiations. Such embodiment is especially suitable where the image radiation and the prepolarization radiation are of the same approximate wave length.

In another embodiment, it is contemplated using at least two separate, exchangeable electrodes 1 with one electrode being transparent to the prepolarizing radiation and the other electrode being transparent to the image radiation. Such embodiment is especially warranted where the prepolarizing light and image light are of substantially different wave lengths.

The latter embodiment is preferred where the PIP layer is irradiated with image radiation having a wave length outside the visible range. Thus, where the image radiation comprises X-rays of infra-red rays, it is contemplated that the prepolarization radiation may be of a different wave length, typically in the visible or ultraviolet range.

In a particular embodiment of this invention, the PIP layer is prepolarized with light in the visible range or of any other suitable wave length and then irradiated with X-rays so as to project an image positioned internally within a given body or structure. Such an embodiment is especially suitable in the field of internal medicine for projecting and immediately viewing a picture image of the internal organs of a human body. As noted hereinbefore, a camera or other means can be used to permanently record the image picture before the erasure thereof.

If this invention is used to X-ray the internal organs of a living animal, especially a human being, it is contemplated using a PIP material such as a Zn-Cd phosphor having the property of high X-ray absorption or stoppage. By selectively varying the thickness of such PIP material, substantially all of the X-rays may be absorbed in the PIP material such that the patient's X-ray exposure time and the quantity of X-rays required are significantly reduced.

The electrode materials of construction will vary with the light to be transmitted therethrough. Thus, if light in the visible or ultraviolet range is to be transmitted, a conductive glass electrode is used. For gamma rays, X-rays, and high energy beta rays, the electrode is constructed out of very thin metal. The conductive glass electrodes are well known in the art as well as the methods of preparing same. Reference is made, for example, to Belgian Pat. 610,765. Usually, the electrode comprises a layer of glass lightly coated with a semi-conductive compound such as tin oxide.

In a system which comprises pre-polarizing visible light and X-ray image radiation, it is contemplated constructing electrode 1 from a transparent plastic layer lightly coated with a transparent conductive film, e.g. tin oxide. After the pre-polarizing image light has been passed therethrough, an X-ray transparent shutter is positioned across the face of the electrode 1. The shutter is constructed out of a suitable material, e.g. a thin layer of metallic aluminum, which is not transparent to radiation outside the X-ray range. If desired, the shutter may actually be used as a second electrode 1 after appropriately disconnecting the coated plastic electrode from the source E.

The layer 3 is constructed out of any material capable of developing PIP when simultaneously exposed to irradiation and an electric field. The phenomenon of PIP can be achieved in any material which exhibits the following characteristics:

(1) The material must have a high resistivity in the dark (a low density of free charges) whereby it is a good insulator in the absence of penetrating radiations such as light or high energy particles.

(2) The material must be photoconductive; that is, it must have decreased resistivity when penetrated and excited with appropriate radiation.

(3) The material must have a high density of carrier traps for trapping and freezing the charges separated by the simultaneous irradiation and application of the electric field.

Typical organic and inorganic PIP materials or substances contemplated in the practice of this invention include not by way of limitation zinc sulfide, cadmium sulfide, zinc selenide, cadmium selenide, zinc oxide, cadmium oxide, selenium, tellurium, anthracene, chrysene, alkaline earth halides, and mixtures of same, especially mixtures of selenium with tellurium, zinc-cadmium selenides, and zinc-cadmium sulfides. It is also contemplated that a small effective amount of a suitable activator, e.g. gold, silver, or copper, may be incorporated with the photoconducting PIP substance.

The commonly used powdered PIP materials are typically dispersed or mixed with a suitable resin binder such as a cellulose acetate, ether, or ester, silicones, vinyl resins, and/or epoxy resins.

The liquid electrophoretic developer in chamber 4 comprises a suspension of very fine solid particles dispersed in a suitable dielectric liquid such that the particles uniformly acquire a negative or positive charge.

Although it is not intended that this invention be limited or bound by any particular theory, it is believed the dispersed particles acquire a negative or positive charge because of the generation of an interfacial potential difference (between the particles and the liquid) due to one or more of the following mechanisms:

(1) Contact potential
(2) Adsorption potential
(3) Lyoelectric potential

When the solid particles are dispersed in a non-polar organic liquid, it is believed that the mechanism is contact potential although one or more other mechanisms could also be involved. When any two phases are in contact (e.g. liquid-solid), it is believed that the phase with the higher dielectric constant tends to be positively charged.

If an EMF (electromotive force) is applied to a dispersion of charged solid particles in a liquid medium, the charged particles will migrate in the electric field in the direction of that pole or electrode having the opposite charge. This is called an electrophoretic movement of the particles (electrophoresis).

In accordance with the practice of this invention, it is contemplated that the liquid electrophoretic developer (liquid-toner combination) should have certain properties and characteristics:

(1) The liquid and particles should be compatible with the insulating opaque film or layer **5** if such film forms one wall of the chamber **4**.

(2) The liquid may have any suitable dielectric constant but should have a relatively high electrical resistivity and relatively low viscosity.

(3) The solid toner particles should be capable of being uniformly charged with one sign and maintaining the charge indefinitely.

(4) The particles may be of any suitable size and density. However, for good resolution the toner particles should be of submicron size to make a colloid suspension, or alternatively, the particles should be of a large particle size with a density equal to that of the liquid. The particles can be of a large size with a different density from that of the liquid such that the particles either float or settle; however, in such case it is contemplated that the chamber **4** will have to be tilted or turned at an appropriate angle so as to cascade the toner particles over the surface of the film **5** or over the inner surface of the chamber **4** wall adjacent to the film **5**.

(5) The amount of toner in the liquid should be suitably calibrated such that all of the toner is used for an average exposure except where the chamber **4** is to be tilted as noted in (4) hereinbefore.

Typical toner particles contemplated in the practice of this invention include not by way of limitation inorganic and organic pigments such as titanium oxide, barium sulfate, lead chromate, manganese dioxide, calcium silicates, Cadmium Red, Vermilion Red, zinc oxide, iron oxides, chromium oxide, Prussian Blue, Hansa Yellows, Phthalocyanine Blues, Phthalocyanine Greens, Indanthrone Blue, Ultramarine Deep, charcoal, precipitated diazo pigments, polymers such as low molecular weight polyethylenes and vinyl chloride, cupric hydroxide, gilsonite, Polymethyl Methacrylate, and Special Maroon.

Typical carrier fluids include not by way of limitation aliphatic and aromatic liquid hydrocarbons, chlorinated and fluorinated liquid hydrocarbons, silicones, and liquid organic solvents having a relatively high electrical resistivity. Suitably the liquid carrier has a dielectric constant of less than 10, e.g. 2 to 4, although liquids having a higher dielectric constant are contemplated. Preferred liquid carriers include mineral spirits or petroleum naphtha, gasoline, kerosene, turpentine, benzene, carbon tetrachloride, cyclohexane, and Freons such as CCl_3F and $CCl_2F \cdot CClF_3$.

In addition various control agents may be added to the toner-carrier fluid suspension as noted on page 358 of Xerography and Related Processes, The Focal Press, London and New York, (1965).

It has been discovered that best results are obtained with toner-carrier fluids wherein the charge (positive or negative) on the toner is at least 80%, preferably 90 to 100%.

Suitable combinations of toner-carrier fluid suspensions which may be used in the practice of this invention include not by way of limitation vinyl chloride with an average molecular weight of about 16,000 suspended in naphtha or trichlorotrifluoroethane, charcoal suspended in toluene, polymethyl methacrylate suspended in naphtha, and Special Maroon suspended in CCl_4.

In the practice of this invention, the picture of the image may comprise any two color combinations depending upon the selected toner color and the color of the opaque layer. Generally the color combination will include black toner on a white layer, or vice versa.

The following example hereinafter represents the best mode contemplated by the inventor in the practice of this invention.

EXAMPLE

The embodiment of FIGS. I, IIA, and IIB was used.

A PIP plate **3** was prepared by mixing an Ag-Cl-Ni activated zinc-cadmium sulfide phosphor with an alkyd binder in a suitable solvent (xylene-toluene) and layering the suspension (with a doctor knife) on the conductive side of a conductive glass electrode plate **1** to form a wet film of about 0.1 millimeter in thickness.

The conductive glass electrode **1** was initially formed by depositing a conductive layer of tin oxide on one side of a 7 inch by 8 inch glass plate. Such glass is commercially available being sold as Nesa glass by the Pittsburgh Plate Glass Co. of Pittsburgh, Pa.

After the PIP material was layed with the doctor knife on the tin oxide surface, it was dried to a hard film. A very thin layer of opaque black plastic was then put on top of the PIP film using Rust-Oleum Quick Drying Black No. 634 and a thin layer of opaque white plastic was put on top of the black plastic using Sears Alkyd White No. 6500–0, the two plastic films (black and white) together forming the opaque layer **5**.

A confined chamber **4** was then added to the assembly with opaque layer **5** forming one wall of the chamber. The other side of the chamber **4** was provided by the conductive side of a tin oxide coated glass electrode **2**.

The liquid toner combination used in the chamber **4** consisted of a carbon black toner and kerosene diluted with low viscosity silicone oil.

The two electrodes **1** and **2** were then connected to a source of 510 volts (direct currernt) electrode **1** serving as the positive pole and electrode **2** as the negative pole. Simultaneously, the PIP layer **3** was flooded with light transmitted through electrode **1**.

The polarity of the electrodes were then reversed and the PIP layer exposed to the image light. The image was clearly viewable in normal room light through transparent electrode **2**.

The image was erased by reversing the polarity and flooding the PIP layer with light transmitted through electrode **1**.

Although this invention has been described and illustrated in terms of using both a prepolarizing light and an image light, it is possible to eliminate the former and use the same light source simultaneously as both the prepolarizing and imaging light.

The voltage requirements for the system will vary with the materials of construction and the thickness. Typically, any magnitude of applied voltage will suffice so long as the voltage drop across the system generates adequate persistent internal polarization in the PIP plate **3** and also attracts the charged toner particles (in chamber **4**) at a reasonable rate of electrophoretic movement. In general, the voltage drop across the entire panel can be enhanced by making the PIP plate **3** thicker than the liquid layer in chamber **4**, and/or by making the dielectric constant of the liquid much higher than the effective dielectric constant of the photoconductive PIP material.

Although this invention has been described with reference to certain specific embodiments it will be apparent to others skilled in the art that various modifications of this invention can be made or followed in light of the foregoing specification without departing from the scope of the following claims.

I claim:

1. An electrophotographic five layered image panel system comprising in order: a first conductive radiation transparent electrode, a photoconductive layer capable of developing persistent internal polarization when simultaneously exposed to activating radiation and an electric field, a substantially opaque insulating layer, a layer comprising a suspension of fine solid toner particles dispersed in a dielectric liquid, said particles being capable of acquiring a positive or negative charge under the influence of an applied electric field, and a second conductive transparent electrode.

2. An electrophotographic process for reproducing and viewing an image which comprises establishing an electric field across the system of claim **1** while simultaneously flooding said photoconductive layer uniformly with a

pre-polarizing radiation, reversing the polarity of the electric field while irradiating said photoconductive layer with polarizing image radiation, whereby said toner particles are charged and electrophoretically moved toward the substantially opaque layer so as to form a picture of the image.

3. The process of claim 2 wherein said process is continuous and the photoconductive layer is uniformly flooded with light so as to simultaneously erase the preceding pictures and prepolarize the layer or projection of radiation from a subsequent image.

4. The process of claim 2 wherein the photoconductive layer comprises a Zn-Cd phosphor.

5. The process of claim 4 wherein the pre-polarizing radiation is in the visible range and the image radiation is in the X-ray range.

References Cited

UNITED STATES PATENTS

2,898,279	8/1959	Metcalfe et al.	204—181
3,257,304	6/1966	Johnson	204—181
3,268,331	8/1966	Harper	96—1
3,384,565	5/1968	Tulagin et al.	204—181

GEORGE F. LESMES, Primary Examiner

J. C. COOPER, Assistant Examiner

U.S. Cl. X.R.

96—1, 1.3; 117—37; 204—180, 181