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ELECTROPHORETIC IMAGING APPARATUS INCLUDING MEANS TO COAT AND ELECTRIFY THE IMAGING ELECTRODE

Original Filed Jan. 2, 1969

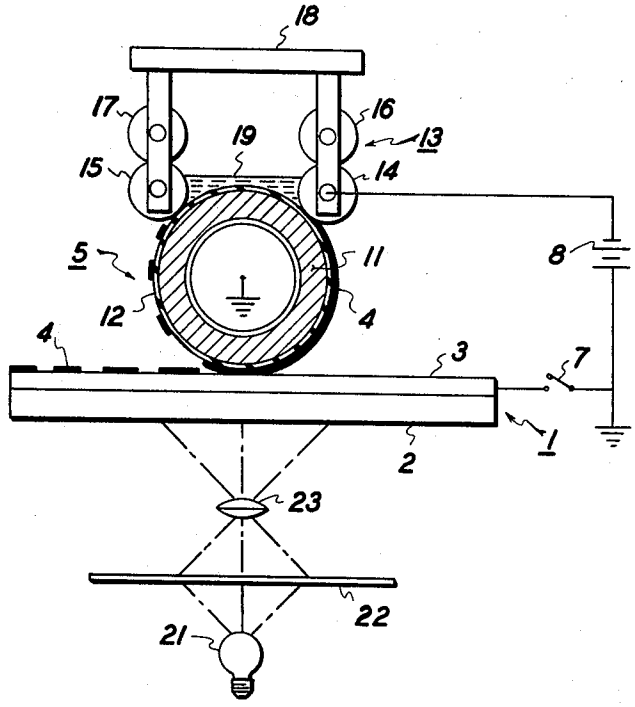


FIG. 1

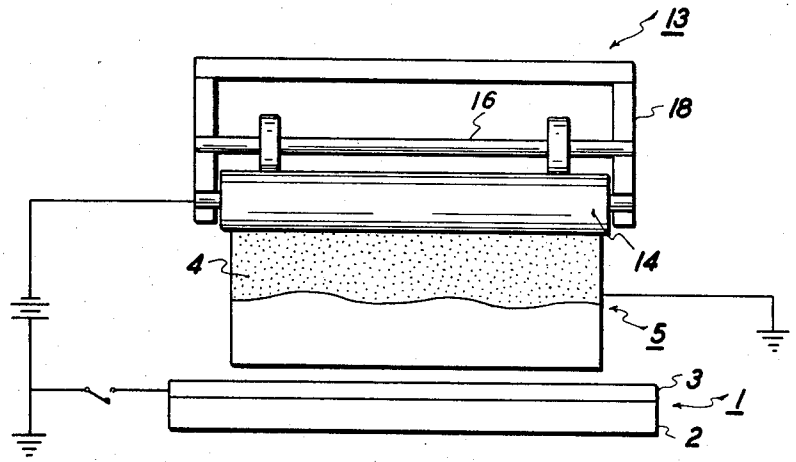


FIG. 2

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ELECTROPHORETIC IMAGING APPARATUS INCLUDING MEANS TO COAT AND ELECTRIFY THE IMAGING ELECTRODE

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Int. Cl. B01k 5/00; G03g 15/00

U.S. Cl. 204—300 5 Claims

ABSTRACT OF THE DISCLOSURE

It has been determined that by applying DC voltage to a coating means in the electrophoretic imaging system that it is possible to establish the necessary field for imaging as well as eliminating the buildup of unwanted residual charge on the surface of the blocking electrode. In addition, the application of the potential in this manner has been found to decrease mottling of the imaging suspension on the surface of the blocking electrode.

This is a division of application Ser. No. 789,088, filed in the United States, Jan. 2, 1969 now Pat. No. 3,586,615.

BACKGROUND OF THE INVENTION

This invention relates to an imaging system and more specifically to an improved photoelectrophoretic imaging system.

In photoelectrophoretic imaging colored photosensitive particles are suspended in an insulating carrier liquid. This suspension is placed between at least two electrodes one of which is generally conductive and referred to as the injecting electrode and the other which is generally insulating and called the blocking electrode. The suspension is subjected to a potential difference and exposed to an image to be reproduced. Ordinarily, in carrying out the process, the imaging suspension is placed on a transparent electrically conductive plate in the form of a thin film and exposure is made through the transparent plate while a second generally cylindrically shaped biased electrode is rolled across the suspension. The particles are believed to bear an initial charge when suspended in the liquid carrier which causes them to be attracted to the transparent base electrode and upon exposure, to change polarity by exchanging charge with the base electrode so that the exposed particles migrate to the second or roller electrode thereby forming images on both of the electrodes by particle subtraction each image being complementary to the other. The process may be used to produce both polychromatic and monochromatic images. In the latter instance a single color photoresponsive particle may be used in the suspension or a number of differently colored photoresponsive particles may be used all of which respond to the same wavelength of light exposure. An extensive and detailed description of the photoelectrophoretic imaging techniques as described may be found in U.S. Pat. Nos. 3,383,993, 3,384,488, 3,384,565 and 3,384,566.

In the case of the polychromatic imaging process the imaging suspension will contain a plurality of at least two differently colored finely divided particles in a carrier liquid each of said particles comprising an electrically photosensitive pigment whose principal light absorption band substantially coincides with its principal photosensitive response. Thus, the pigment represents both the primary electrically photosensitive ingredient and the primary colorant for the specific particle in suspension. The particles utilized in the polychromatic system should

preferably have intense pure colors and be highly photosensitive. It is preferred that the particles migrate with minimum exposure to activating electromagnetic radiation and that particles of each color migrate to an equal extent upon exposure to light of the complementary color. When the suspension is exposed to a multicolored image, particles will migrate to one electrode in proportion to the intensity of the light which they absorb. This migration should take place with a minimum of electrical interaction between the particles of different colors. Thus, it is preferred and desired that particles selectively remain on one of the electrodes in image configuration with unwanted particles migrating to the other electrode in the system. For example, when a mixture comprising cyan, magenta and yellow particles is exposed to an image by yellow light, the cyan and magenta particles should migrate leaving behind an image made up of yellow particles. Similarly, when exposed to a multicolored image, different colored particles absorb light of their complementary color in appropriate image areas and migrate thereby leaving a full colored image corresponding to the original.

This system, using a conductive injecting electrode, a substantially insulating blocking electrode and photosensitive particles dispersed in an insulating carrier liquid between the electrodes, has been found to be capable of producing excellent images. Most of the polymeric materials utilized as the blocking layer on the respective electrode vary in resistivity from 10^8 to 10^{15} ohms cm. or greater. Those materials in the lower resistivity range, i.e. 10^8 to 10^{12} ohms cm., such as baryta paper, although capable of producing excellent image are humidity sensitive (in that their resistivities vary depending upon the relative humidity they are subjected to). As a result, these materials are cleaned between imaging steps. Blocking layers of materials having higher resistivities with less humidity sensitivity are therefore generally preferred. However, with those materials of higher resistivities of from about 10^{12} ohms cm. or greater, e.g. Myler and Telflon, the image quality progressively decreases particularly where several images are made using the same electrode in rapid succession. Therefore, while a great many substantially insulating materials have been found operative when used as the blocking layer of the blocking electrode, due to the apparent charge retention on the specific material during the image formation step, the quality of the images formed on these highly insulating materials when recycled is substantially reduced. Thus, the overall image quality is reduced as a result of the accumulation of the undesirable charges on the blocking electrode. For example, conventionally used blocking electrode polymers such as Mylar and Tedlar, having resistivities of about 10^{17} and 10^{13} ohms cm. respectively, illustrate the charge retention problem.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide an electrophoretic imaging system which will overcome the above-noted disadvantages.

It is another object of this invention to provide a novel photoelectrophoretic imaging system.

It is a further object of this invention to provide a photoelectrophoretic imaging system capable of producing a plurality of images in rapid succession of uniform high quality.

Yet, still a further object of this invention to provide an electrophoretic imaging system capable of utilizing a wide range of blocking electrode materials.

The foregoing objects and others are accomplished in accordance with the present invention generally speaking by providing an imaging apparatus consisting of an electrode system utilized in conjunction with an imaging

suspension comprising a plurality of light absorbing photoelectrophoretic imaging particles in an insulating carrier liquid. The imaging apparatus utilizes at least one electrode in roller configuration, generally the imaging or blocking electrode, and at least one additional electrode, the injecting electrode. One of these electrodes is at least partially transparent to activating electromagnetic radiation. Rotatably mounted in close proximity to the roller electrode in the system is a coating means which continuously applies the imaging suspension to the surface of the roller electrode. The imaging suspension is exposed selectively to an electromagnetic radiation source through the transparent electrode in the system while simultaneously developing an electrical field across the imaging suspension by applying a DC voltage to the coating means. The coating means in the form of a rod is in surface contact with the blocking layer of the blocking roller electrode. The coating rod coats the surface of the roller electrode with a uniform film of the imaging suspension while at the same time distributing charge to the surface of the blocking electrode. Imaging is then completed at the surface of the injecting electrode as a result of the particle migration within the system whereby complementary color images are formed on the surfaces of each of the electrodes. The roller or imaging electrode is then recoated by the above mentioned coating device so as to replenish the imaging suspension while simultaneously eliminating or neutralizing buildup of unwanted charge on the surface of the insulating blocking electrode. In effect, the charging of the coating rod both contact charges the blocking electrode so as to establish the necessary field between the blocking and injecting electrode during imaging and, in addition, as the roller recycles, eliminates the buildup of residual charge on the surface of the blocking electrode. In an alternate embodiment of the present invention charge buildup on the blocking electrode may be eliminated in a sequential manner in a system where the field is established between the blocking and injecting electrodes by applying the field charge directly to the blocking electrode, by first cutting off the potential to the core of the blocking electrode then applying charge to the coating rod to neutralize the residual charge on the surface or blocking layer of the blocking electrode, then cutting off the potential to the coating rod and reestablishing the field between the blocking electrode and the injecting electrode.

It has been determined in the course of the present invention that by applying a DC voltage directly to the coating device in the above described imaging apparatus it is possible to eliminate the buildup of residual charge on the blocking electrode which effects the quality of the image attained when rapid imaging is desired. In addition to neutralizing the residual charge effect on the surface of the blocking electrode, it is possible to simultaneously establish the necessary field across the imaging suspension for purposes of imaging. In addition to eliminating charge buildup on the surface of the blocking layer the charging of the coating rod also provides a means of eliminating mottled or a spotted appearance sometimes obtained during the coating of the imaging suspension on the surface of the blocking electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention illustrated in the accompanying drawings wherein:

FIG. 1 represents a side sectional view of a simple exemplary system for carrying out the steps of the present invention; and

FIG. 2 shows a frontal view of the imaging apparatus of the present invention.

DETAILED DESCRIPTION OF DRAWINGS

Referring now to FIG. 1 there is seen a transparent electrode generally designated **1** which, in this exemplary

instance, is made up of a layer of optically transparent glass **2** overcoated with a thin transparent layer **3** of tin oxide. The latter configuration is commercially available under the trade name NESA glass. This electrode will hereinafter be referred to as the injecting electrode. In close proximity to the injecting electrode **1** is a rotary electrode **5** having a conductive central core **11** which is covered with a layer of blocking electrode insulating material **12**. The latter electrode is referred to as the blocking or imaging electrode. A detailed description of the improved results and the types of material which may be used as the blocking layer may be found in detail in U.S. Pat. 3,383,993. A thin layer **4** of the imaging suspension of the present invention, which consists of finely divided photosensitive particles dispersed in an insulating carrier liquid, is coated on the surface of the blocking electrode by coating means generally designated **13** which meters the application of the imaging suspension so that it is applied to a uniform thickness. The coating means comprises coating rods **14** and **15** with pressure rollers **16** and **17**. The coating and pressure rods are suspended by support **18**. The ink reservoir **19** inherently develops on the upper surface of the blocking electrode **5**. During this initial part of the description of the invention the term "photosensitive" may be thought of as any particle which once attracted to the injecting electrode will migrate away from it under the influence of an applied electric field when it is exposed to actinic electromagnetic radiation. The imaging suspension may also contain a sensitizer and/or binder for the pigment particles the latter being at least partially soluble in the suspending or carrier liquid. As the blocking or imaging roller **5** is passed across the surface of the injecting electrode **1**, switch **7** is closed which as the result of the presence of potential source **8** establishes an electric field across the imaging suspension **4**. The central core of the blocking electrode is connected to ground. The pigment suspension is exposed by way of a projection mechanism made of a light source **21**, transparency **22** and lens system **23**. For purposes of this illustration a positive color transparency is utilized during the process. As the imaging roller passes across the surface of the NESA electrode, ink from the reservoir **19** is applied in a uniform manner to the surface of the imaging electrode. Simultaneously, as a result of the application of a DC potential to the coating rod **14** the necessary electrical field is established across the apparatus so as to allow for imaging at the surface of the injecting electrode and to eliminate the buildup of residual charge on the surface of the insulating blocking electrode. Exposure causes the exposed particles originally attracted to the injecting electrode **1** to migrate through the liquid carrier and adhere to the surface of the imaging electrode **5** leaving behind an image on the surface of the injecting electrode which is a duplicate of the original transparency **22**.

Referring now to FIG. 2 there is seen in a frontal view the imaging apparatus of FIG. 1. The coating means **13** comprising the support **18**, coating rod **14** and pressure roller **17** applies the imaging suspension **4** to the surface of the blocking electrode **5**. The injecting electrode **1** comprising the conductives substrate **2** and tin oxide coating **3** is situated beneath the blocking electrode **5**. Electrical connection is made between the coating rod **14** and the NESA or injecting electrode **1**.

It is preferred that the injecting electrode be composed of an optically transparent material such as glass overcoated with a conductive material such as tin oxide, copper, copper iodide, gold or the like in order to obtain optimum results; however, other suitable materials including many semiconductvie materials such as raw cellophane, which are ordinarily not thought of as conductors but which are still capable of accepting injected charge carriers of the proper polarity under the influence of the applied field may be used within the course of the present invention. The use of more conductive materials

allows for cleaner charge separation and prevents possible charge buildup on the electrode which tends to diminish the interior electrode field. The blocking electrode on the other hand is selected so as to prevent or greatly retard the injection of electrons into the photosensitive pigment particles when the particles reach the surface of this electrode. The blocking electrode base or core generally will consist of a material which is fairly high in electrical conductivity. Typical conductive materials utilized are conductive rubber, and metal foils of steel, aluminum, copper and brass. If, however, a low conductivity material is used a separate electrical connection may be made to the back of the blocking layer of the electrode. Although the blocking electrode material need not necessarily be used in the system the use of such a layer is preferred because of the markedly improved results which it is capable of producing. Generally speaking, the blocking electrode material or layer consists of a material having a resistivity of about 10^8 ohms cm. or greater with the preferred materials having a resistivity in the range of from about 10^{12} to 10^{17} ohms cm. Exemplary of the preferred blocking layer materials used are baryta paper, which consists of paper coated with barium sulfate suspended in a gelatin solution, Tedlar, a polyvinylfluoride, and polyurethane. Any other suitable material having the desired resistivity properties may be utilized. Typical materials include cellulose acetate coated papers, polystyrene, polytetrafluoroethylene, and polyethyleneterephthalate. The blocking electrode layer when utilized may be a separate replaceable layer which is easily fixed in some manner to the blocking electrode such as by mechanical fasteners or any other similar device which is capable of simply holding the layer on the electrode. In the alternative, the layer may be an integral part of the electrode itself being adhesively bonded, laminated, spray coated or otherwise applied to the surface of the electrode.

Where the above imaging steps are repeated with cleaning of the blocking electrode but without discharging the blocking electrode before repetition of the imaging step it has been found that there is a steady decrease in the image quality of the successive copies. It has been found that this general gradual decrease in image quality is due to the accumulation of undesired electrostatic charge on the surface of the blocking electrode. Therefore, in accordance with the present invention, the voltage supplied to the system is applied by way of the coating means used which itself makes rolling contact with the blocking electrode layer or material on the surface of the roller electrode core. Generally, a potential of about 3,000 to 7,000 volts has been applied to the coating means so as to establish the necessary field across the imaging suspension during imaging. Preferred operating potentials generally fall within the range of from about 4500 to about 5500 volts. The coating device utilized may comprise at least more than one roller to disperse this suspension on the imaging or blocking electrode. However, the number of rollers utilized in conjunction with the imaging apparatus will be determined by the particular application of the imaging system with respect to the degree to which the suspension is to be coated on the imaging electrode. Representative coating thicknesses range from about 1 to about 6 mils with a coating thickness of about 4 mils generally being preferred. Any suitable coating rod may be used such that it will transmit upon contact with the blocking electrode surface a potential which both neutralizes charge buildup on the blocking electrode layer and establishes the necessary electric field across the imaging suspension at the area of contact between the blocking and injecting electrodes. Typical coating rods which may be used include a conductive glass coating rod, a conductive rubber coating rod, and a wire wound metal coating rod otherwise known as a Meyer rod.

Although various electrode spacings may be employed, spacings of less than 1 mil and extending down even to the point where the electrodes are pressed together constitutes a particular preferred form of the invention in that this configuration produces better resolution and, in a polychrome imaging system, superior color separation results. This improvement is believed to take place because of the high field strength across the suspension during imaging.

In the polychromatic system, the particles are selected so that those of different colors respond to different wavelengths of light in the visible spectrum corresponding to their principal absorption band and further so that their spectral response curves do not have substantial overlap thus allowing for color separation and subtractive multicolor image formation. Several different particles are employed namely a cyan colored particle sensitive mainly to red light, a magenta colored particle sensitive mainly to green light and a yellow colored particle sensitive mainly to blue light. Although this is the simplest combination, additional particles having different absorption maximum may be added to improve color synthesis. When mixed together in the carrier liquid, these particles produce a generally black liquid and when one or more of the particles are caused to migrate from the suspension the remaining particles produce a color equivalent to the color of the impinging light source. Thus, for example, red light exposure causes the cyan colored pigment to migrate thereby leaving behind the magenta and yellow pigment which combine to produce red in the final image. In the same manner, blue and green color is produced by removal of yellow and magenta pigment respectively and of course when white light impinges upon the mix all pigments migrate leaving behind the color of the white or the transparent substrate. No exposure leaves behind all pigments which combine to produce a black image. It should be recognized that this is an ideal technique of subtractive color imaging in that the particles are not only each composed of but one component but in addition they perform a dual function in that they act both as the final image colorant and as the photosensitive medium of the system. Accordingly, the system represents virtually the ultimate in eliminating the complexity of prior art methods of subtractive color imaging. In a monochromatic system, particles of a single color or particles of more than one color but responding to substantially the same wavelength of light are dispersed in the carrier liquid and exposed to a black and white image. A single colored image results corresponding to black and white photography.

The roller blocking electrode configuration shown in the drawing is of course merely representative, and any other similar configuration may be used. For example, the blocking electrode may be in the form of a movable or stationary flat plate or in the form of a continuous belt. It is also possible to provide a transparent blocking electrode with the imaging or exposure lamp being located inside the respective electrode.

Any suitable carrier liquid may be used in the course of the present invention. Materials found suitable include decane, dodecane and tetradecane, molten paraffin wax, molten beeswax and other molten thermoplastic materials. Sohio Odorless Solvent, a kerosene fraction commercially available from the Standard Oil Co. of Ohio and Isopar G, a long chain saturated aliphatic hydrocarbon commercially available from the Humble Oil Co. of New Jersey have been found suitable. Mixtures of the above defined compositions have also been found to satisfy the requirements of the present invention.

Any suitable differently colored photosensitive pigment particle having spectral responses such as disclosed in U.S. Pats. 3,384,488 and 3,384,566 may be used to form the imaging suspension of the present invention. The percentage of pigment in the insulating liquid carrier is not considered critical; however, for reference purposes it is noted that from about 2 to about 10 percent pigment

by weight has been found desirable to produce acceptable results. As previously stated once the particle image is formed it may be fixed to the respective electrodes such as by spraying a binder onto the surface, by laminating an overlay over the imaged surface or by including a binder in the liquid suspension medium. Generally, it will be found preferable to transfer the image from the electrode and fix it to a secondary surface so that the electrode may be reused. The transfer step may be carried out by an adhesive pick off technique, such as with adhesive tape, or preferably by electrostatic field transfer. Transfer may also be affected by photoelectrophoretic means.

To further define the specifics of the present invention the following examples are intended to illustrate but not limit the subject matter of the present invention. Parts and percentages are by weight unless otherwise indicated.

PREFERRED EMBODIMENTS

In the following examples four different imaging suspensions are employed utilizing the apparatus of the general type illustrated in FIG. 1. The injecting electrode is made up of NESA glass and the surface of the glass connected to ground. The blocking electrode consists of a hard conductive rubber core approximately 2 inches in diameter coated with a layer of Tedlar. A negative potential of about 3,000 volts is imposed on the coating rod during exposure. Exposure is made through a photographic transparency with a light intensity of about 1800 foot candles. The imaging suspension used in this examples consists of about 17 parts by weight of the pigment particles dispersed in about 100 parts mineral oil. A wire wound metal rod is used as the coating rod in Examples 1 and 2 and a conductive rubber roller is used in Examples 3 and 4. The imaging suspension is coated on the surface of the blocking electrode to a thickness of about 3 mils for Examples 1 and 2 and about 4 mils for Examples 3 and 4.

Example I

A tri-mix is prepared dispersing equal parts of a cyan pigment, Monolite Fast Blue, G.S., the alpha form of metal-free phthalocyanine, C.I. No. 74100, available from Arnold Hoffman Co.; a magenta pigment, Watchung Red B, a barium salt of 1-(4′-methyl-5′-chloro-2′-sulfonic acid) azobenzene-2-hydroxy-3-naphthoic acid, C.I. No. 15865, available from E. I. du Pont de Nemours & Co., and a yellow pigment, Algol Yellow, G.C., 1,2,5,6-di-(C,C′-diphenyl)thiazole anthraquinone, C.I. No. 67300, available from General Dyestuffs, in mineral oil. The tri-mix is coated and images as described above forming a full colored image conforming to the original transparency.

Example II

A tri-mix is prepared by dispersing equal parts of a cyan pigment, Diane Blue, 3,3′-methoxy-4,4′-diphenyl-bis-(1″-azo-2″-hydroxy-3″-naphthanilide), C.I. No. 21180, available from Harmon Colors, a magenta pigment, Calcium Lithol Red, a calcium lake of 1-(2′-azonaphthalene-1′-sulfonic acid)-2-napthol, C.I. No. 15630, available from Collway Colors; and a proprietary yellow pigment, N - 2″ - pyridyl-8,13-dioxodinaphtho-(2,1-6,2′,3′-d-furan-6-carboxyamide, discolsed in U.S. patent application No. 421,281, filed Dec. 28, 1964 now Pat. No. 3,447,922 and having a common assignee, in mineral oil. The tri-mix is imaged as described above forming a full colored image conforming to the color transparency.

Example III

Seven parts by weight of the metal-free phthalocyanine pigment disclosed in Example I is blended with 100 parts mineral oil. The resulting uni-mix is coated on a NESA electrode and imaged as described above. A single color cyan image on a background of white is formed.

Example IV

An imaging suspension comprising equal amounts of Bonadur Red B, 1-(4′-chloro-5′-ethyl-2′-sulfonic acid) azobenzene-2-hydroxy-3-naphthoic acid, available from American Cyanamide; Monolite Fast Blue G.S., and the proprietary yellow pigment disclosed in Example I in Sohio Solvent 3440 is prepared and imaged as described above. A full colored image conforming to the original color transparency is obtained.

Although the present examples were specific in terms of conditions and materials used, any of the above listed typical materials may be substituted when suitable in the above examples with similar results being obtained. In addition to the steps used to carry out the process of the present invention, other steps or modifications may be used, if desirable. Other materials may also be incorporated in the imaging suspension and other facets of the invention which will enhance, synergize or otherwise desirably effect the properties therein desired. For example, various sensitizers may be utilized in conjunction with the imaging suspension.

Anyone skilled in the art will have other modifications occur to them based on the teachings of the present invention. These modifications are intended to be encompassed within the scope of this invention.

What is claimed is:

1. A photoelectrophoretic imaging apparatus comprising in combination a rotatably mounted first electrode, conductive means to coat continuously and uniformly an imaging suspension on the surface of said first electrode, a second electrode adapted to contact said suspension opposite said first electrode and spaced up to about one mil therefrom, at least one of said electrodes being substantially transparent, and at least one of said electrodes having a blocking surface facing said imaging suspension, means for applying a potential to the conductive coating means thereby developing an electric field across said suspension between said electrodes and means to expose said suspension to an image with actinic electromagnetic radiation, whereby an image is produced.

2. The apparatus as disclosed in claim **1** wherein said coating means comprises at least one wire-wound metal rod.

3. The apparatus as discolsed in claim **1** wherein said coating means comprises at least one conductive glass rod.

4. The apparatus as disclosed in claim **1** wherein said coating means comprises at least one conductive rubber roller.

5. The apparatus as disclosed in claim **1** wherein said second electrode is rotatably mounted in close proximity to said first electrode, such that the surface of said second electrode is in area contact with the suspension on the surface of said first electrode, the axis of said second electrode being parallel to the axis of said first electrode, and further including means to rotate said first and second electrodes synchronously.

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