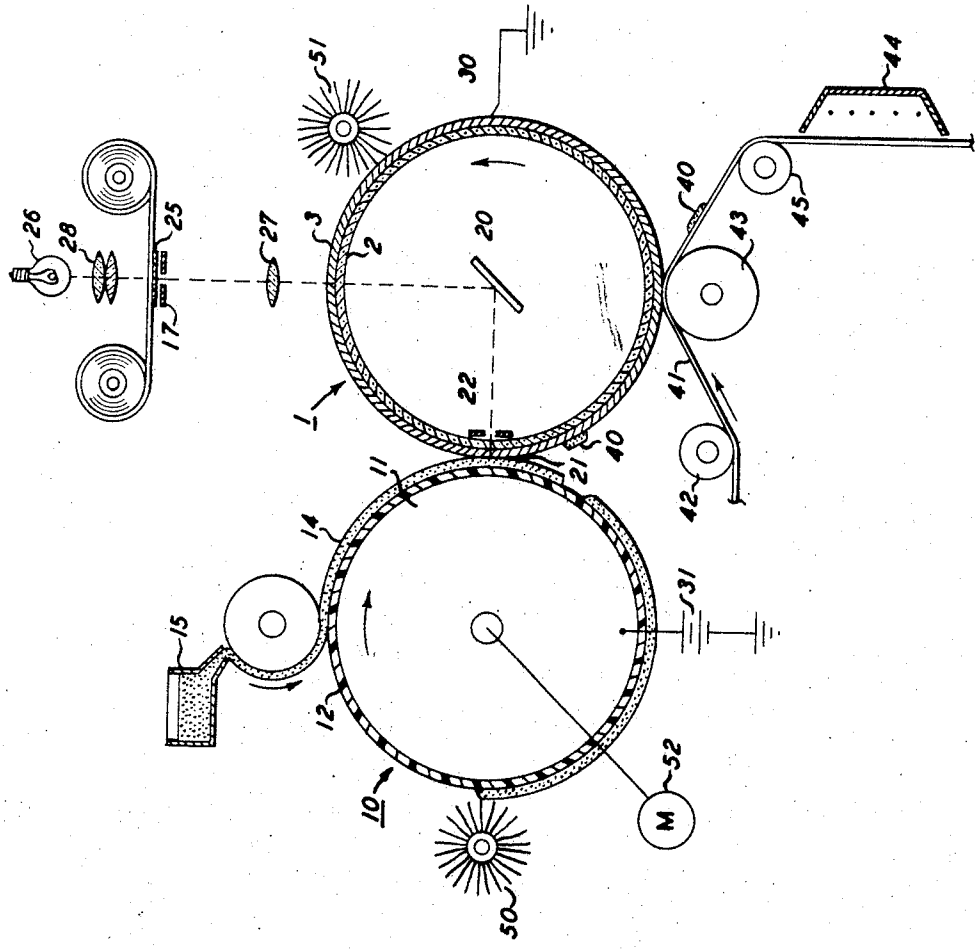
Feb. 11, 1969 V. S. MIHAJLOV 3,427,242

APPARATUS FOR CONTINUOUS PHOTOELECTROPHORETIC IMAGING

Filed April 18, 1966



INVENTOR.
VSEVOLOD S. MIHAJLOV
BY James J. Ralabate
ATTORNEY

United States Patent Office 3,427,242
Patented Feb. 11, 1969

3,427,242

APPARATUS FOR CONTINUOUS PHOTOELECTROPHORETIC IMAGING

Vsevolod S. Mihajlov, Rochester, N.Y., assignor to Xerox Corporation, Rochester, N.Y., a corporation of New York

Filed Apr. 18, 1966, Ser. No. 543,125
U.S. Cl. 204—300 11 Claims
Int. Cl. B01k 5/00

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

In photoelectrophoretic imaging colored particles are suspended in an insulating carrier liquid. This suspension is then placed between a pair of electrodes, 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 bottom of this plate while a second cylindrical shaped electrode is rolled over the top of the suspension. The particles are believed to bear an initial charge when suspended in the liquid which causes them to be attracted to the transparent base electrode and to change polarity by exchanging charge with the base electrode upon exposure so that exposed particles migrate across to the roller electrode to form an image on the base electrode by particle subtraction. The system may be used to produce monochromatic images by using a single color particle in the suspension or a number of differently colored patricles in the suspension which all respond to the same wavelengths of light exposure. In polychromatic systems, mixtures of two or more differently colored particles, each of which are sensitive only to light of specific, different and generally narrow wavelengths are used. Thus, for example, a full color image may be produced by using a mixture of cyan, magenta and yellow particles which respond to red, green, and blue light, respectively. An extensive and detailed description of the photoelectrophoretic imaging technique as described above is found in copending U.S. applications Ser. Nos. 384,737 now U.S. Patent 3,384,565; 384,681; now abandoned and 384,680 now abandoned, filed Jan. 23, 1964.

Although it has been found that good quality images can be produced, especially when a relatively insulating "blocking electrode" surface is used on the roller, the photoelectrophoretic imaging process is relatively slow, generally utilizing reciprocating movement as the imaging technique. A continuous imaging system based on particle migration techniques has been suggested in the prior art as described, for example, in U.S. Patent No. 2,940,847. However, this syestem has proven to be so light insensitive, producing such poor images, and is so complex and difficult to prepare that it has never been accepted commercially. This continuous prior art system employs complex particles including at least two, and frequently more, layers of various different materials including, for example. photoconductive cores with varying high resistivity light filtering overcoatings and sometimes includes glass cores, encapsulated dyes and similar complicating components, which were previously thought to be necessary to provide light filtering action to prevent particle interaction and oscillation in the system, and perform other functions. Furthermore, the exposure station and image source is detrimentally located within the imaging drum. It has, however, been discovered quite unexpectedly and surprisingly in accordance with the present invention that this complex system is not only unnecessary but also undesirable and that instead the continuous system of the present invention may incorporate single component

particles made up of colored photosensitive pigments in a conveniently operable arrangement to produce excellent results as described hereinafter.

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

It is a further object of this invention to provide a novel continuous imaging system capable of direct positive imaging.

Another object of this invention is to provide a continuous imaging system for producing images in one or more colors.

Still a further object of this invention is to provide a novel continuous photoelectrophoretic apparatus.

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing an apparatus whereby an image is internally projected upon the surface of an imaging roller, the imaging roller contacting at the position of image reflection a development roller which has coated on the surface thereof photosensitive pigment particles dispersed in an insulating liquid carrier. By the process of photoelectrophoresis, as described above, a direct positive image is formed on the surface of the imaging roller. The imaging roller is referred to as the injecting electrode and consists of a transparent electrode which may, for example, be made up of a layer of optically transparent glass overcoated with a thin optically transparent layer of conductive material, such as tin oxide. The development roller is made up of a central core which preferably has a fairly high electrical conductivity and is usually covered with a layer of blocking electrode material, such as Baryta paper. It is referred to as the blocking electrode. The positive, developed image is then contacted with a transfer substrate, such as paper, for the purpose of transferring the developed image from the imaging roller onto the surface of the substrate. The transferred pigment image is then fixed in a suitable manner to the surface of the transfer sheet.

The invention is illustrated in the accompanying drawings in which there is shown a side sectional view of an exemplary continuous photoelectrophoretic printing apparatus of the present invention.

Referring now to the drawing, there is seen a rotary transparent electrode **1** in the form of a drum which, in this instance, is made up of a layer of optically transparent glass **2**, carrying on its outer surface a thin optically transparent conductive layer **3** of tin oxide. Tin oxide coated glass of this nature is commercially available under the trade name "NESA glass." This rotary base electrode is referred to as the injecting electrode. In close proximity to electrode **1** and parallel thereto is a rotary developing electrode **10** made up of a central core **11** which is preferably of fairly high electrical conductivity and is covered with a layer of blocking electrode material **12** which may, for example, be Baryta paper. Although a blocking electrode material such as **12** need not necessarily be used on the surface of electrode **10**, the use of such a layer is preferred because of the markedly imporved results which it is capable of producing. For obvious reasons the latter electrode, as stated above, is referred to as the blocking electrode. A detailed description of these improved results and the types of materials which may be employed as the electrode coating material is described in detail in copending U.S. application Serial No. 384,689 referred to above. During the imaging process a thin suspension layer **14** of finely divided photosensitive particles dispersed in an insulating carrier liquid is formed on the surface of the developing or blocking electrode **10** supplied from reservoir **15**. Within the rotary imaging roller (electrode) **1** is located

a stationary, first-surface mirror **20** which receives the image projected from the transparent subject to be copied **25** and directs the reflected image through the exposure slit **22** and onto the surface of the suspension at the line of contact **21** where the injecting electrode **1** contacts the developer coated blocking electrode **10**.

The transparency **25** that is to be printed is shown passing under the light source **26** and moving synchronously with the rotary imaging drum **1**. From the image formation station or lens **27** by way of the imaging slit **17**, the image is projected onto the surface of the first surface mirror **20** which is located within the imaging drum and, in turn, reflected onto the surface of the suspension at the line of contact **21**. The image is preferably projected in a plane normal to the surface of the drum so as to minimize distortion of the image and loss of image density. The imaging injecting electrode drum is grounded by connection **30** and the developing blocking electrode is connected with a potential source **31** which is in turn connected to ground. The polarity of the charge on the developing electrode **10** is opposite to that of the polarity that is carried on the surface of the imaging electrode **1**.

The image projector made up of light source **26**, double lens complex **28**, transparency **25** and a single lens **27** is provided to expose the suspension **14** made available from reservoir **15** to the light image of the original transparency to be reproduced. During imaging, drive means **52** rotates the development electrode **10**, synchronously with the imaging electrode **1**, thereby carrying the imaging suspension containing the photosensitive radiant energy particles into intimate contact with the surface of the injecting electrode at the site of projection of the image from transparency **25** onto the surface of the suspension at the line of contact **21**. This slit exposure causes selective particles to migrate through the dispersion liquid and adhere to the surface of the rotating blocking electrode **10** leaving behind a positive particle image on the surface of the injecting electrode **1** which is a duplicate of the original transparency **25**.

The image **40** now developed on the surface of the imaging (injecting) electrode is carried so as to contact an adhesive copy web **41** which is passed up against the drum surface by two idler rollers **42** and **45** so that the web moves at the same speed as the periphery of the drum. A transfer roller **43** is placed behind the web **41** and between rollers **42** and **45**. Thus, the developed image is adhesively transferred from the surface of the imaging or injecting electrode onto the surface of the copy web. The copy web may consist of adhesive tape which will pick up the complete image as it passes over the transfer roller. The transferred image may then be fixed in place as, for example, by placing a lamination over its top surface or by virtue of the presence of a dissolved binder material in the carrier liquid such as a paraffin wax or other suitable binder that comes out of solution as the carrier liquid evaporates. In fact, the carrier liquid itself may be a molten paraffin wax or other suitable binder in a liquid state which is self-fixing upon cooling and return to the solid state. The fixing step is represented by fixing unit **44**. The remnants of the photosensitive dispersion are removed from the surface of the developing electrode **10** by brush **50** and from the surface of the imaging electrode by brush **51**.

It is to be understood that during the imaging process of the present invention as a result of the nature of photoelectrophoretic imaging when a positive image is formed on the surface of the injecting electrode a corresponding negative image is formed on the surface of the blocking electrode. When the system is a monochromatic one it may be desirable to transfer both the positive and negative developed images to respective transfer sheets. Therefore, if desired a transfer system similar to that described above in conjunction with the injecting electrode transfer may also be included in the apparatus to enable the transfer of the image formed on the blocking electrode. Alternatively, when used, the blocking electrode layer of material, such as Baryta paper, may be removed from the development roller to preserve the negative image recorded thereon. A conductive imaging substrate, such as a conductive cellophane web, may be driven between the blocking and imaging electrodes so as to permit the formation of the positive image on the surface of the imaging substrate thereby eliminating the transfer step required by the embodiment disclosed in the illustration and further eliminating the need for cleaning the surface of the imaging or injecting electrode. Any suitable transparent conductive material may be used as the imaging substrate. Typical optically transparent conductive materials are cellulose acetate (optical grade), polyesters such as Mylar, a polyethylene terephthalate, and polycarbonates, such as Plestar, overcoated by any suitable means such as by vacuum deposition with a transparent metal coating such as aluminum, copper, gold, silver or chromium.

Materials which may be used as the photosensitive particles and carrier liquid, the injecting electrode and blocking electrode, are to be found in the copending U.S. applications, Ser. Nos. 384,737, 384,680, and 384,681, mentioned above and copending U.S. applications, Ser. Nos. 468,935 and 473,607, all of which are accordingly incorporated herein by reference. Processing parameters such as the magnitude of the applied potential and the like may also be found in these copending applications. The present system has been found to be capable of producing either monochromatic or polychromatic images depending upon the color, sensitivity and number of different pigments suspended in the carrier liquid and the color light to which the suspension is exposed. Furthermore, it is to be understood that it is not intended that the structural arrangement of the apparatus described in the present invention be restricted to the design as set-out herein, and it is intended to include all similar configurations which will satisfy the requirements of the present invention. For example, it is not necessarily required that the blocking and injecting electrodes be of the same dimension as they appear in the accompanying illustration. Nor is it necessary to limit the number of development electrodes in the system, and when multiple development is desired two or more electrodes may be incorporated in the apparatus.

The term injecting electrode when used in the course of this invention should be understood to mean that it is an electrode which will preferably be capable of injecting electrons into the bound photosensitive particles of the dispersion when it is exposed to light so as to allow for a net change in the charge polarity on the particle. By the term blocking electrode is meant one which is incapable of injecting electrons into or receiving electrons from the above-mentioned photosensitive particles at more than a very slow rate when the particles come into contact with the surface of the electrode. Obviously, if all polarities in the system are reversed the function of the electrodes will also be reversed.

It is preferred that the injecting electrode be composed of an optically transparent glass drum overcoated with conventional conductive materials such as tin oxide, copper, copper iodide, gold or the like to obtain optimum results; however, other suitable materials including many semi-conductive 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 in the course of this invention. Even highly insulating materials such as polytetrafluoroethylene may be placed over the surface of the injecting electrode and such electrodes still may be operative because charge, which leaves the photosensitive particles initially bonded on this surface, upon exposure to light, can merely move out of the particles and remain on the insulating surface thereby allowing the exposed particles to migrate. However, as mentioned above, the use of the more conductive

materials is preferred because it allows for cleaner charge separation and the charge leaving the particles upon exposure can move into the underlying surface and away from the particles in which it originated. This also prevents possible charge buildup on the electrode which might tend to diminish the inter-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 particles when the particles reach the surface of this electrode. The blocking electrode drum generally will consist of a very soft central core which may be of fairly high electrical conductivity. Typical conductive materials are conductive rubber, and metal foils of steel, aluminum, copper, and brass. Preferably, the central core will have a high electrical conductivity in order to establish the required polarity differential. However, if a low conductivity core is used, a separate electrical connection may be made to the back of the blocking layer of the electrode when the latter is utilized. It is preferred that the blocking layer when used be either an insulator or a semi-conductor which will not allow for the passage of sufficient charge carriers under the influence of the applied field to discharge the particles finally bound to it thereby preventing particle oscillation in the system which results in enhanced image density and image resolution. Even if this blocking electrode will allow for the passage of some charge carriers through it to the photosensitive particles, it will still be considered to come within the class of preferred materials if it does not allow for the passage of sufficient carriers to recharge the particle to the opposite polarity because even a discharge particle will tend to adhere to this blocking electrode by Van Der Waals forces. Here again, other suitable materials not coming within the preferred class may be used, as defined in copending U.S. application Ser. No. 384,680. Exemplary of the preferred blocking material is Baryta paper which consists of a paper coated with barium sulfate suspended in a gelatin solution. The Baryta paper and the other suitable materials used as the blocking layer may be wetted on their back surfaces with tap water or coated on these back surfaces with electrically conductive materials. The blocking electrode layer, when used, may be a separate replaceable layer which is either taped on the developing electrode roller or held by mechanical fasteners or any other device which is capable of releasably holding the layer on the roller. In the alternative, the layer may be an integral part of the roller itself, being either adhesively bonded, laminated, spray coated or otherwise applied to the surface of the roller.

Any suitable voltage may be applied, depending upon the thickness of the materials used, to produce a preferred field strength of from about 400 to about 1,000 volts per mil across the suspension at the time of exposure in order to obtain optimum results. For example, using a seven mil thick plastic coated Baryta paper over a conductive Neoprene (polychloroprene) backing as the blocking electrode, when this electrode contacts the injecting electrode in the presence of the imaging suspension, it has generally been found that voltages of from about 1,000 to about 7,000 may be employed and that ordinarily better images are produced if the applied voltage is in the higher end of this range. Different voltages may be used with different components of varying thickness to attain approximately the same field strength in the system.

Although this invention has been described for the most part in connection with a Baryta paper blocking electrode, any suitable material having a resistivity of about 10^7 ohms/cm.^{2} or greater may be employed. Typical materials in this resistivity range which may be employed in the system of the present invention include cellulose acetate and polyethylene coated papers, cellophane, nitro cellulose, polystyrene, polytetrafluoroethylene, polyvinyl fluoride, and polyethylene terephthalate.

Any suitable means may be used to transfer the developed image from the surface of the injecting electrode. The transfer step may be carried out by means of an adhesive pick-off technique such as is shown and described above or the transfer of the image may be carried out in the presence of electrostatic field. In addition, other transfer methods may be used such as those disclosed in copending U.S. application Ser. No. 542,050, having a common assignee.

Any suitable fixing means may be used in the course of the present invention to fix the transferred image to the surface of a copy web such as by placing a lamination over the top surface of the transferred image or by virtue of the inclusion of a suitable binder material in the carrier for the photosensitive particles, such as a wax. In the latter case, the binder material will solidify upon cooling thereby fixing the developed image to the surface of the copy web. For ease of operation it is preferred to use the lamination technique.

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

In the following examples, four different imaging suspensions are employed with the apparatus of the present invention as shown in the accompanying illustration. The imaging or injecting electrode is made up of NESA glass, as described above, and the surface of the glass is connected to ground. The injecting electrode roller is approximately 7 inches in diameter. The development or blocking electrode consists of a hard conductive rubber core of approximately 7 inches in diameter coated with a layer of water-proof Baryta paper. A negative voltage of 2,500 is applied across the imaging suspension. The imaging suspension used in these examples consists of about 7 parts by weight of photosensitive particles in Sohio Odorless Solvent 3440, a kerosene fraction. The image source used is a "Kodachrome" color transparency.

Example I

A tri-mix is prepared by dispersing equal parts of a cyan pigment, Monolite Fast Blue GS, a mixture of the alpha and beta forms of metal-free phthalocyanine; a magenta pigment, Watchung Red B, 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydrox-3-naphthoic acid, C.I. No. 15865, and a yellow pigment, Algol Yellow GC, 1,2,5,6-di (C,C'-diphenyl)-thiazole-anthraquinone, C.I. No. 67,300, in the above-mentioned Sohio Odorless Solvent 3440. The tri-mix is imaged, as described above, forming a full color image conforming to the original transparency.

Example II

A tri-mix is prepared by dispering equal parts of a Cyan pigment, Diane Blue, 3,3'-methyoxy-4,4' diphenyl-bis (1''-azo-2''-hydroxy-3''-naphthanilide), C.I. No. 21180; a magenta pigment, Calcium Lithol Red, a calcium lake of 1 - (2' - azonaphthalene - 1' - sulfonic acid) - 2-naphthol, C.I. No. 15,630, and a yellow pigment, 8, 13-dioxodinaphtho-1,2-2',3') - furan - 6 - carbox - 4'' - methoxyanilide, disclosed in U.S. Patent application No. 421,377 filed Dec. 28, 1964, in the Sohio Odorless Solvent 3440 mentioned above. The tri-mix is imaged, as described above, forming a full color image conforming to the original transparency.

Example III

Seven parts by weight of the metal-free phthalocyanine pigment disclosed in Example I is blended with the Sohio odorless Solvent and imaged as described above. However, in this instance, a black-and-white transparency is used. A single color cyan image on a background of white is formed conforming to the original transparency.

Example IV

The photo sensitive particles of this example consist entirely of Quindo Magenta RV–6803, a substituted quinacridone. After blending the pigment with the Sohio

Solvent 3440, the mixture is imaged as in Example III. A magenta image conforming to the original transparency is formed.

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. In addition to the steps used to carry out the process of the present invention, other steps or modifications may be used, if desirable. For example, exposure of the transparent image may take place along the longitudinal axis of the imaging (injecting) electrode. In addition, other materials may be incorporated in the developing suspension, image projector, injecting electrode, blocking electrode, copy web, or fixing unit, which will enhance, synergize or otherwise desirably affect the properties of the systems for their present use. For example, the developer suspension may contain sensitizers and/or binders for the photosensitive particles which are dissolved or suspended in the carrier liquid.

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

What is claimed is:

1. An apparatus for photoelectrophoretic imaging comprising in combination a rotatably mounted first electrode, means to apply a film of an imaging suspension to the surface of said first electrode, an optically transparent second electrode rotatably mounted in close proximity and parallel to the axis of said first electrode such that the surface of said second electrode is in area contact with the film on the surface of said first electrode, means to rotate said first and second electrodes, means to project an image onto said suspension at the area of contact of said second electrode with said film coated first electrode, and means to apply an electric field across said suspension at said area contact whereby an image is produced on at least one of said electrodes.

2. The apparatus as described in claim **1** wherein said projecting means comprises an exposing mechanism located external to said second electrode and a reflecting mechanism located internal to said second electrode.

3. The apparatus as described in claim **2** wherein said exposing mechanism is adapted to project an image in a plane perpendicular to the surface of said electrode.

4. An apparatus for continuous photoelectrophoretic imaging comprising in combination a blocking electrode cylindrically shaped and rotatably mounted for continuous imaging, means to apply a film of an imaging suspension to the surface of said blocking electrode, an optically transparent, cylindrically shaped injecting electrode rotatably mounted in close proximity and parallel to the axis of said blocking electrode such that the surface of said injecting electrode is in area contact with the film on the surface of said blocking electrode, means to rotate said blocking and injecting electrodes, means to project an image into said suspension at the area of contact of said injecting electrode with said film coated blocking electrode, and means to apply an electric field across said imaging suspension at said area contact whereby an image is produced on at least one of said electrodes.

5. The apparatus as described in claim **4** further including a means to transfer the image from the surface of at least one of said imaged electrodes to a copy web.

6. The apparatus as described in claim **4** wherein said projecting means comprises an exposing mechanism located external to said injecting electrode and a reflecting mechanism located internal to said injecting electrode.

7. The apparatus as described in claim **6** wherein said exposing mechanism is adapted to project an image in a plane perpendicular to the surface of said injecting electrode.

8. An apparatus for continuous photo-electrophoretic imaging comprising in combination a blocking electrode cylindrically shaped and rotatably mounted for continuous imaging, means to apply a film of an imaging suspension to the surface of said blocking electrode, an optically transparent, cylindrically shaped injecting electrode rotatably mounted in close proximity and parallel to the axis of said blocking electrode, means to direct a transparent conductive imaging substrate between said blocking electrode and said injecting electrode in such a manner so as to form a single continuous area of contact between said injecting electrode and film coated blocking electrode, means to rotate said blocking and injecting electrodes, means to project an image onto said suspension at said area of contact, and means to apply an electric field across said imaging suspension at said area of contact whereby an image is produced on the surface of said imaging substrate.

9. The apparatus as described in claim **8** wherein said conductive imaging substrate comprises a metallized polyethylene terephthalate film.

10. The apparatus as described in claim **1** wherein said projection means comprises an exposure mechanism located such that exposure takes place along the longitudinal axis of said second electrode.

11. The apparatus as described in claim **4** wherein said projection means comprises an exposure mechanism located such that exposure takes place along the longitudinal axis of said injecting electrode.

References Cited

UNITED STATES PATENTS

2,732,775	1/1956	Young et al.	96—1
3,043,684	7/1962	Mayer	117—372 X
2,940,847	6/1960	Kaprelian	96—1.4
3,043,684	7/1962	Mayer	117—372 X
3,276,896	10/1966	Fisher	118—637
3,281,857	10/1966	Kaiser	118—637
3,384,566	5/1968	Clark	204—181

FOREIGN PATENTS

624,328	7/1961	Canada.

JOHN H. MACK, *Primary Examiner.*

E. ZAGARELLA, *Assistant Examiner.*

U.S. Cl. X.R.

96—1, 1.3; 204—181