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Ohno et al.

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[45] **Dec. 4, 1973**

[54] **ELECTROSTATIC PRINTING METHOD AND APPARATUS**

[75] Inventors: **Genji Ohno,** Yokohama; **Eiichi Inoue,** Tokyo, both of Japan

[73] Assignee: **Research and Development Laboratories of Ohno Co., Ltd.,** Yokohama-shi, Japan

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[52] **U.S. Cl.** .... **355/10,** 355/16, 96/1 LY, 117/37 LE, 118/637, 118/DIG. 28

[51] **Int. Cl.** **G03g 15/10**

[58] **Field of Search** .... 355/3, 10, 16, 17; 96/1 LY; 117/37 LE; 118/627, DIG. 28

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Primary Examiner—Robert P. Greiner

Attorney—Staas, Halsey & Gable

[57] **ABSTRACT**

Apparatus is disclosed for electrostatically printing, comprising a photosensitive plate composed of a conductive substrate having fine pores distributed uniformly all over the surface thereof and a liquid-repellent photoconductive layer coating the surface of the substrate except the part of the pores. An electrostatic latent image is formed on the photoconductive layer, and a liquid developer is supplied from the back side of the photosensitive plate. Next, a voltage is applied between the plate and an opposing electrode contacting a paper to be printed, disposed in an opposing relation to the plate so that the latent image is developed and transferred to the paper.

9 Claims, 12 Drawing Figures

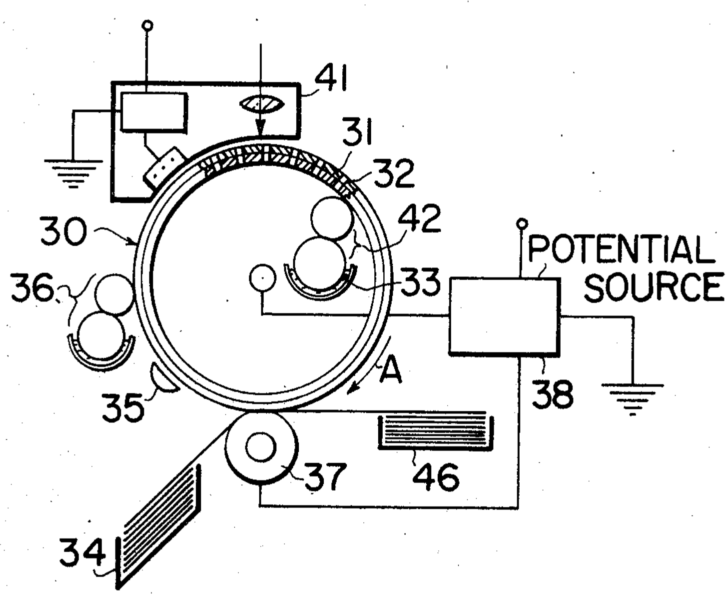


FIG. 1

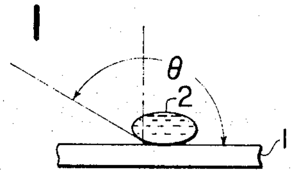


FIG. 2

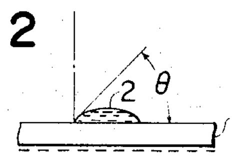


FIG. 4

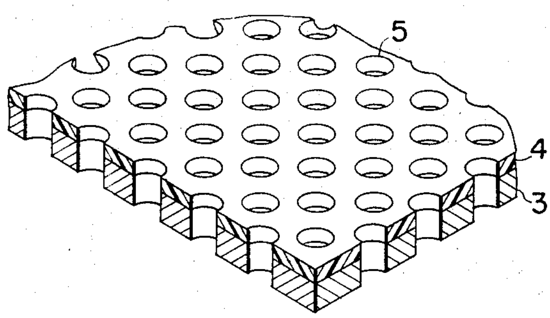


FIG. 3

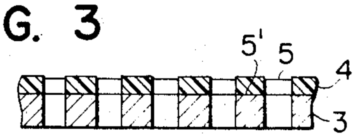


FIG. 5

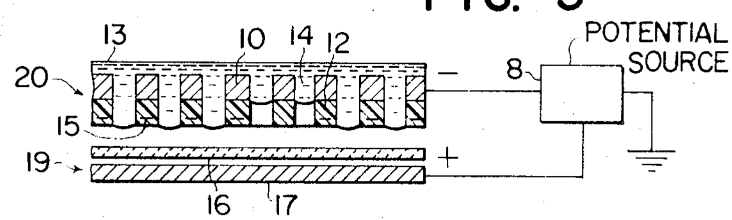


FIG. 6

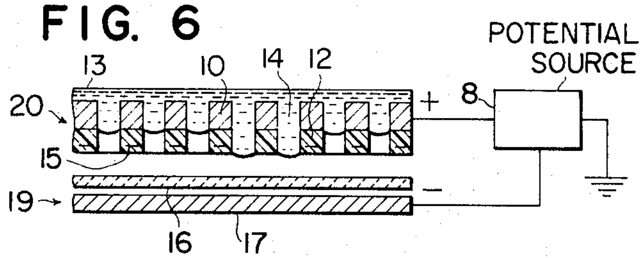


FIG. 7

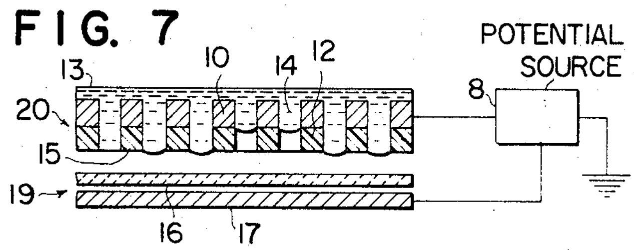


FIG. 8

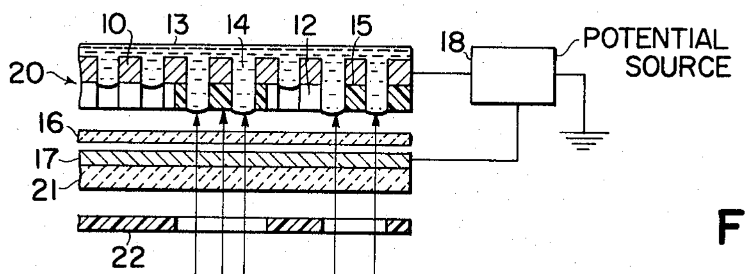


FIG. 9

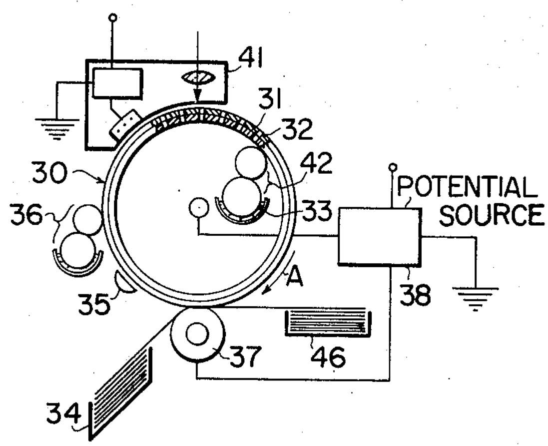


FIG. 10

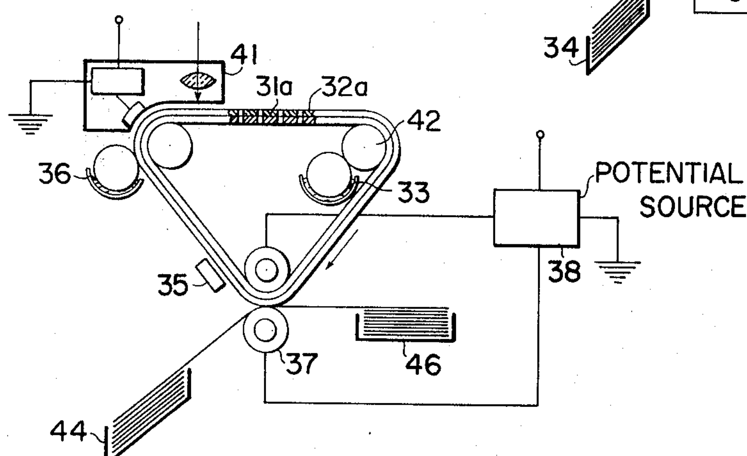


FIG. 11(a)

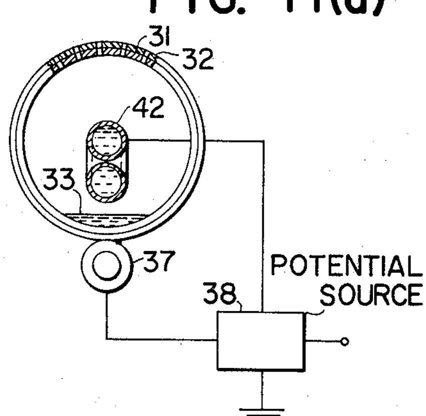
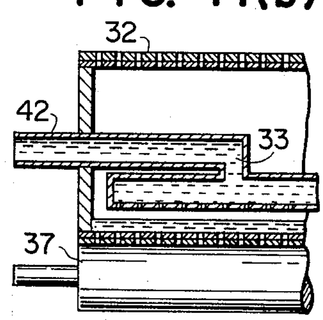


FIG. 11(b)



ELECTROSTATIC PRINTING METHOD AND APPARATUS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an electrostatic printing method and an apparatus thereof, and in particular to such a method and an apparatus, wherein liquid developers are used.

2. Description of the Prior Art

Conventional electrostatic printing methods of the prior art require that an electrostatic latent image be formed on an electrophotographic plate and that colored fine particles to be suppled to be electrostatically attracted to the latent image so that image development is carried out and the colored fine particles are electrostatically transferred to a print paper. In the above method, a photoconductive, photosensitive selenium plate (or other space charge type of photosensitive plate including an insulating layer formed on the surface of a photoconductive layer), may be used as the electrophotographic sensitive plate. The colored fine particles may be suspended in a high-resistant, low dielectric constant carrier liquid.

Among the known conventional methods, dry developing methods have the following defects: 1) the developer particles are apt to be scattered 2) the developing unit is complex, and 3) the resolving power is inadequate. The known liquid developing methods have the following defects: 1) the liquid developers may have objectionable odors and be poisonous; and 2) the voltages required may cause fires due to discharges.

SUMMARY OF THE INVENTION

An object of this invention is to provide an electrostatic printing method and an apparatus used therein, wherein a positive image can be reproduced from both positive and negative originals by a liquid developing method without danger of fire, odor and poison.

In accordance with the teachings of this invention, a photosensitive plate comprises a conductive substrate with fine pores distributed uniformly over the entire surface of the substrate; the surface of said substrate is coated except the part of the pores, by a photoconductive layer which is repellent against liquid developers. One surface of the photosensitive plate is exposed to a light image to form an electrostatic latent charge thereon corresponding to the light image. Next, a liquid developer is applied to the other side of the photosensitive plate and a voltage is applied between the photosensitive plate and an opposing electrode arranged near the photophotosensitive plate. The opposing electrode contacts a paper to be printed so that the latent image on the photosensitive plate can be developed and transferred to the paper.

The opposing electrode may be previously attached to the print paper or may be designed as a separate member from the paper to provide an electrode surface disposed to contact the back side of the paper and to apply a voltage thereto.

According to a significant feature of this invention, the surface of the photosensitive layer is liquid-repellent and hence, the contamination of the printed image thereby is minimized and the optimum print can be reproduced by adjusting the applied voltage. Another significant feature of this invention is that a positive print can be made from both positive and negative

originals by changing the polarity of the applied voltage. A still further feature of this invention is that the developer comprises water as the carrier and hence, the developer is not objectionable in odor, poisonous and does not present a fire hazard.

BRIEF DESCRIPTION OF THE DRAWINGS

While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter which is regarded as the invention, preferred embodiments are disclosed in the following detailed description taken in conjunction with the accompanying drawings, in which:

FIG. 1 shows the contact angle of a liquid drop on a liquid-repellent insulating film when the film is uncharged;

FIG. 2 shows the same insulating film as shown in **FIG. 1**, except that the film is charged;

FIG. 3 shows a cross-sectional view of a photosensitive plate according to this invention;

FIG. 4 shows a perspective view of the photosensitive plate shown in **FIG. 3**;

FIGS. 5 to **8** show apparatus for producing latent images in various embodiments of this invention;

FIGS. 9 and **10** show illustrative embodiments of the electrostatic printing apparatus according to this invention; and

FIGS. 11A and **11B** show the illustrative embodiment of a developer supply unit to be incorporated into the apparatus of this invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THIS INVENTION

Referring to **FIG. 1**, when a liquid drop is placed on an uncharged surface of a liquid-repellent insulating film **1**, the contact angle is more than 90° and the liquid drop does not wet the film surface. In contrast, as shown in **FIG. 2**, if the film is charged (indicated by a broken line), the contact angle θ is decreased to a value less than 90° and the liquid drop wets the film surface. This phenomenon depends on the liquid-repellent property of the film surface, the kind of liquid and the applied voltage. For instance, when a water drop is placed on a 3-fluoroethylen chloride resin film, the contact angle is 108° before it is charged and decreases to 56° to wet the film surface when it is charged by −500V.

In **FIGS. 3** and **4**, a conductive substrate **3** has a large number of fine pores **5** uniformly distributed over the surface. A part **5'** of the substrate where no pores exist is coated by a liquid-repellent photoconductive layer **4**. Thus, the photosensitive plate includes the substrate **3** and the photoconductive layer **4**. The size of the fine pores **5** is determined by the resolution required in the printed matter. For example, the pore size may be 10 to 100μ, preferably 30 to 50μ, in case of usual business. The space between pores is determined by the kinds of paper and ink used and is selected to permit the developer in one pore to spread and contact the developer in an adjacent pore upon transfer and printing; the space is preferably 10 to 100μ.

The thickness of the liquid-repellent photoconductive layer **4** is selected to be in the range of 3 to 400μ, preferably 3 to 100μ. If the thickness is less than 3μ, contamination may be induced by non-uniformity of the pores and roughness of the paper. If the thickness is more than 400μ the effect of the latent charge upon the developer is reduced and development is not sufficiently carried out. If the size of pores is less than 10μ, they are often plugged up by impurities contained in the developer, and if the size is over 400μ, a uniform image is not obtained. If the space between pores is less than 10μ or more than 100μ, the accuracy of image is not good.

Such finely porous substrate can be easily made by conventional methods of making a porous metal filter. A metal plate such as copper, having a 5 to 100μ thickness, may be photoetched so that pores are formed over the entire surface of the metal plate. Alternatively, a mesh can be used as a substrate of the photosensitive plate.

The developer taking the form of a mixture of photoconductive particles and a resin solution, is applied to the porous substrate **3** by an electrostatic painting method (the substrate **3** having been used as an electrode) to a predetermined thickness so that a photoconductive layer is formed on the surface of the substrate **3.** Alternatively, a solution of the particles charged in a polarity opposite to that of the substrate are electrodeposited onto the substrate by spray coating. If an inorganic photosemiconductor such as amorphous selenium is used as photosensitive material, the layer can be easily formed by vacuum deposition under suitable voltages.

In order to obtain the liquid-repellent photoconductive layer, liquid-repellent resins such as polyethylene, polystyrene, alkyd resin, silicone varnish or 3-fluoroethylene chloride resin are used as a binder in the developer solution. Next, the photoconductive material is mixed with the binder (see Example 1, for a binder-type photoconductive layer). Alternatively, a film of the above mentioned liquid-repellent resins may be formed on the photoconductive layer (see Example 2); this layer may be formed by vacuum deposition of an inorganic semiconductor. Thus, a liquid-repellent photoconductive photosensitive plate having fine pores over the surface is obtained. Other known photoconductive layers, if they are porous and liquid-repellent, may be used in this invention.

FIGS. **5** and **6** show a unit for development used in this invention. In FIG. **5,** a conductive substrate **10** has fine pores **4** distributed uniformly over the entire surface of the substrate **10.** A liquid-repellent photoconductive layer **12** coats the surface except for the exposed pores **14.** A photoconductive photosensitive plate **20** comprises the substrate **10** and the layer **12.** An electrostatic image of charges indicated by the numeral **15** is formed on the surface of the plate **20** by a conventional method, and a liquid developer **13** is supplied to the back side of the plate **20.** The contact angle of the liquid developer being less than 90° with respect to the substrate **10** and more than 90° with respect to the photoconductive layer **12,** the developer wets and enters into the pores **4** until it reaches the interface between the substrate **10** and the layer **12.** An electrode **17** which provides a contact surface to a paper to be printed, is arranged to oppose the plate **20** as shown. A DC voltage is applied between the substrate **10** and the electrode **17** by a potential source **18,** so as that the polarity of the substrate **10** is the same as that of the charge of the latent image **15** and the polarity of the opposing electrode **17** is opposite. An electric field is formed between the plate **20** and the electrode **17;** the resulting field is much stronger through the portion of the plate **20** where the latent image is present than in the part where the image does not exist. Accordingly, the liquid developer does not exude through the pores to the surface of those portions of the plate **20** where no latent image exists due to repulsing influence of the liquid-repellent layer. Where the image exists, however, electrostatic polarization or induction is caused under the influence of the latent image charge and the applied voltage, so that the contact angle is decreased and the liquid developer wets the internal surfaces of the pores in the layer. As a result, the liquid penetrates through the pores of the layer to the surface of the plate **20.** Thus, the exuded developer may be contacted, absorbed and transferred to a print paper **16** so that a positive image can be obtained in correspondence with the image of electrostatic charges.

Next, if the electrostatic voltage is applied so as that the polarity of the electrode **17** is the same as that of the charge of the latent image **15** and the polarity of the substrate **10** of the plate **20** is opposite, the electric field between the plate **20** and the electrode **17** is decreased where the latent image exists and increased where the latent image does not exist.

If the applied voltage is properly adjusted, the field where the latent image exists, assumes a minimum value so that electrostatic polarization or induction of the liquid developer in the pores cannot occur and the field does not drive the liquid developer to the electrode **17.** In contrast, where no image exists, the liquid is electrostatically polarized or induced in the pores due to the electric field, and the contact angle is decreased so that the liquid developer is attracted to the electrode **17.** Thus, in a similar manner as discussed above, an inverse image of the electrostatic charge image is transferred and printed onto the paper **16.** The value of the electrostatic voltage for developing the electrostatic charge latent image according to this invention depends on the developing speed and on the kinds of the electrostatic latent image, the charge, the liquid-repellent layer and the developer. Experiments indicate that a voltage of 0 to 2,000 V (preferably 0 to 1,500 V) is required when the electrostatic latent image is a positive one. If the voltage exceeds 2,000 V, the image becomes blurred due to creeping discharge. When the latent image is a negative one, the voltage should be in the order of 20 to 2,000 V, preferably 30 to 1,500 V.

FIGS. **7** and **8** show a unit for developing a latent image according to this invention. If a large amount of material remains on the photoconductive layer of the photosensitive plate, the influence of the exposure remains for a long time after exposure (i.e., pre-exposure fatigue). Under such conditions, electrostatic printing can be carried out due to the conductivity resulting from irradiation of light without electrostatic charge. In FIG. **7,** the liquid developer is supplied from the back side of the photosensitive plate **20,** whose photoconductive layer **12** is formed on the surface of a finely porous conductive **10** substrate and contains trapping material, such as a low grade polymer including carboxylic acid or diphenyl picrye hydrazyle, and has a property of pre-exposure fatigue. Next, an electrostatic voltage is applied between the conductive substrate **10** of the photosensitive plate **20,** and the electrode **17** which opposes the plate and provides a contact surface to apply a voltage from source **18** to the paper to be printed. The field between the plate **20** and the opposing electrode is much more intensive where the plate has been irradiated than where the plate **17** has not be radiated, because the capacitance and conductivity of irradiated portions are increased thereby. Accordingly, the liquid developer does not exude through the pores to the surface of the plate due to inhibiting influence of the non-irradiated portion of the liquid-repellent layer. Where the layer has been irradiated, the developer is electrostatically polarized or induced under the intensive field to be attracted to the opposing electrode, and exuded to the surface of the plate **20** because the contact angle of the developer with the pore's surface is decreased. Thus, the exuded developer may be contacted, absorbed and transferred to the paper **16** so that a reverse image can be obtained.

If the photoconductive layer has little or no pre-exposure fatigue effect, development can be carried out at the same time as the irradiation of the light image. In FIG. **8**, the liquid developer is supplied to the back side of the photosensitive plate **20** composed of a finely porous conductive substrate **10** and a liquid-repellant photoconductive layer **12** formed on the substrate. A transparent paper to be printed is placed on a transparent opposing electrode **17**, which is disposed near and opposed to the photosensitive plate and has a transparent conductive layer **21** such as NESA layer (tin dioxide transparent conductive film). The light image is irradiated onto the back side of the plate **20** through the light image plate (negative or positive film) **22**, and simultenously an electrostatic voltage is applied between the conductive substrate **10** of the photosensitive plate **20** and the transparent opposing electrode **17**. A reverse image is obtained on the paper by the same process as shown in FIG. **7**. The voltage for development should be in the range of 30 to 2,000 V. preferably 30 to 1,500 V. If it is less than 30V, the intensity of the field is too weak to obtain uniform development, and if the voltage exceeds 2,000 V, the image obtained becomes blurred.

Because of the principle of this invention mentioned above, it is not always necessary for the developer of this invention to have a high electric resistance and a low dielectric constant.

Developers used in this invention are liquid and include coloring agents, contact angle adjusting agents, and viscosity adjusting agents. The liquid used in the developer of this invention has a contact angle not less than 90° with respect to uncharged surface of the photoconductive, photosensitive plate and less than 90° on the electrostatic latent image of the plate to thereby wet the surface. If the liquid-repellent material is made of polyethylene, polystyrene, 4-fluoroethylene, 3-fluoroethylene chloride, silicone varnish or akyd resin; water glycerol or ethylene glycol may be used as the developer solvent.

The coloring agent may be added to a solution, suspension or mixture of these aforementioned components. When water is used, hydrophilic dyes such as malachite green, methyl violet, victoria blue and persian orange are used. If a small amount of ethyl alcohol is contained as a contact angle adjusting agent, alcohol soluble dyes such as pigment green and carmine FB are used.

An organic pigment such as carbon black and phthalocyanine may be dispersed into liquid by a suitable dispersing agent and is used as suspended coloring agent.

Contact angle adjusting agents are used for obtaining optimum contact angle in relation with the liquid-repellent property of the photoconductive photosensitive plate and the desired printing speed. Suitable contact agents are prepared by mixing two liquids having different surface tensions or utilizing a small amount of surface activator.

Viscosity adjusting agents are used for adjusting the fluidity of ink in relation with the printing speed. Liquid-soluble resins, for example,polyvinyl alcohol, dextrin, gelatine as methylol melamin, are used when the liquid is water. Viscosity adjusting agents also serve to fix the coloring agent to the paper when the developer has dried.

FIG. **9** shows an embodiment of this invention wherein a cylindrical photoconductive photosensitive plate is used. A cylindrical plate **30** is composed of a conductive substrate **31** having fine pores over the entire surface and a liquid-repellent photoconductive layer **32** arranged on the substrate **32**. After a latent image is formed on the surface of the plate **30** by an electrostatic latent image forming unit **41**, the plate **30** is rotated in the direction of the arrow A as shown by a driving unit (not shown), and a developer **33** is applied onto its back side from a developer supply unit **42** which is disposed within a supply of the developer **33** and contact the inside surface of the plate as shown in FIG. **9**. The developer can be discharged in numerous ways, for example, in a manner shown in FIGS. **11A** and **11B**. That is, the developer flows down to the inner surface of the plate by means of the axis of the cylindrical plate. The developer may be applied before or at the same time as the development and transfer.

The cylindrical plate **30** supplied with the developer is further rotated to a conductive roll **37**, where the plate **30** comes into contact with a paper which is supplied by the roll **37**. An electrostatic voltage is applied between the plate **30** and the roll **37** by a source **38**, and the liquid developer supplied to the back side of the plate is exuded to the surface of the plate in the form of a positive or negative image of an orginal picture. The developer exuded in the form of the image is at once transferred to a paper to be printed. The printed paper is deposited to a receiver **44**.

After printing, the processed part of the plate is erased by a latent image erasing unit **35** and cleaned by a cleaning unit **36**. The latent image can be erased by a known method, for example, by irradiating the entire area of the surface of the latent image by light. Further, the developer still remaining on the plate after printing can be removed by a wet, soft brush roll, a felt roll or the like. Again a latent image is formed by the latent image forming unit **41** to be continuously printed.

FIG. **10** shows the other embodiment of this invention wherein a photoconductive photosensitive plate in the form of a flexible, endless belt **30***a* is used. Similar elements are identified by corresponding numbers in FIGS. **9** and **10**.

Example 1 - A photosensitive liquid was prepared of the following components:

Zink oxide	100g
Bromophenol blue (1% solution)	1.5cc
Flueorescein (1% solution)	1.5cc
Rose bengal (1% solution)	1.5cc
Styrene-buthadien copolymer	30g
Toluene	60cc

Brass particles (grain size - 40μ) were press-sintered to form a 5 mm thick finely porous substrate. The surface of the substrate was polished to serve as an electrode. A photosensitive liquid is sprayed onto the polished surface by a nozzle. A 1 KV voltage is applied between the nozzle and the substrate. The photosensitive liquid is sprayed from the nozzle in the form of charged particles with a polarity opposite to that of the substrate. Thus, the liquid is electrodeposited to 30μ thickness onto the plate, and after drying, silicone varnish was electrodeposited thereon to an average thickness in the order of 10μ in the same manner as the photosensitive liquid.

The resultant photoconductive photosensitive plate was given a negative electrostatic charge latent image by conventional means, such as 9 KV corona discharging unit.

A liquid developer composed of the following components was supplied to the back side of the plate:

Methylene blue	6g
Polyvinyl alcohol (8% solution)	50cc
Glycerol	5cc
Water	50cc

The plate was carried to oppose a paper placed on an opposing electrode; then, a 300V electrostatic voltage was applied between the conductive substrate of the photosensitive plate and the opposing electrode, the former being negative and the latter positive. A distinct blue positive image was printed on the paper corresponding with the original.

Example 2 - The process was performed in the same manner as in Example 1, except that the plate was placed at a positive voltage, the opposing electrode being negative, and the voltage therebetween being 450V. A distinct negative image was obtained. Example 3 - A 100μ thick, brass plate was photoetched to produce fine pores having a diameter in the order of 40μ and a density of 225 pores per mm^2. The photosensitive liquid of Example 1 was sprayed and electrodeposited at 1KV onto this conductive plate to provide a photosensitive layer with a thickness of 35μafter drying.

Dilute silicone varnish (1 percent solution) was coated on the dried layer by air blown from the back side. A negative electrostatic latent image was formed on the surface of this photosensitive plate in correspondence with the original by a conventional method; then the plate was moved to oppose a paper placed on the opposing electrode

Next, a liquid developer composed of the following components was supplied to the back side of the photosensitive plate:

Carbon black	7g
Victoria blue	0.15g
Gelatin	2g
Glycerol	15g
Water	100cc

A 280V electrostatic voltage was applied between the plate and the opposing electrode, the former being negative and the latter positive. A distinct blue-black positive image was obtained in correspondence with the original. When a 530V electrostatic voltage was applied in reverse polarity, the negative image was obtained.

Example 4 - Charged, liquid particles of a photosensitive liquid composed of the following components were electrodeposited to the surface of a stainless steel mesh (250 mesh):

Zinc oxide	100g
Bromophenol blue (1% solution)	2cc
Rose bengal (1% solution)	2cc
Diphenyl picryl hydrazyl	0.4g.
Styrene-buthadien copolymer	40g
Toluene	60cc

The photosensitive liquid was sprayed by a nozzle under 3KV electrostatic voltage applied between the mesh and the nozzle. After drying a silicone varnish was coated on the photosensitive layer in the same manner as described in Example 2.

The resultant photosensitive plate was exposed to latent image in correspondence with the original, by a tungsten filament lamp. The plate was then moved to a paper placed on an opposing electrode.

Next, a liquid developer composed of the following components was supplied to the back side of the plate:

Victoria blue	3g
Persian oragne	5g
Dextrin	8g
Glycerol	8g
Water	100cc

A 480V electrostatic voltage was applied between the plate and the opposing electrode, and a distinct negative image was obtained.

Example 5 - A photosensitive plate was prepared by forming the liquid-repellent photoconductive layer of Example 1 on the mesh of Example 4. The developer of Example 3 was supplied to the back side of the plate, and the plate was then disposed adjacent to a transparent film placed on a conductive NESA film formed on a transparent glass plate. A light image was irradiated from the back side of the glass plate, as shown in FIG. 8, and at the same time a 500V electrostatic voltage was applied between the photosensitive plate and the conductive layer of the glass plate. A blue-black negative image was obtained in correspondence with the original.

Example 6 - A liquid developer was prepared of the following components:

Zink oxide	50g
Silicone varnish (resin 5%)	50g
Rose bengal (2% methanol solution)	15cc
Thinner	150cc

A 100μ thick copper plate was photo-etched to provide fine pores having a diameter in the order of 40μ and a density of 140 pores per mm^2. The prepared photosensitive liquid developer was electrodeposited on the surface of this plate by a spary nozzle disposed at 1KV. The thickness of the developer was 40μ after drying. Development and transfer was carried out at 600V, the photosensitive plate being positive and the opposing electrode negative. A distinct negative image was obtained in correspondence with the original.

Numerous modifications and adaptations of the system of the invention will be apparent to those skilled in the art and thus it is intended by the dependent claims to cover all such modifications and adaptations as fall within the true spirit and scope of the invention.

What is claimed is:

1. Apparatus for electrostatically reproducing an original image onto an image bearing medium, said apparatus comprising:

transfer means including an electrically conductive substrate having a first exposed surface and a photoconductive layer disposed upon said conductive substrate to form a composite assembly, said photoconductive layer having a liquid repellent second surface, said composite assembly having a plurality of uniformly spaced openings disposed therethrough;

means for forming an electrostatic latent image on said second surface corresponding to the original image;

means for supplying a liquid developer to said first surface to direct the developer through said openings and onto those portions of said second surface in accordance with the electrostatic latent image formed thereon;

electrode means disposed in an opposing relationship to said composite assembly contacting the image bearing medium; and

means for applying a voltage between said electrode means and said composite assembly to thereby effect the development of the electrostatic latent image on the image bearing medium, which is disposed adjacent said second surface of said transfer means.

2. Apparatus as claimed in claim **1**, wherein said transfer means comprises a cylindrical member comprising said substrate and said photoconductive layer.

3. Apparatus as claimed in claim **1**, wherein said transfer means comprises a continuous, flexible belt comprising said substrate and said photoconductive layer.

4. Apparatus as claimed in claim **1**, wherein said photoconductive layer comprises a liquid-repellent resin binder and a photoconductive material.

5. Apparatus as claimed in claim **1**, wherein said photoconductive layer comprises a first layer having a liquid repellent property and a second layer having a photoconductive property.

6. Apparatus as claimed in claim **1**, wherein said photoconductive layer has a thickness in the range of 3μ to 400μ.

7. Apparatus as claimed in claim **1**, wherein said openings have a diameter in the range of 10μ to 100μ.

8. Apparatus as claimed in claim **1**, wherein said openings are uniformly spaced from each other by a distance in the range of 10μ to 100μ.

9. Apparatus as claimed in claim **1**, further including means for erasing the latent image formed upon said composite assembly, and means for removing the developer remaining on the second surface from said second surface.

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