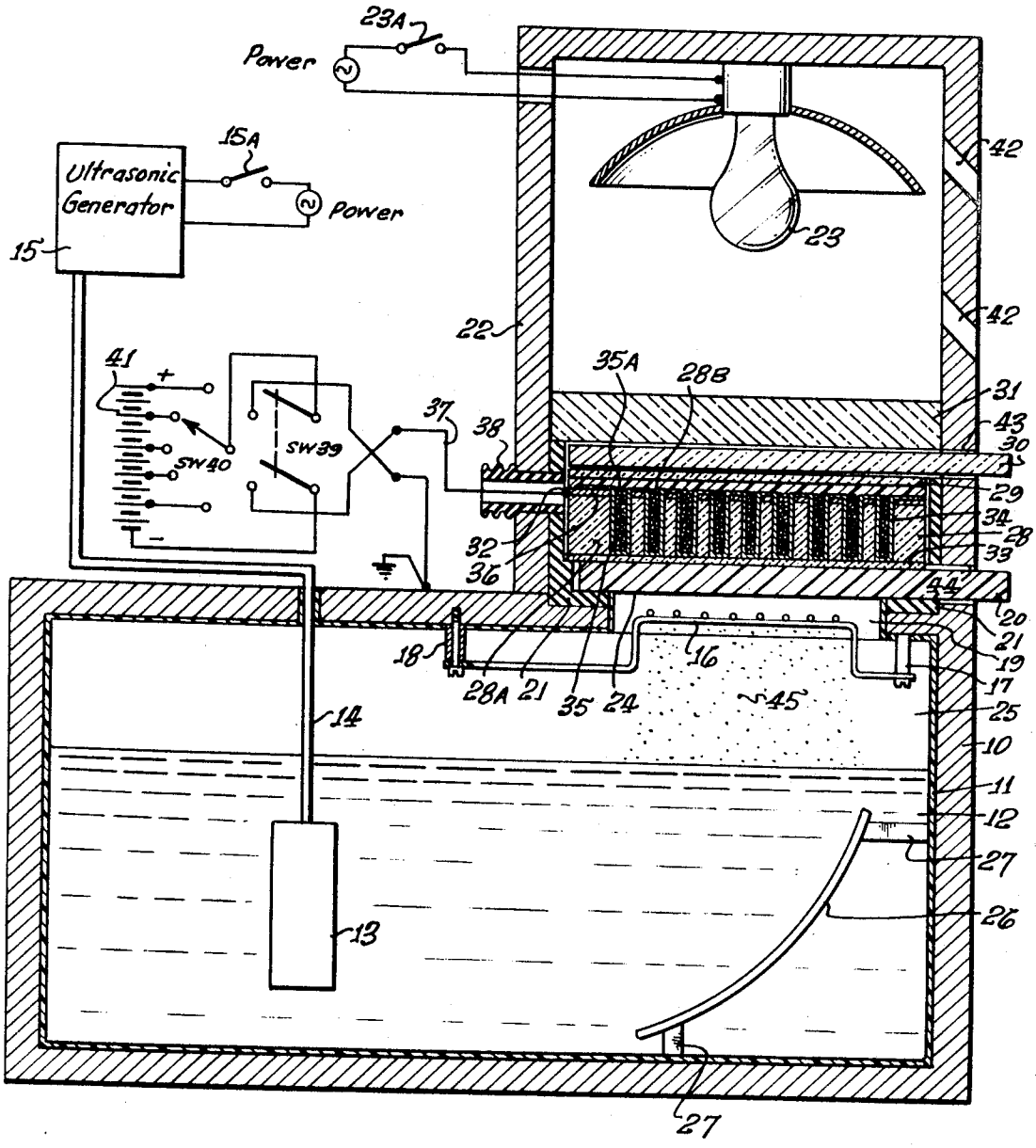
June 2, 1970 W. HOTINE 3,514,847

PROCESS FOR MAKING PHOTOCONDUCTIVE MATRICES

Original Filed May 10, 1966 3 Sheets-Sheet 1

FIG. 1.



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PROCESS FOR MAKING PHOTOCONDUCTIVE MATRICES

Original Filed May 10, 1966 3 Sheets-Sheet 2

FIG. 2.

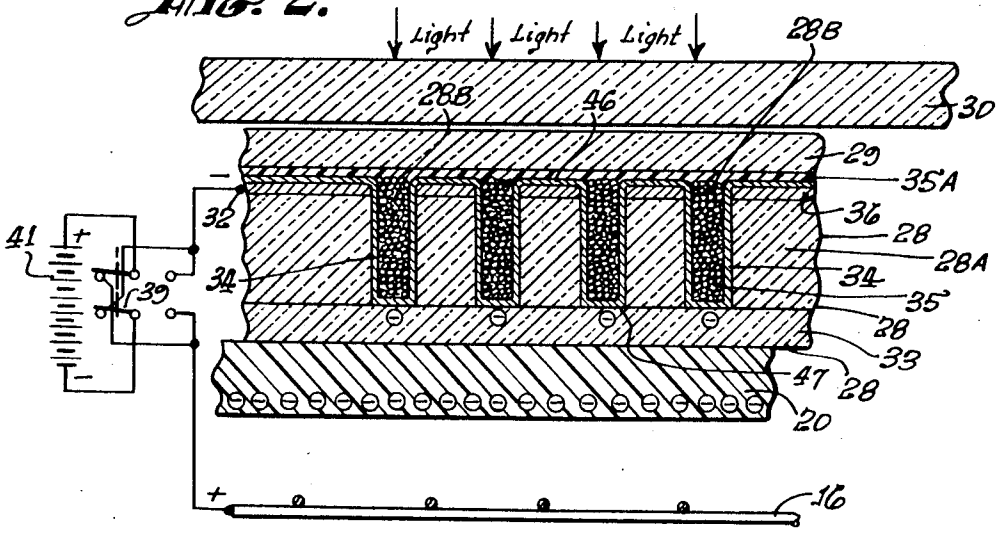
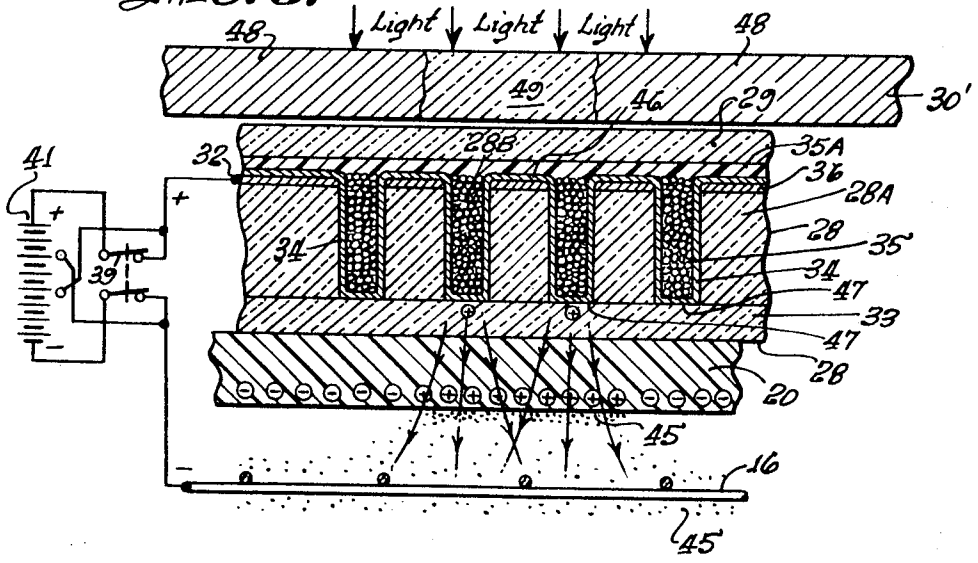


FIG. 3.



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PROCESS FOR MAKING PHOTOCONDUCTIVE MATRICES

Original Filed May 10, 1966 3 Sheets-Sheet 3

FIG. 4.

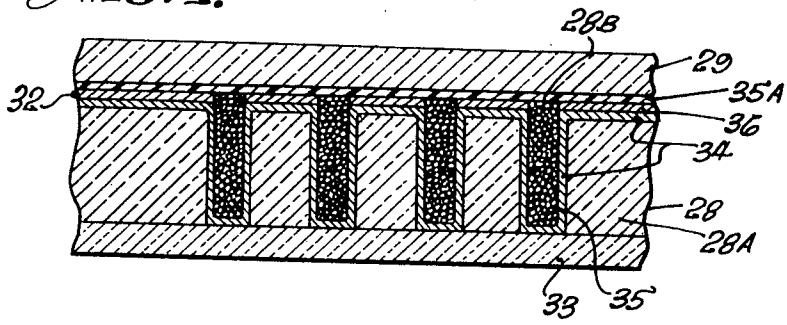
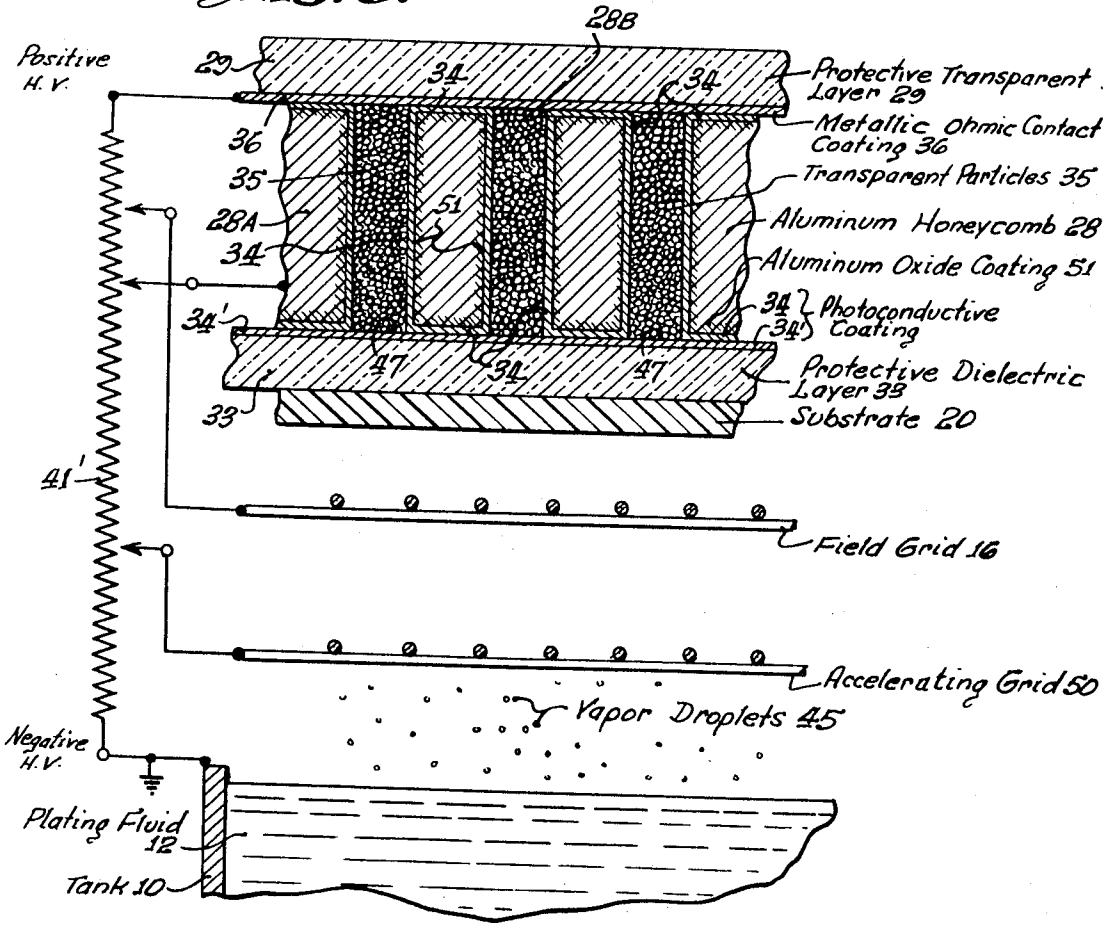


FIG. 5.



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3,514,847

PROCESS FOR MAKING PHOTOCONDUCTIVE MATRICES

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Original application May 10, 1966, Ser. No. 548,888. Divided and this application Oct. 22, 1968, Ser. No. 803,495

Int. Cl. H01l *15/02*

U.S. Cl. 29—572 3 Claims

ABSTRACT OF THE DISCLOSURE

A process for making photoconductive matrices by forming a layer of aluminum oxide by anodizing perforated aluminum, a photoconductive coating is then applied to the oxide layer, the perforations are masked, a metallic layer is then applied on the exposed photoconductive coating and the mask removed. Next a layer of photoconductive material is applied across the perforations opposite the metallic layer, connecting the protective layer to the photoconductive material, insering light scattering material is the perforations and finally attaching a protective transparent layer.

This application is a division of Ser. No. 548,888, filed May 10, 1966.

This invention relates to vapor plating, and particularly to an electrostatically controlled method and apparatus for vapor plating utilizing an electroless plating solution to deposit a printed circuit on an insulating substrate without the use of masking processes.

Previous maskless or screenless electrostatic printing devices have utilized a thin layer of homogeneous photoconductive material as a medium for the generation of an electrostatic analogy of a visible pattern. The electrostatic analogy or image is a graduation of the values of electrostatic charges of one polarity on the surface of the photoconductive layer. A layer of insulating material has been placed in an electrostatic field above this electrostatic image so that minute particles charged to the opposite polarity are accelerated toward and attracted to the image and are deposited on the surface of the insulating material to form a visible reproduction of the original visible pattern. In this prior system, there is no positive means to positively prevent the unwanted deposition of particles in blank white areas of a black pattern.

The present invention is an improved system for electrostatic control of the deposition of either solid or liquid particles of one polarity on the surface of an insulating layer or substrate. The present invention provides an electrostatic image composed of charges of two polarities, one of which attracts the particles to form black areas of a visible pattern, the other polarity repels the particles to prevent their unwanted deposition on blank white areas of a black pattern.

The electrostatic image of the present invention is formed on the surface of an insulating layer or substrate by means of an underlying novel, snythetic photoconductive matrix which is fabricated in such a manner that it has the necessary desirable properties for the generation of an electrostatic analogy of a visible pattern.

Therefore, it is an object of this invention to provide an improved maskless method and apparatus for electrostatic deposition of a visible pattern on a substrate which employs charges of two polarities on said substrate to enable improved contrast and definition.

A further object of the invention is to provide an improved maskless method and apparatus for electrostatically controlling the deposition of an electroless plating solution on an insulating substrate to form a printed circuit.

Another object of the invention is to utilize a film negative of a visible pattern to control the deposition of either solid or liquid particles on a substrate to form a reproduction of the visible pattern on the film.

Another object of the invention is to provide a method for an automatic continuous process of production of printed circuits without the use of masking or etching processes.

Another object of the invention is to provide a method and apparatus for electroless vapor plating on a layer of plastic.

Another object of the invention is to provide a method and apparatus for depositing different thicknesses of plating on selected areas of an insulating substrate without the use of masking or screening processes.

Another object of the invention is to accomplish the above objects in air at normal barometric pressure, and at normal temperatures.

Other objects of the invention will become readily apparent from the following description and accompanying drawings wherein:

FIG. 1 is a view partially in cross section of a first embodiment of the inventive apparatus for carrying out the method thereof;

FIGS. 2 and 3 are enlarged views illustrating the operation of the method by the FIG. 1 apparatus;

FIG. 4 illustrates an alternate construction of the conductive matrix assembly; and

FIG. 5 is a partial view, partly in cross section, of another embodiment of the inventive apparatus.

Broadly, the invention relates to an electrostatically controlled method and apparatus for vapor plating, using an electroless plating solution to deposit a printed circuit on an insulating substrate without the use of masking processes. More particularly, the subject apparatus includes a tank of electroless plating solution for providing a cloud of small droplets of said solution, a grid suspended over said tank for imparting a negative charge to said droplets, a substrate on which a printed circuit is to be vapor deposited, a photoconductive glass or aluminum matrix plate for conveying a desired charge to said substrate, a film negative for selectively illuminating said matrix plate, and a source of light.

With the conductive matrix plate being constructed of glass, for example, as shown in the FIG. 1 embodiment, the glass plate is provided with closely spaced holes over its area with a thin opaque glass layer cemented to the bottom surface thereof for covering the bottoms of said holes. A metallic conductive layer is placed on the upper surface of said glass plate, said holes extending therethrough. The inside surfaces of said holes and the top of the metallic conductive layer are coated with a thin layer of photoconductive material. Transparent particles are used to fill said holes and are there retained by a transparent plastic covering deposited over the thin layer of photoconductive material. A voltage source is connected to the conductive layer for selectively applying positive and negative charges thereto.

By way of operation of the FIG. 1 embodiment, for example, a negative charge is placed on the metallic conductive layer of the matrix. The light source is then energized for a period long enough to allow a negative charge to be conveyed to the substrate. A film negative having the pattern of the desired printed circuit is then placed between the matrix and the light source while the metallic conductive layer is positively charged. The light source is again energized and the pattern of positive charges in the design of the desired printed circuit is caused to be placed on the substrate. Negatively charged vapor droplets are thereby attracted to the positively charged portions of the substrate forming a vapor deposited printed circuit.

The FIG. 5 embodiment is generally similar to the above

briefly described FIG. 1 embodiment except that the photoconductive matrix plate is constructed of aluminum, and that a different type electrical control arrangement is utilized.

Referring now to FIG. 1, a metal tank **10** which is provided with a noncorrosive lining **11** contains an electroless plating solution **12**. An ultrasonic transducer **13** is suspended and submerged in solution **12** by its electric leads **14** connecting to an ultrasonic generator **15**, which is supplied power from a source through switch **15A**. A wire grid **16** of noncorrosive material is held by conductive supports **17** and **18** and is placed in an opening **19** which is in the upper side of tank **10**. Above opening **19** is placed a substrate **20** which is made of an insulating plastic such as Mylar. The edges of substrate **20** rest on an insulating lining **21** of metal enclosure **22** which contains a light assembly **23**, supplied with power through switch **23A**. The underside **24** of substrate **20** is exposed to the air indicated at **25** in tank **10**. A polished curved metal reflector **26** is located on supports **27** at a position below opening **19** in solution **12**, and in a position to reflect output energy of transducer **13** to the surface of the solution. Above the substrate **20**, within lining **21** of enclosure **22**, are located, lying in order, a photoconductive matrix plate **28**, a film negative **30**, and a transparent retaining plate **31**. As shown in FIG. 1, the last described elements are greatly enlarged for clarity.

The photoconductive matrix plate **28** is a glass plate **28A** having closely spaced small through holes **28B** over its area with a cemented-on thin opaque bottom layer **33** of opaque glass or other insulating material which closes the bottoms of the holes **28B**. The inside surfaces of the holes and areas on the top of a conducting metal layer **36** are coated with a thin layer of a photoconductive material **34** such as cadmium sulphide. The holes **28B** are filled with micron sized transparent particles **35** made of glass or plastic, and a transparent plastic coating **35A** is used to retain the particles in the holes. The conductive layer **36** of metal is deposited on the top of glass plate **28A** before the deposition of the cadmium sulphide, to act as an electrical contact to the areas of photoconductive layer **34** at the top of the holes **28B**. An electrical connection **32** is made to layer **36** and brought out by lead **37** through insulator **38** mounted in enclosure **22**. Lead **37** is connected to double pole polarity reversing switch **39**, which is wired to voltage selector switch **40** and tapped power supply **41**, symbolized by a battery of polarity shown. Tank **10** is grounded permanently for safety and the power supply **41** is ungrounded. Ventilation openings **42** are provided in enclosure **22**, which do not admit external light but which admit cooling air for light assembly **23**. A slit **43** is also provided in enclosure **22** for insertion and removal of film negative **30**. Another slit **44** in enclosure **22** is provided for insertion and removal of substrate **20**, the upper side of which is in contact with the lower side of the photoconductive matrix **28**.

Referring to FIG. 2, a greatly enlarged sectional view is shown of portions of the illuminated photographic negative **30**, the photoconductive matrix **28**, the substrate **20**, and the grid **16** which are located in or above opening **19** of tank **10**. In FIG. 2, operation of the process is started by throwing switch **39** to the left to establish the voltage polarities shown, with the metallic conductive layer **36** connected to the negative, and grid **16** connected to the positive of the power supply **41**. A completely transparent film **30** is inserted in slot **43** and switch **23A** is closed to light assembly **23** thus illuminating film **30**. The light, as indicated by the arrows, shines through film **30**, transparent layer **29**, transparent layer **35A**, and impinges on holes **28B**. The light which penetrates holes **28B** is scattered by particles **35** as it penetrates the holes, so that the photoconductive coating **34** on the sides of the holes is illuminated. When coating **34** is illuminated its resistance is lowered by a factor of approximately 10^4 to 10^5 thus providing a relatively good conductive path of 10^3 to 10^4 ohms from the top areas **46** of coating **34** to the bottom **47** of the holes. The top areas **46** are deposited on conductive layer **36** and are thereby electrically connected to layer **36**. Electron movement caused by the E.M.F. between grid **16** and the bottom **47** of holes **28B** will cause the bottom surface of the substrate **20** to acquire negative charges as shown in FIG. 2. The bottom surface of substrate **20** is thus charged negatively over its entire surface area. Light assembly **23** is then extinguished by opening switch **23A**, and switch **39** is opened. The above-described sequence requires only a few milliseconds to charge substrate **20**, with power supply **41** giving suitable voltage.

A film negative **30'** of the desired printed circuit is substituted for the transparent film **30** as previously set forth above to continue the operation sequence. As can be seen in FIG. 3, the enlarged view shows film negative **30'** in position, having a circuit pattern defined by opaque areas **48** and transparent areas **49**. Switch **39** is then closed to the right, as shown in FIG. 3, thus reversing the former voltage polarities and making the metallic conductive layer **36** positive and the grid **16** negative. Switch **23A** is now closed, lighting assembly **23** and illuminating the top of film negative **30** as shown by arrows. The transparent portions **49** of negative **30'** will allow light to strike the tops of holes **28B** underneath these areas, the light penetrating the holes and being scattered by particles **35** to illuminate the layer **34** on the sides of the holes. When layer **34** is illuminated, its resistance is lowered by a factor of about 10^4 to 10^5 thus providing a relatively good conductive path from the positively polarized layer **36** and the top areas **46** of coating **34** to the bottoms **47** of the holes **28B**. Positive charges at the bottoms **47** of the illuminated holes will migrate through the dielectrics to the under surface of substrate **20**, following the approximately vertical electrostatic lines of force which extend to the negative electrode **16**, as indicated by the arrows, and these positive charges will first cancel the existing negative charges in the local areas under the illuminated holes, and then will accumulate on the under surface of substrate **20** in these areas as shown in FIG. 3. Where light cannot penetrate the opaque portions **48** of film **30'**, the layer **34** will remain a very high (dark) resistance, so that comparatively little negative charge will leak off, thus leaving the negative charges on the under surface of substrate **20** under opaque areas **48** of film **30**. The electrostatic charges on the under surface of substrate **20** are now a replica of the printed circuit pattern on film negative **30**, with positive charges on this surface denoting circuit paths, while negative charges on the surface denote the blank insulating spaces between the circuit paths.

At this point in the process power is applied to the ultrasonic generator **15** of about 50 watts power output, for example, by closing switch **15A**. The output of generator **15** is at a frequency of approximately 2 megacycles and is applied to transducer **13**, which transforms the electrical energy input to sonic vibration. This vibrational energy is directly transmitted in solution **12** to impinge on reflector **26**, which changes the direction of the ultransonic energy to a direction toward the surface of solution **12**. Due to the curvature of reflector **26** random direction interferences of the sonic energy take place at the solution surface which act to break up the surface and produce very small droplets **45** of approximately one micron diameter which are impelled upwards into the atmosphere. The droplets **45** are denoted by the dots in FIGS. 1 and 3. The cloud of droplets rises, forming a vapor which passes through grid **16**, the individual droplets **45** acquiring negative charges from grid **16**. The electrostatic field gradient between grid **16** and the positive charges on the under surface of substrate **20** accelerates these negatively charged droplets **45** toward these positively charged areas, where the droplets are deposited and are merged together by their surface tension. Negatively charged areas will repel the droplets so they are not deposited on these areas as shown on FIG. 3. Switch **40** is adjusted for optimum

voltage for vapor plating at this point in the process. The plating can then be continued for the time required to deposit the desired thickness of metal on substrate **20**. When this desired thickness is attained, all switches are opened and substrate **20** is removed via slit **44**, rinsed and dried.

The chemical preparation of the surface of substrate **20** includes the following steps for a silver electrostatic electroless vapor plating of a printed circuit on a plastic substrate. In the following procedure, a rinsing stage in clean water occurs between each of the steps.

(1) Roughen under surface of substrate for mechanical bonding of the deposited metal to this surface.

(2) Clean in alkaline solution or detergent.

(3) Oxidize slightly in chromic acid solution for surface wettability.

(4) Treat surface to be deposited on with stannous chloride solution, which acts as a catalyst to cause metal precitation from an electroless plating solution.

(5) Dry.

At this point in the preparation process the substrate **20** is ready to use in the plating process described above. Solution **12** in the plating process, for example, may be a standard well known silver electroless plating solution. Other metals may be deposited by using other suitable electroless solutions.

The method of generating the vapor droplets **45** which was described above is known in the prior art, but has not been previously applied in an electroless plating process. Other alternate well known methods of forming vapor droplets, or a mist, such as an atomizer gun, may be used, with suitable modifications of the tank **10** of FIG. 1.

The mechanical arrangement of the apparatus of FIG. 1 is novel, in that only by such an assembly can the provision be made for exposure of only one side of the substrate to the plating vapor, while the substrate itself is utilized to protect the photoconductive matrix from undesired deposit of metal.

The method of operation described above is novel, in that it enables the charging of the under surface of substrate **20** with an electrostatic analogy of the circuit pattern on film negaive **30'**, and which enables maintaining this charge pattern while the deposition of charged vapor droplets **45** is taking place on desired oppositely charged areas while the droplets are repelled and excluded from undesired areas charged to the same sign (polarity) as the vapor droplets. This method of operations dispenses with mechanical masks or screens formerly used in electrostatic depositions.

The method described also enables the thickening of the plating deposition in selected areas by first depositing these areas only, controlled by one negative, and then depositing the entire pattern over these thickened areas, by use of a second negative registered in position with the first. This method enables great accuracy in dimensions of printed circuits as it eliminates the steps of masking and mask fabrication with their accompanying errors.

Also, the above described method is adaptable to a continuous process of production by suitable modifications. The film can be made a continuous strip, and the substrate a continuous tape, fed through a machine in synchronism while the plating deposition takes place. Various solutions in succeeding tanks may be used to deposit various metals such as resistor materials, and to deposit other materials such as dielectrics for capacitors.

A major element of the invention is the novel photoconductive matrix **28**. The use in matrix **28** of the transparent particles **35** to scatter light entering the hole and thus illuminate the photoconductive layer **34** on the sides of the hole is new. The particles **35** may have an optimum size and can be made of an optimum material for the particular wavelengths of light employed to illuminate the hole. Other methods or materials might be here employed if they accomplish the purpose of scattering the light which enters the hole vertically, to illuminate the sides of the hole, such as fiber optical elements which are finished with smooth end and roughened side surfaces. The holes are formed in glass sheet **28A** by chemical machining or etching, and have been produced as small as 800 holes to the linear inch or 640,000 holes per square inch. The resolution of the system, or resultant definition and tolerance of the printed circuit conductor outline and size in a direct function of the hole size and hole spacing.

The process of making the photoconductive matrix, for example, follows the steps given below:

(1) Clean the perforated glass sheet **28A**.

(2) Vacuum deposit conductive layer **36**, while masking holes **28B'**. Layer **36** may be of metal indium if the photoconductive layer **34** is cadmium sulphide.

(3) Remove the masking from holes **28B**.

(4) Cement plate **33** on the bottom of glass sheet **28A**, thus closing the bottoms of holes **28B**. Plate **33** is opaque to light.

(5) Vacuum deposit photoconductive layer **34** over the surface of conductive layer **36** and on the sides and bottoms of holes **28B**. Layer **34** may be cadmium sulphide.

(6) Vacuum deposit sensitizer on top of photoconductive layer **34**. Sensitizer may be 0.6% copper by weight of the cadmium sulphide layer.

(7) Fill holes **28B** with transparent micron size particles of glass or plastic **35**.

(8) Deposit transparent layer **35A** over the top of layer **34** and particles **35**. Layer **35A** may be a transparent plastic cement.

(9) Cement protective transparent layer **29** over layer **35A**. Layer **29** may be glass.

FIG. 4 illustrates an alternate construction of the photoconductive matrix **28** wherein layer **36** is deposited on top of layer **34** after holes **28B** are filled with masking particles, removing these masking particles after the deposition of layer **36** and then filling the holes with operative transparent particles **35**. This construction makes an ohmic connection from layer **36** to the top surface of layer **34** instead of to the bottom surface thereof as shown in FIGS. 1–3.

The operating voltages have not been given for the operation of the FIG. 1 electrostatic plating apparatus as these are subject to variation according to dimensions and thicknesses of apparatus components.

FIG. 5 illustrates a modified embodiment of the FIG. 1 apparatus having a matrix plate of aluminum, perforated with holes like a honeycomb, anodized to produce a coating of aluminum oxide over the entire surface of the plate including the interior of the holes This construction enables the use of the aluminum plate as an element of the electrostatic control circuit, which enables a more simplified operation of the electrostatic control of the vapor droplet deposition than previously described. Briefly, the potential of the aluminum matrix plate is such as to maintain a repellent charge over its area except at the photoconductive holes which are illuminated. An illuminated hole conducts an attractive charge potential through the matrix plate and thus attracts charged vapor droplets to its location.

Referring now to FIG. 5, wherein like elements are given the same numerals as set forth with respect to the FIGS. 1–3 apparatus, the photoconductive matrix **28** is fabricated from an aluminum base **28A** by forming holes **28B** over its area to produce an aluminum honeycomb. A layer of aluminum oxide **51**, indicated by cross hatching, is formed on the entire surface of the aluminum plate, including the holes **28B**, by an anodizing process. A photoconductive coating **34** is deposited by vacuum evaporation techniques to cover the entire surface area, over the aluminum oxide **51** which is an insulator. After masking holes **28B** on the top surface by filling them with particles, a metallic ohmic connection layer **36** is also deposited by vacuum evaporation or other suitable techniques, to make an ohmic contact with the upper surface of the photoconductive coating **34** Conductive layer **36**

covers the top of holes **28B** but is sufficiently thin to be transparent, thus allowing light to pass therethrough. The masking particles are removed from holes **28B** and a protective dielectric layer **33**, which has a photoconductive coating **34'** on its upper surface, is cemented to the bottom of the matrix **28**, so that the holes **28B** are closed at the bottom by the photoconductive coating **34'**. Transparent particles **35** are used to fill the holes **28B** and are retained by a protective transparent layer **29** cemented to the top of matrix **28**. The transparent particles **35** act to scatter light entering holes **28B** in a vertical direction so that the light illuminates the photoconductive coating **34** on the sides of the illuminated holes **28B** and lowers the resistance of the coating. Thus, when light enters a hole, the charging potential of the connection layer **36** will be conveyed to the bottom **47** of that hole. If light does not enter a hole, the charging potential at the bottom of that hole will be very small due to the very high resistance of the photoconductive layer **34** on the sides of that hole. Therefore, a pattern of charges on the bottom of matrix **28** can be generated, which will be the image of the light pattern falling on the top surface of the matrix **28**.

In the electrical control arrangement of the FIG. 5 embodiment, an accelerating grid **50** has been added to provide control of vapor droplets **45** and to enable the reduction of the potential of the field grid **16**. No switching of potentials is necessary in this embodiment because the aluminum matrix **28** is at a higher potential than the potential of the field grid **16** which results in a repellent charge effect which was obtained in the FIG. 1 apparatus by switching potential polarities. In the FIG. 5 embodiment, the potential may be varied by movement along the resistor **41'** supplied by a power source as previously described.

It has thus been shown that the present invention provides an electrostatically controlled method and apparatus for vapor plating utilizing an electroless plating solution to deposit a printed circuit on an insulating substrate without the use of masking processes.

While specific embodiments have been illustrated and described, modifications will become apparent to those skilled in the art, and it is intended to cover in the appended claims all such modifications as come within the true spirit and scope of the invention.

What I claim is:

1. A process for making photoconductive matrices adapted for electrostatic vapor plating comprising the steps of: anodizing perforated aluminum to provide a layer of aluminum oxide over the entire surface thereof, depositing a photoconductive coating over the entire surface of the oxide layer, masking the perforations, applying a metallic layer on the exposed surface of the photoconductive coating on one side of the aluminum; removing the masking; applying a layer of photoconductive material across at least the end of the perforations opposite the metallic layer; connecting a protective layer of dielectric material to at least the photoconductive material; inserting light scattering material in the perforations; and attaching a protective transparent layer to the metallic layer for retaining the light scattering material within the perforations.

2. The process defined in claim **1**, additionally including the step of perforating the aluminum prior to the anodizing step.

3. The process defined in claim **1**, wherein the layer of photoconductive material is first attached to the layer of dielectric material prior to attaching same to the photoconductive coating opposite the metallic layer.

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U.S. Cl. X.R.

136—89