Dec. 4, 1956 P. G. HERKART 2,772,654

APPARATUS FOR APPLYING A CONDUCTIVE COATING TO THE INSIDE OF A TUBULAR GLASS ENVELOPE

Filed June 6, 1952 2 Sheets-Sheet 1

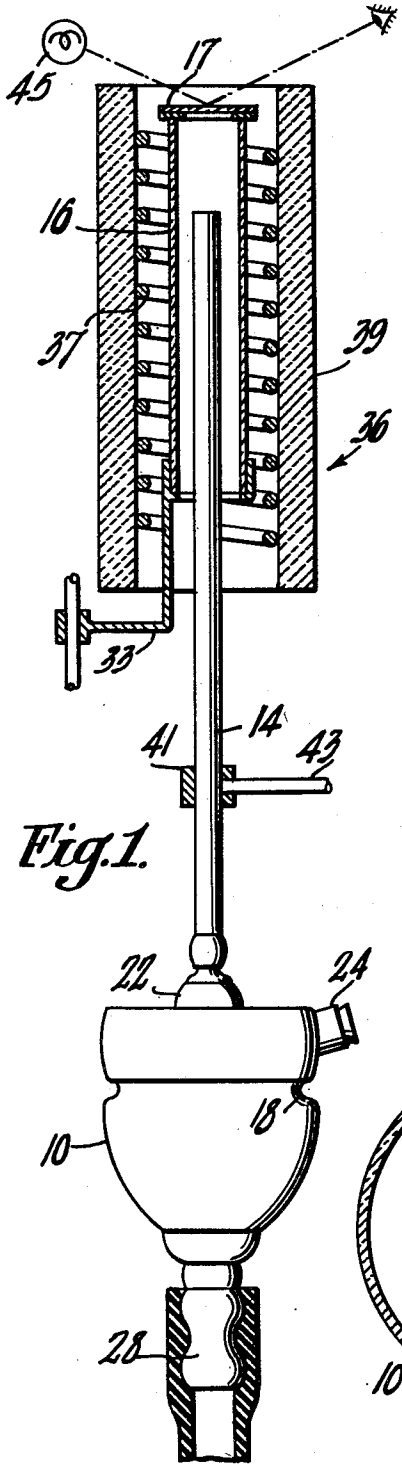


Fig. 1.

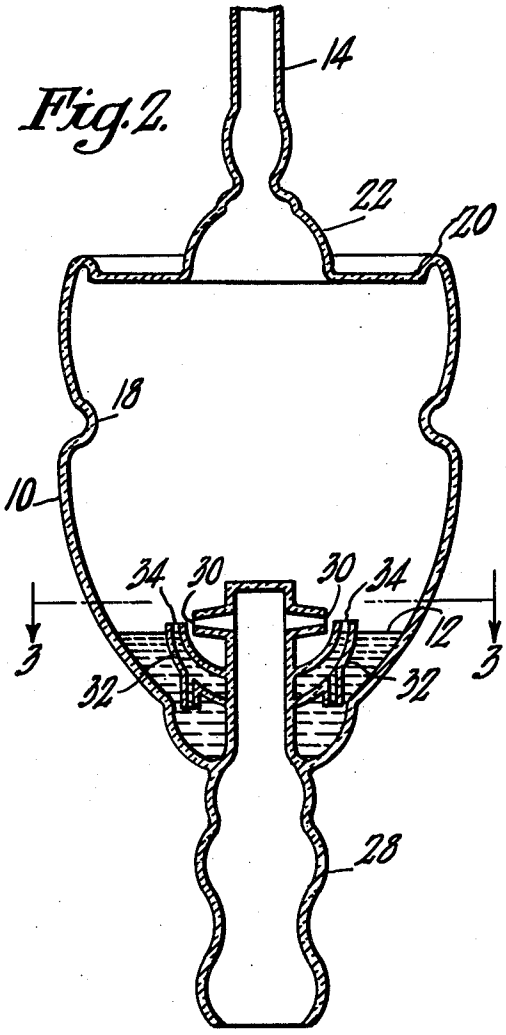


Fig. 2.

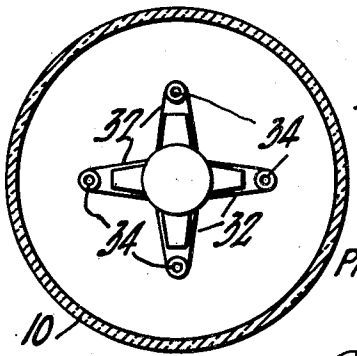


Fig. 3.

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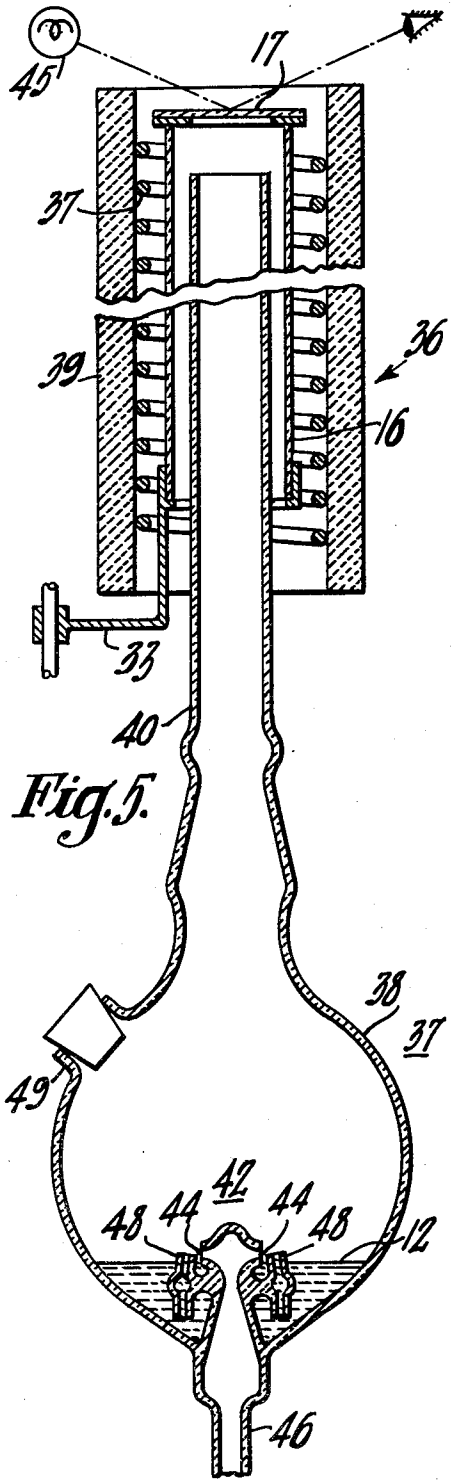


Fig. 5.

Fig. 4.

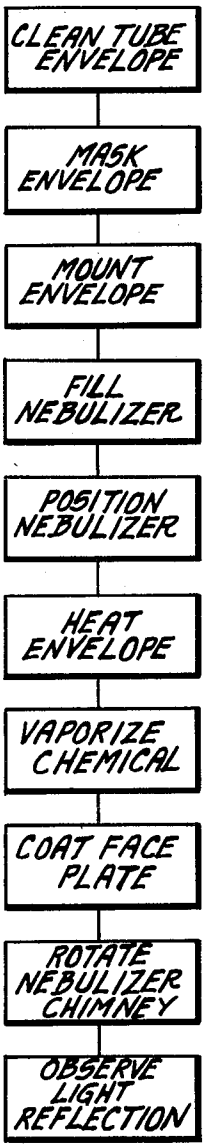
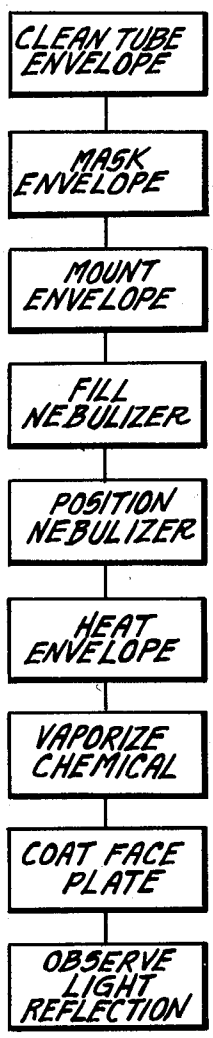


Fig. 6.



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APPARATUS FOR APPLYING A CONDUCTIVE COATING TO THE INSIDE OF A TUBULAR GLASS ENVELOPE

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Application June 6, 1952, Serial No. 292,156

The terminal fifteen years of the term of the patent to be granted has been disclaimed

3 Claims. (Cl. 118—48)

This invention relates to apparatus for applying a coating of a chemical substance to a predetermined area on the inner surface of a hollow vessel, more particularly to an electron tube envelope of elongated tubular structure.

There are at present many types of electron tubes which utilize coatings of the type which may be applied by the apparatus of this invention. One type of coating is the transparent conductive coating which is used in many electronic devices including camera pickup tubes, viewing tubes and the like. One example of a pickup tube includes an envelope having a target assembly formed with a supporting transparent face plate sealed to the envelope by means of a conductive ring made of a cobalt-nickel-iron alloy or the like. The face plate is first coated with a transparent conductive film or signal plate and then, secondly, with a layer of known photoconductive material, over the conductive film. This target assembly is prepared on the end or face plate of an elongated tubular envelope with the photoconductive coating facing an electron gun structure which produces an electron beam substantially normal to the photoconductive surface. Either electrostatic fields or electromagnetic fields can be used to cause the electron beam to scan, in closely spaced parallel lines, over the surface of the photoconductive target layer.

The scanning of the electron beam over this photoconductive layer establishes an electrical charge on the photoconductive layer and stabilizes the surface of the photoconductive film at an equilibrium potential. A potential is applied to the conductive signal plate of the target assembly which is several volts removed from the equilibrium potential established on the photoconductive surface. In this manner, then, a difference of potential is established between the two surfaces of the photoconductive film. Due to the photoconductive properties of the material used, when light is focused upon the photoconductive film, a current will flow through the film in the illuminated areas, and will change the potential of these areas in the direction of the potential of the conductive film. Areas of the film not illuminated by the light will have little or no current flow depending upon the resistivity of the photoconductive material in the dark and will thus remain at the equilibrium potential established by the beam. The electron beam upon scanning over the photoconductive film areas illuminated by light, will return the illuminated film areas to equilibrium potential. Since the signal plate is capacitively coupled with the scanned surface of the photoconductive film, the instantaneous charging of the film by the beam to equilibrium potential will be evidenced by a voltage change in the circuit of the signal plate. This voltage change becomes the output signal of the tube.

Previously, conductive coatings of the type under consideration have been applied to work pieces by a spraying process. However such a process is unsatisfactory for applying a conductive coating to the interior of a container or vessel, such as an elongated electron tube envelope. When the spraying process is attempted with electron tube envelopes, it is found that a very fine vapor or spray is required but that such a vapor cannot be introduced into the envelope and directed to the area to be coated with ease. A further defect is that large droplets of the chemical material in the vapor produce a spotted, blemished and nonuniform surface or film. Such a defective conductive film prevents proper operation of the completed tube due to abrupt changes in the resistance of the film. In addition, the spots and blemishes may appear in a transmitted picture.

In addition it is necessary to control the thickness of deposition of the conductive film in order to control the resistance of the film since for optimum results, the resistance of the film must fall within a comparatively narrow range of values. Techniques previously used made it difficult to do this.

Accordingly, the principal object of this invention is to provide an improved apparatus for applying a coating to a predetermined area within a container.

A further object is to provide an improved apparatus for depositing a transparent conductive film of conductive chemical material on a predetermined area within an elongated electron tube envelope.

Another object is to provide an improved apparatus for applying a uniform film to a predetermined area within a container.

A further object is to provide an improved apparatus for introducing a fine vapor of a chemical into a tube envelope and for depositing the vapor as a uniform film on a predetermined area within the envelope.

A still further object of the invention is to provide an improved apparatus for forming a fine vapor spray of a chemical and for removing comparatively large droplets from the spray.

Another object of the invention is to provide an improved apparatus for accurately controlling film thickness and resistance of the transparent conductive film being formed.

In general the purposes and objects of this invention are accomplished by the provision of a device having a bulb portion for containing the chemical material or fluid to be deposited as a coating within an electron tube envelope. The bulb portion is provided with means for atomizing and vaporizing the chemical fluid contained therein. An elongated outlet tube or pipe extends from the bulb and serves both as an outlet for the vaporized chemical and as a means for vaporizing fine droplets of chemical. As an important feature of the invention, the bulb is designed and provided with structure for breaking up and/or retaining large droplets of the vaporized chemical within the bulb and allowing only a fine spray to pass through the outlet tube. By arranging the apparatus to provide visual observation of the color changes of reflected light from the area being coated the thickness of the film and the resistance can be determined and the operation terminated at the proper time to obtain the desired results.

The invention is described in detail with reference to the drawings wherein:

Fig. 1 is an elevation view, partly in section, of the apparatus of the invention in operating position with respect to an electron tube envelope;

Fig. 2 is an enlarged sectional view of a portion of the apparatus shown in Fig. 1;

Fig. 3 is a sectional view along the line 3—3 in Fig. 2 and shows the atomizer arrangement of the invention;

Fig. 4 is a flow chart of some of the steps of a method in which the apparatus of the invention is used;

Fig. 5 is an elevation view, partly in section of a modification of the apparatus shown in Fig. 1; and

Fig. 6 is a flow chart of some of the steps of a method in which the apparatus of Fig. 5 is used.

This invention is of general interest in the coating art, however it is described with particular reference to the application of a transparent conductive coating within an elongated tubular electron tube envelope of the type utilized in camera pickup tubes. One type of pickup tube, to which this invention applies, and its operation, are fully described in the copending United States Patent application, Serial Number 198,130 of S. V. Forgue, filed November 29, 1950, and assigned to the same assignee as the present invention.

According to the invention, apparatus is provided for vaporizing a quantity of the chemical to be introduced into an electron tube envelope closed at one end by a transparent face plate sealed to a metal ring made of a cobalt-nickel-iron alloy or the like. The apparatus is also utilized for introducing the vaporized material into the envelope where it is deposited as a film on the inner surface of the face plate of the envelope and in contact with the metal ring. The apparatus includes a bulb **10** made of glass or some similar non-reactive material in which the chemical material **12** is retained and in which the chemical is vaporized. Also included is an elongated pipe or chimney **14** through which the chemical vapor is carried directly into a tube envelope **16** having a face plate **17**. In one form of apparatus built for coating an envelope having approximately a one inch diameter, the pipe **14** had a diameter of approximately three-eighths of an inch.

The bulb **10** is generally heart-shaped and its inner wall is provided with a peripheral ridge **18** which circles the bulb approximately in the middle thereof. The bulb is also provided with another peripheral ridge **20** running substantially around the top edge thereof. The pipe or chimney **14** is connected to the bulb by means of a stepped connecting portion **22**.

The bulb **10** is provided with an atomizer or nebulizer arrangement for atomizing and vaporizing the chemical retained therein. The atomizer includes a gas inlet tube **28** which extends into the bulb from the center of the bottom thereof. The upper portion of the inlet pipe **28** is formed with a plurality of constricted orifices **30** extending radially outwardly toward the side wall of the bulb. These orifices constitute jets for supplying fine streams of gas which serve to atomize the chemical fluid **12** in the bulb **10**. Also provided within the bulb are a plurality of liquid supply tubes **32** which communicate directly with the pool **12** of chemical so that liquid rises in them to the same level as in the rest of the bulb. These chambers are formed with constricted openings **34** which are positioned adjacent to the jet-like orifices **30** of the gas inlet pipe. By this arrangement the jet-like orifices **30** cooperate with the liquid filled channels **32** to provide a vapor or spray of chemical directed outwardly toward the inner wall of the bulb. This spray includes vapor, fine droplets and large droplets of chemical.

The peripheral ridges **18** and **20** and the connecting piece **22** for the elongated pipe **14** serve to break up or remove large droplets from the chemical vapor or spray formed in the bulb **10**. As the chemical is atomized and the spray is blown toward the inner wall of the bulb, the vapor and fine droplets tend to rise toward the chimney **14**. Whatever vapor or fine droplets are directed against the wall can maneuver easily around the ridges **18** and **20** and the connecting portion **22** on their way upwardly toward the chimney. However, large droplets which strike the ridges **18** and **20** and the portion **22** connot maneuver around these obstacles and are either broken up into fine droplets which are carried along to the chimney by the air flow or they fall back into the pool of chemical **12**. By this means only a fine vapor, including very fine droplets, escapes from the bulb **10** and passes through the pipe **14** and onto the area being coated. The bulb is also provided with a short lateral tube **24** through which the chemical fluid **12** may be introduced.

Referring to the flow chart in Figure 4, in operation of the apparatus, the electron tube envelope **16** to be coated internally is cleaned thoroughly with a cleaning agent, for example a mixture of potassium nitrate and sulfuric acid. The envelope is washed with distilled water and dried. This is necessary because particles of dirt or other foreign matter might cause a spotted and unsatisfactory conductive film. A layer of a suitable masking material is then applied to the inner wall of the envelope **16** to prevent undesired coating of the wall. The envelope is then mounted on a conventional support post or the like by means of a clamping device **33** fastened around the tube envelope.

Next, a quantity of the chemical **12** to be coated is introduced into the bulb **10** through the inlet **24** provided for that purpose. The chemical material concerned herein is a mixture of stannic chloride, water, and methanol. However, the principles of the invention are applicable to other chemicals. The bulb is then positioned with the elongated pipe **14** within the tube envelope **16**. The top of the pipe is disposed relatively close to the target area and for envelopes of the type used in small camera pickup tubes having diameters on the order of one inch, this distance "*s*" actually used was on the order of 2½ to 3 inches. However, this distance depends on the size of the tube envelope, the size of the elongated pipe, and the air pressure to be used in operation of the atomizer and may be varied accordingly.

Next a heating device **36** which may comprise a suitable heating coil **37** surrounded by an insulating member **39** is disposed around the tube envelope, and the temperature of the envelope and the pipe is raised to a temperature as close as possible to the annealing temperature of the glass surface to be coated, such as the face plate glass **17**. If the temperature is too low, the chemical coating deposited thereon becomes cloudy. This is probably due to the fact that the vapor passing up through the pipe is cooled sufficiently to form droplets. Or, it may be that the fine droplets in the vapor spray are not completely vaporized. In any case, the presence of such fine droplets may cause the cloudy appearance of the conductive film. If the temperature is too high, for example on the order of 600° C. for some glasses having annealing temperatures on the order of 500° C., the film may also be cloudy. This is considered to be due to a reaction between the conductive material or the glass and the conductive ring by which the face plate is sealed to the tube envelope. Another possible explanation of the cloudy appearance is set forth below.

A gas, for example air or the like is then admitted to the inlet pipe **28** and is forced through the jet-like orifices **30** at a flow of approximately 20 liters per minute. This pressure is critical for any particular combination of apparatus. However the optimum pressure is different with other bulbs, pipes and tube envelopes in any one case. If the pressure is too low, the coating process takes too long for convenience. If the pressure is too high, the spray entering the pipe **14** contains too many large droplets and a non-uniform, spotted film results. As described above such non-uniformity produces excessive resistance differentials from point to point in the film and, in addition, the non-uniformities often appear in the transmitted picture. By this gas flow means, chemical material **12** is atomized into a fine spray including vapor, fine droplets and large droplets. As the chemical is atomized, it is forced outwardly toward the wall of the bulb. Large droplets in the spray of chemical are blown close to the wall and, as described above, are trapped by the peripheral ridge **18** or are broken up thereby. As the spray rises toward the pipe, other droplets of smaller

size are trapped by the ridge **20** and the stepped structure **22** of the support for the pipe **14**. Finally, a fine spray including vapor and, possibly, a certain amount of fine droplets, is carried upwardly through the pipe **14** to be deposited on the face plate within the envelope. As described above, if the envelope and pipe are sufficiently hot, the fine droplets are converted to vapor and substantially only a uniform vapor reaches the face plate to be coated. As the chemical vapor rises in the pipe **14**, the pipe is slowly rotated around its center position by hand or other suitable means to promote the deposition of chemical uniformly over the entire inner surface of the face plate **17**. One such other means may comprise a collar **41** mounted on the pipe **14** and connected by means of a connecting rod **43** to a conventional device for converting rectilinear motion into rotary motion. After the conductive coating has been formed, the temperature of the oven is slowly lowered and the coated envelope is removed for further processing.

The chemical reaction which takes place as the coating is formed is considered to be as follows: The chemical liquid **12** is a water solution of stannic chloride and methanol. As the chemical solution is atomized, it is carried up the pipe toward the face plate by the mechanical action of the atomizer. At the hot face plate the water and stannic chloride react to form stannic acid and hydrochloric acid. The heat immediately dehydrates the stannic acid to form stannic oxide which frequently exists in a colorless and transparent amorphous state. This is the desired form in the present case. The methanol does not enter into the reaction; it forms the liquid solution for dissolving the stannic chloride pentahydrate into stannic chloride and water. It sometimes happens that, after the chemical solution has been used or exposed to air for a period of time or under other circumstances, a white crystalline precipitate often forms. This is stannic acid. It is possible that this crystalline formation of stannic acid causes the deposited layer to appear cloudy when the tube envelope is not heated to a sufficiently high temperature during the procedure set forth above.

One chemical mixture actually applied as a coating included approximately 92% of stannic chloride pentahydrate and approximately 8% of methanol. Using such a mixture, it has been determined that a resistance between the edge and center of the layer of approximately 1000 ohms is desirable. It has also been determined that light reflected from a source **45** by the conductive layer has a color which depends on the thickness of the layer. As the conductive material is deposited on the face plate and as the thickness of the coating increases, the color of the reflected light changes in the following order: white, first yellow, red, violet, blue, green, second yellow. Resistance measurements as described above have indicated that a coating which has a resistance of approximately one thousand ohms reflects light which is blue-green in color. Accordingly, the evaporation procedure is carried out until such a color appears in the light reflected from the deposited screen. For an electron tube of the type described above having a diameter of approximately one inch, the evaporation procedure is carried out for a time on the order of one to two minutes to achieve the desired coating.

If it is desired to coat the side wall of the tube envelope, a shield is first inserted into the envelope to protect the coated face plate from further condensation of the conductive chemical. After such provision has been made the envelope is raised the desired distance above the outlet of the elongated pipe and the vaporization process is continued as desired.

In another embodment of the invention shown in Figure 5, a nebulizer apparatus is shown by which a coating of conductve material may be deposited on the face plate of the electron tube envelope without rotating any portion of the device to achieve the desired coating. This

nebulizer **37** includes a generally heart-shaped bulb **38** which, in this instance has substantially smooth inner and outer walls. If desired, the ridges **18** and **20** utilized in the apparatus shown in Figure 3 may be employed. Extending from the bulb is a comparatively wide pipe or chimney **40** having a diameter substantially larger than the diameter of the pipe shown in Figure 3 and approaching in size the diameter of the tube envelope **16**. In this embodiment the pipe had a diameter between ⅝ and ¾ of an inch for a tube envelope having a diameter of one inch. The bulb is also provided with an atomizer arrangement **42** including a jet-like orifice **44** connected to a gas inlet pipe **46** and a liquid storage tube **48** communicating with the fluid **12** within the bulb. The orifice **44** and the storage tube **48** are designed and positioned so that when the liquid **12** is atomized, it is blown toward the wall of the bulb where large droplets are broken up or condensed. A tube **49** is also provided in the wall of the bulb for filling the bulb with the chemical liquid **12**.

The operation of this apparatus is similar to that set forth for the apparatus shown in Figures 1–3 except for certain variables determined by the geometry of the system. A flow chart for this apparatus is shown in Figure 6. The nebulizer **37** is positioned with the chimney **40** within the tube envelope to be coated so that the axis of the pipe or chimney is concentric with the axis of the tube envelope **16**. Because of the relationship set forth above whereby the spacing *"s"* is inversely proportional to the diameter of the chimney, the open upper end of the chimney is positioned comparatively close to the face plate to be coated. In this instance the optimum spacing *"s"* is on the order of ⅜ of an inch. With the apparatus thus assembled the heating device **36** is positioned around the envelope **16** and the portion of the chimney contained therein and the parts are heated as close as possible to the annealing temperature of the glass envelope. Air is then introduced into the air line **46** from which it emanates through the jet-like orifice **44** and atomizes a quantity of liquid in the storage tube **48**. With the shape of bulb employed in this instance, to achieve as fine a spray or vapor as possible, an air flow on the order of ten cubic feet per hour is employed. This flow is satisfactory for a bulb of the type shown and having no auxiliary droplet trapping means. With this air flow, the chemical fluid is atomized and blown in the direction of the wall of the bulb. Substantially only vapor and a small quantity of very fine droplets are blown up into the chimney **40** in the direction of the face plate **17**.

The remainder of the procedure is substantially as described above. With the apparatus of this embodiment the layer of conductive material is somewhat thicker at the center than it is at the sides. However, the difference in thickness is so gradual and of such light magnitude that no appreciable defects in operation result.

In this embodiment a chemical mixture was employed which included approximately 83% of stannic chloride pentahydrate and approximately 17% of methanol. For this mixture, a resistance from the edge to the center of the conductive layer in the range of 200 to 300 ohms is desirable. To achieve such a layer, the chemical vapors are deposited until light reflected from the center of the coating passes through the color range set forth above and reaches the second yellow.

What is claimed is:

1. Apparatus for forming a transparent conductive coating on the inner closed end of an elongated tubular glass envelope, said apparatus comprising a support for said envelope, heating means near said support and adapted to surround said envelope and apply heat thereto, a hollow container near said heating means for holding a quantity of coating substance at one end thereof, a vaporizer within said container at said one end thereof for vaporizing said substance and directing the vaporized substance against the inner wall of said container, said vaporizer including a gas inlet tube provided with a plu-

rality of restricted orifices extending radially outward towards the wall of said container and a plurality of liquid supply tubes having restricted openings positioned adjacent to said restricted orifices, a tubular member at another end of said container extending from and communicating with the interior of said container and adapted to have one end inserted within said tubular envelope with said one end closely adjacent to the area to be coated, and means including a peripheral ridge on the inner wall of said container intermediate said vaporizer and said tubular member for removing droplets from the vaporized substance.

2. Apparatus for forming a transparent conductive coating on the inner end of an elongated tubular glass envelope having a diameter on the order of one inch, said apparatus comprising a support for said envelope, heating means near said support and adapted to surround said envelope and apply heat thereto, said heating means including a heating coil and an insulating member surrounding said coil, a container near said heating means for holding a quantity of the coating substance, a vaporizer within said container at one end thereof for vaporizing said substance and directing the vaporized substance against the inner wall of said container, said vaporizer including a gas inlet tube provided with a plurality of restricted orifices extending radially outward towards the walls of said container and a plurality of liquid supply tubes having restricted openings positioned adjacent to said restricted orifices, a tubular member at another end of said container having a diameter of approximately ⅜ of an inch and extending from and communicating with the interior of said container and adapted to have one end inserted within said tubular envelope with said one end approximately 2½ inches from the area to be coated, means for removing droplets from said vaporized substance including a peripheral ridge on the inner wall of said container intermediate said vaporizer and said tubular member and a restriction in said tubular member, and means for rotating said tubular member around the

longitudinal axis of said envelope to apply an even coating on the surface to be coated.

3. Apparatus for forming a transparent conductive coating on the inner end of an elongated tubular glass envelope having a diameter on the order of one inch, said apparatus comprising a support for said envelope, a heating coil near said support and adapted to surround said envelope and apply heat thereto, a container near said heating means for holding a quantity of the coating substance, a vaporizer within said container at one end thereof for vaporizing said substance and directing the vaporized substance against the inner wall of said container, said vaporizer including a gas inlet tube provided with a plurality of restricted orifices extending radially outward towards the wall of said container and a plurality of liquid supply tubes having restricted openings positioned adjacent to said restricted orifices, a tubular member at another end of said container having a diameter of approximately ⅝ to ¾ of an inch, said tubular member having one end extending from and communicating with the interior of said container and the other end extending within said heating coil and adapted to be inserted within the tubular envelope with said other end approximately ⅜ of an inch from the area to be coated and means including a peripheral ridge on the interior wall of said container intermediate said vaporizer and said tubular member for removing droplets from the vaporized substance.

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