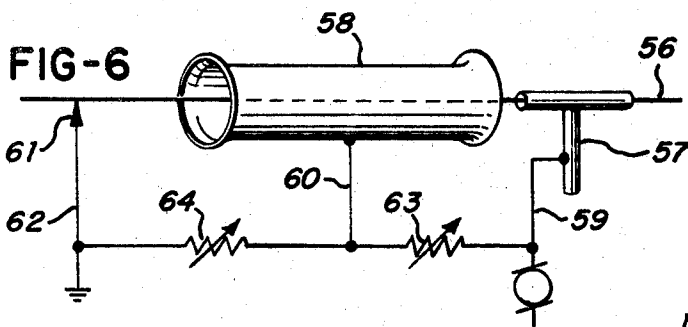
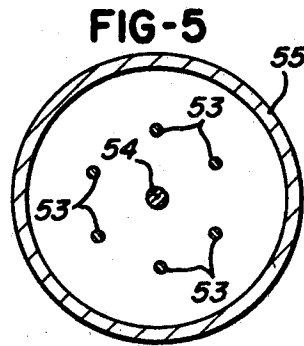
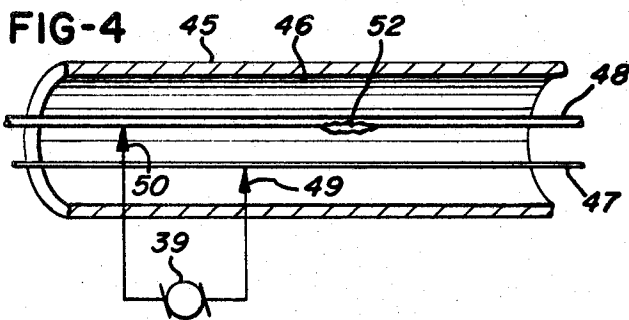
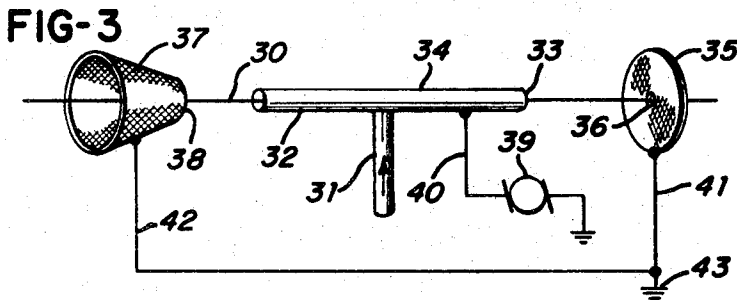
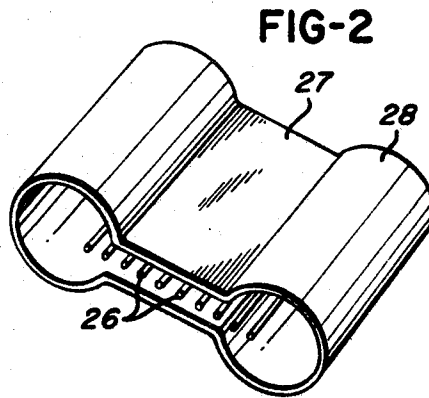
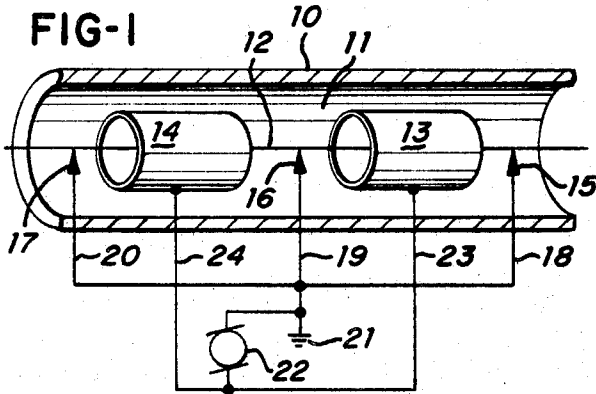


June 4, 1968

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 APPARATUS FOR DEPOSITING MATERIAL ON A FILAMENT FROM
 IONIZED COATING MATERIAL
 Filed Dec. 8, 1964

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1

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APPARATUS FOR DEPOSITING MATERIAL ON A FILAMENT FROM IONIZED COAT- ING MATERIAL

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Filed Dec. 8, 1964, Ser. No. 416,936
4 Claims. (Cl. 204-312)

ABSTRACT OF THE DISCLOSURE

Method and apparatus for the deposition of a conductive or nonconductive material on a conductive or nonconductive moving filamentary substrate in a chamber filled with a gaseous suspension of ionized particles or plasma of the material by establishing an electrical field that continuously increases in intensity from an electrode situated in the plasma to the substrate in the case of a conductive substrate or to an electrode positioned as close as possible to the substrate in the case of a nonconductive substrate.

This invention relates to a new and improved method and apparatus for the formation of materials or for the coating of materials by deposition from a gaseous atmosphere, particularly from a gaseous suspension or plasma of ionized particles.

Considerable attention of late has been focused upon so-called "vapor plating," particularly of refractory substances such as pyrolytic graphite, borides, carbides, nitrides and the like. These prior art ventures have for the most part involved a gas-phase solidifying reaction upon contact of a volatilized precursor with a heated substrate. While recent developments have represented substantial advancements in the art, most if not all of the prior art expedients for accomplishing vapor deposition have required costly apparatus, careful production control and a relatively low product yield, the severity of which has been accentuated by a lack of uniformity requiring close inspection and rejection of large quantities of the finished material.

Moreover, because of various process requirements of the prior art methods such as extremely high temperatures on the order of up to 4800° Fahrenheit, the maintenance of such temperatures while the substrate is in motion within the vapor plating atmosphere and the like, only a limited number of substrate and plating materials have been available. At the same time, whereas one method might be satisfactory for a particular substrate and plating gas combination, it could not be adapted to accommodate a change in either the substrate or the plating material. Similarly, because most methods have relied upon electrical resistance heating of the substrate to sustain the gas-phase surface reaction, the prior art has been largely confined to electrically conductive substrate materials and to the deposition of electrically conductive coatings thereon.

It is accordingly an object of this invention to provide an improved method and apparatus for the vapor deposition of a wide variety of materials.

It is a further object of this invention to provide such a method and apparatus which may be easily modified in a variety of particulars to accommodate a broad range of different precursory materials and to provide a diversity of end products.

Still another object of this invention is to provide such a method and apparatus which will yield a uniform product with a minimum of control and inspection.

Still another object of the present invention is to provide such a method which will not require several en-

2

vironmental conditions or energy levels and will therefore be amenable to almost all substances, regardless of their electrical conductivity, heat resistance and the like.

It is yet another object of this invention to provide an apparatus for the practice of the method according to this invention.

To achieve these and other objects and advantages which will appear from a reading of the following disclosure, the present invention teaches a plating or deposition atmosphere which, while it might be characterized as a vapor, is more precisely a gaseous suspension or plasma of ions of the material or materials to be extracted by or otherwise involved in the vapor plating or deposition operation. The precursors representing the source of the plated coating or deposit to be derived from the present invention may accordingly comprise all materials that are capable of ionization; and this category includes not only the refractory compositions that have been the principal subject of pyrolytic vapor deposition but also a wide variety of electrical conductors, non-conductors, metals and non-metals. Precursors which are useable in this invention also include a wide range of organic and inorganic materials; and, subject only to practical limits on extremes of energy which might be required to ionize a limited number of substances, any material might be formed as a film or deposited as a coating according to the teachings herein.

The ion-laden plasma in the method and apparatus of this invention may be formed or otherwise obtained according to a wide variety of procedures; but, as will be hereinafter explained, certain ionization techniques, when combined with the other teachings hereof, produce unique and unobvious improvements in and advantages over the prior art. Thus, while the ionized gas may be pre-formed or may in fact be obtained from naturally-occurring sources and thereupon placed in the deposition zone or chamber by suitable ducting and compartmentalization, it may also be formed in situ within the deposition zone by such expedients as establishing a substantial vacuum and volatilizing the precursory material therein or by the energization as by electrically charging and heating of a solid until it achieves an ionized gaseous state within the chamber. According to one modification of the invention, particular advantages seem to be obtainable where the injection of the ionized plasma into the plating zone is confined or at least concentrated in the vicinity of the substrate by establishing a jet flow along its surfaces.

Once the ionized precursory material is in proximity with the substrate upon which it is to be plated, it has been found that the establishment of an electrical gradient or electromotive force between the substrate and some area of the enveloping plasma spaced from the substrate will result in the deposition of a film, coating or other build-up of the ionized material. In one preferred practice the electrical energization of the ionized gas is accompanied by the establishment of a non-uniform electrical field as between the substrate and the enveloping plasma; and one means for achieving such a non-uniform electrical field is the positioning of high-surface-area electrodes within the plasma but spaced from the substrate surface which is of relatively small area as compared with the electrodes. The desired variation of the electrical field may also be achieved simply by effecting topological changes resulting in a reduction of the surface area of the electrodes as they near the substrate surface. Yet another means of establishing the non-uniform electrical field wherein the field or electron density is higher at or near the substrate than in the remainder of the enveloping plasma is the provision of a second electrode of relatively low surface area and in relatively close spacing to the substrate surface as compared to the high-surface-area electrodes positioned in the plasma cloud. The pro-

vision of this second electrode eliminates the requirement that the substrate or its coating be electrically conductive.

In still other modifications of this invention, the electrode of larger surface may be the precursor which, upon electrical energization, itself becomes ionized and at the same time maintains the plasma envelope in proper juxtaposition to the substrate so that the desired deposition thereon can take place. To facilitate this ionization, it is usually preferred that a substantial vacuum be maintained in the ionization-plating zone. Where the voltages that might be required to ionize the material of the electrode in this instance are higher than those desired in the deposition operation, the ionization may occur at and emanate from a third electrode more substantially spaced from the substrate. The ion-containing atmosphere thus established will then come under the influence of the non-uniform field-establishing components of the type discussed above which may thereupon accomplish the desired deposition at lower voltages.

It will be observed that a great number of variables can be manipulated with relative ease to influence the nature and characteristics of the deposited material and the variety of precursors and substrates that may be employed therefor. The electrical gradient, electromotive force or voltage between the plasma or the plasma-positioned electrode and the substrate is one such variable. So also is the pressure maintained within the chamber defining the ionization and/or deposition zone as well as the ion content of such atmosphere, both from the standpoint of the substance of the ions and of the degree of their concentration. Similarly, variations in the arrangement and configuration of the electrodes may be effected to change the characteristics of the non-uniform electrical field whereby the ionized plasma is concentrated in the vicinity of the deposition surface to the ultimate improvement of the end product.

By the proper selection and manipulation of these variables a variety of specific procedures may be followed and materials of a wide range of different properties may be processed. For example, where a conductive substrate is to be coated, the electrical energy gradient between the substrate surface and the plasma may be established simply by energizing the high-surface plasma-positioned electrode and grounding the substrate. If the substrate itself is not an electrical conductor but an electrically conductive coating is being deposited thereon, the coated substrate will have the same influence upon the plasma concentration surrounding and approaching the deposition surface.

To form the initial deposition upon a non-electrically conductive substrate or to deposit a non-conductive coating thereon the relatively high field density along and in the area immediately adjoining the substrate may be achieved, as indicated above, by the use of low-surface-area electrodes in closely spaced relationship to the substrate. These closely spaced electrodes may be either a second distinct group of electrodes or a continuation of the plasma-positioned electrodes the surface area of which reduces in the direction of the substrate. In either case, the relatively close spacing between the electrode and the substrate will on many occasions interfere with the buildup of the desired thickness upon the substrate as a result of which it may be desirable to employ several modifications of this invention in tandem. Thus for example, where an electrically conductive coating is to be deposited upon a non-conductive substrate, a continuous operation may be adopted wherein the substrate passes first through a plasma in which are positioned one or more electrodes at least some or parts of some of which are in very close proximity to the substrate. As the electrically conductive coating builds up in this chamber, the substrate of course becomes a conductor and may thereupon be electrically energized as by contact with suitable terminals and acquire its own relatively high electrical density and become the center of the ion concentration

and plating activity responding to the influence of the non-uniform electrical field on the ion cloud.

In still another modification of the invention particularly advantageous where the characteristics of the precursory materials or the process parameters are such that there is a tendency of the plasma to collect or deposit upon the plasma-disposed electrode, this electrode may be in the form of an elongated element in motion along with the substrate in continuous passage through the deposition chamber. In this modification, a wire or filamentous electrode is desirable, the non-uniform electrical field being established by the fact that the diameter and circumference of the electrode wire is substantially larger than that of the substrate wire. In a further variant, the electrode wire may itself be of the material to be deposited upon the substrate and it may be so energized that it is ionized and plated in response to the same electromotive force.

In addition to the ions of the material to be deposited, the envelope surrounding the substrate may contain additional ionized or gas-suspended materials which may act as catalysts or have other influences upon the deposition reaction or on the quality and characteristics of the finished product. Thus, for example where ultra-violet radiation is desired to promote polymerization and deposition of ionized monomers, a small amount of mercury vapor may be ionized in the deposition zone.

The invention thus generally described may be more clearly understood by reference to the following detailed description of certain preferred embodiments thereof in connection with which reference may be had to the appended drawings.

In the drawings:

FIGURE 1 is a schematic illustration of one preferred embodiment of the within invention.

FIGURE 2 is a perspective view in partial cross section of a modified electrode configuration for accommodating a strip or a plurality of laterally spaced filamentous substrates.

FIGURE 3 is a schematic illustration of yet another method and apparatus for practicing the within invention, particularly adaptable for the coating of non-electrically conductive substrates.

FIGURE 4 is a schematic illustration of yet another method for the practicing of the within invention.

FIGURE 5 is a diagrammatic illustration in partial cross section of a modification of the present invention for accommodating a plurality of parallel substrates.

FIGURE 6 is a schematic illustration of a modification of the present invention wherein the forms illustrated in FIGURES 1 and 3 are utilized in tandem.

Referring now to FIGURE 1 there is illustrated what might be termed a concentric conductor arrangement wherein the tubular housing 10, which is an electron tube capable of performing mechanical and/or chemical work, defines a deposition chamber 11 within which may be formed or into which by suitable ducting (not shown) may be introduced an ion-containing atmosphere of a precursory material which is desired to be deposited upon the substrate 12. The ionized precursory material may be any of the above enumerated refractory compositions such as the borides, carbides and nitrides of the prior art or a broad range of other materials including organic polymeric materials which may be ionized in their monomeric form. According to this modification of the invention, the substrate 12 is in the form of a strip or a filament of an electrically conductive material such as tungsten, stainless steel or copper wire which is positioned concentrically of and passes axially through the stationary or static shroud electrodes 13 and 14 which may be in the form of cylindrical shells, toric surfaces or the like and composed of a variety of electrically conductive materials such as the ferrous metals, copper, silver and the like. Moreover, the wall structure of these shells may be of solid sheet material or it may be an interwoven wire mesh or other per-

forate material. The substrate 12 being a conductor may be electrically charged by the spaced sliding contacts 15, 16 and 17 which might be in the form of a slide roller or mercurial miniscus according to established practice. Where the substrate, through contact with the terminals 15, 16 and 17, is connected to ground 21, an electrical current will flow through the substrate upon energization of the electrodes 13 and 14 as by charging the same from the generator 22 through the conductor wires 23 and 24 respectively. Upon such energization of the electrodes 13 and 14, a non-uniform electric field will be established between them and the substrate 12 by virtue of the substantial difference in the areas of the respective components; i.e., the high surface area electrodes 13 and 14 on the one hand and the relatively low surface area substrate 12 on the other. Where the chamber 10 is filled with a gaseous suspension of ionized particles of a precursor such as a methane series gas for the production of graphite or a borohydride for the production of borides for example, and a substantial vacuum on the order of from .01 mm. to 200 mm. of mercury is achieved therein, it has been found that the energization of the electrodes 13 and 14 under voltages as low as 75 to 100 volts will result in a concentration of the ions of the precursory material in the vicinity of the substrate 12 and particularly at the points of its contact with the terminals 15, 16 and 17 and in the deposition of the precursory material on the substrate at these points. While, in certain instances, this deposition may be regarded as a pyrolytic deposition in response to the electrical heating of the substrate and/or of the ionized atmosphere, deposition will take place in many instances without heating to a degree that would suggest a pyrolytic process. It is conceivable therefore that the plating is in response primarily to electrical rather than to heat energy.

By appropriate arrangement and manipulation of supply and take-up reels (not shown) the substrate 12 may be caused to move through the tubular chamber 10 and the ion-containing plasma therein and along the contacts 15, 16 and 17 so that a uniform build-up of the coating will be deposited thereon. The rate of travel of the substrate will of course influence the amount of coating deposited at any one location, and this may be varied according to the desired end product. Adjustment of the substrate's rate of travel will depend further upon the rate of deposition as influenced by the degree of concentration of the ions in the plasma, the pressure within the chamber 10, and by the specific configuration, geometry and spacing of the electrodes 13 and 14 from each other, from the substrate 12 and the contacts 15, 16 and 17. Where the substrate is a web or strip or where a plurality of substrates 26 in transversely spaced alignment as shown in FIGURE 2 are to be coated, the shroud electrode 27 may be shaped to provide an equal-potential surface in the manner illustrated in FIGURE 2 with an intermediate attenuated cross section centrally of the transverse alignment of electrodes and enlarged end portions 28, providing such spacing between the shroud electrode and the substrates that a uniform voltage or electrical potential exists between each of the substrates and the applicable proximate surface of the electrode. In this manner, the degree of non-uniformity of the electrical field between the substrates and the shroud electrodes is identical or constant as to each of the substrates.

In a specific embodiment of concentric electrodes as above described, a .001 inch diameter tungsten wire was used as the center electrode and substrate. Six ground points such as 15, 16 and 17 consisting of mercury-filled jewel electrodes were spaced along the wire at intervals of eight inches. Located half-way between consecutive jeweled electrodes were cylindrical wall electrodes of stainless steel one inch in inside diameter and one and one-half inches in length. The tungsten wire was drawn through the apparatus at a rate of 0.78 feet per minute. Diborane was admitted at 50 milliliters per minute and argon at 200 milliliters per minute. The vacuum was

adjusted to 5.5 millimeters of mercury. The tungsten was made the anode and the cylinders ganged together as cathodes. Under the influence of a 500 volt potential, and a current of not more than 250 milliamps, a hard, smooth deposit of boron was obtained such that the diameter of the moving cathode was increased to .00623 inch yielding a filament of 97.5 percent boron by volume.

Where the substrate such as the filament 30 in FIGURE 3, is a non-conductor or has been coated with an electrical insulator, the teachings of this invention may be practiced as illustrated in FIGURE 3. The pre-formed ion-laden plasma may be introduced to the deposition zone via the passage 31 in communication with the passages 32 and 33 through which the substrate may move. Although shown diagrammatically, the aligned extensions 32 and 33 of the plasma conduits may be provided with appropriate throat or nozzle characteristics to further confine the flow of the plasma escaping therefrom to the area surrounding the substrate 30. Since the substrate itself is not necessarily an electrical conductor however, it is necessary in this instance that the conduit assembly, at least those portions of the surface 34 thereof near the substrate should be electrical conductors which, in cooperation with the static conductors 35 and 37 may establish the desired non-uniform electrical field, the non-uniformity again arising from the substantial differences in the energized area of the substrate-oriented electrode 34 on the one hand and the plasma-oriented static electrodes 35 and 37 on the other. In the case of the electrode 35, it has been found that satisfactory results may be achieved where it is a disc-like conductive member with an opening 36 at least large enough to allow the uninhibited passage of the substrate therethrough. Further variation in the concentration of the electrons or field density may be achieved, however, where electrodes such as that designated as 37 in the form of a conical shell tapering toward its end 38 which is nearer the high-density electrode 34, are employed. Once again the static electrodes 35 and 37 may be of perforate or imperforate material or composed of strips, bands or wire in the form of a fabric or mesh. In this modification, the high voltage potential may be supplied by the generator 39 or other electrical source connected with the conduit member 34 by the conductor 40 while the static electrodes 35 and 37 are maintained at ground potential by their communication via the wires 41 and 42 respectively with the ground 43.

In one specific embodiment of this invention according to the illustration in FIGURE 3, the plasma conduit assembly was composed of two conventional #20 hypodermic needles and one inch diameter metal discs each perforated by a .020 inch diameter hole and located one inch from the needle tip. A .00084 inch diameter filament of glass was drawn through this electrode assembly at 0.78 feet per minute. Diborane was flowed through the needles at 50 milliliters per minute. The vacuum in the apparatus was regulated to 2.1 millimeters of mercury. The needles were made the anode and the discs the cathodes. A potential of 5700 volts, direct current of not more than 100 milliamps, was applied; and a thin, hard, metallic grey coating of boron was obtained on the glass filament. Deposits were also obtained by using reversed polarity. Alternating current is also working but produces a rougher coating.

In the embodiment of this invention illustrated in FIGURE 4 which might be considered as the parallel conductor modification, the tubular housing 45 defines and isolates an ionization and deposition chamber 46 which may be evacuated to provide a substantial vacuum on the order of from .01 to 200 millimeters of mercury. Within this chamber and the attenuated atmosphere it houses, two conductive filaments, webs or strips may be simultaneously passed. The substrate may again be a finely drawn tungsten wire or other conductive filament. In spaced parallel relationship to this is positioned the fila-

ment 48 which may be composed of copper, aluminum, tungsten, carbon or similar material and, being electrically conductive, will operate as the second electrode for establishing the non-uniform electrical field, the non-uniformity in this case being responsive to the fact that the filament 48 is of a larger diameter and circumference than the substrate 47. Both of the filaments 47 and 48 being in motion are brought into electrical contact by virtue of their electrical association with the sliding, rolling or liquid miniscus terminals or contacts 49 and 50 with the power source such as the generator 51 whereby an electromotive force or electrical potential between the two is established. Where sufficient voltage is established to cause a heating of the filaments, the filament 48 may produce ionization (particularly in the substantial vacuum within the tubular housing 45) to provide the plasma which, under the influence of the non-uniform electrical field wherein the higher field density occurs along or upon the substrate 47 will tend to plate out upon the substrate. Since the field-establishing electrode 48 in this case is in motion, the nominal build-up thereon of some of the deposited coating such as at 52 which might represent a discontinuity in or interferences with the constancy of the non-uniform electrical field or the deposition in response thereto is itself moving and its effect upon the substrate will be uniformly distributed where the substrate 47 and the electrode wire 48 are moving at different speeds or in opposite directions, the electrode 48 usually moving more slowly than the substrate 47. Under certain conditions, substantially the same results may be achieved where the filaments such as 47 and 48 are angularly disposed rather than parallel. A plurality of filamentous substrates may be simultaneously coated when arranged as illustrated in FIGURE 5 wherein the substrate filaments 53 corresponding to the filaments 47 of FIGURE 4 are uniformly spaced radially and circumferentially of the plasma-producing or large-diameter filament 54 corresponding to the electrode 48 in FIGURE 4. In the illustration of FIGURE 5, the atmosphere within the tube 55 and the electrical energization of the substrates 53 on the one hand and of the plasma-producing electrode 54 on the other are the same as described in connection with FIGURE 4.

In still another modification of the invention as illustrated in FIGURE 6, a combination of two of the above-described forms of the invention is shown whereby, depending upon the direction of travel of the filament 56 through the jet and electrode assemblies, a conductive coating may be deposited upon a non-conductive substrate or a non-conductive coating may be deposited upon a conductive substrate. Where the substrate 56 is not a conductor of electricity, it may be caused to pass first through the jet member 57 corresponding to 31 in FIGURE 3, by means of which the ionized suspension is discharged along the filament 56 whereby a coating is deposited thereon. This coating being a conductor and the composite filament being thereby electrically conductive, it may then be led through the shroud-type electrode 58, corresponding to the electrodes 13 and 14 in FIGURE 1, and receive a further deposited coating. The jet assembly 57 is connected to a high voltage power source 65 by the conductor wire 59. Similarly, by virtue of its electrically conductive contact with the terminal member 61 which is connected to ground by the wire 62, the substrate 56 is charged with high electromotive force as compared to the voltage acting upon the shroud electrode 58 as a result of its association with the circuitry via the conductor wire 60. The relative differences in the electrical potential between the jet 57 and the substrate 56 on the one hand and between the shroud electrode 58 and the substrate on the other may be further controlled by the variable resistors 63 and 64. Where the filament 56 is an electrical conductor and a non-electrically

trically conductive coating is to be deposited thereon, the direction of travel of the substrate may be from left to right in the illustration, whereby it passes first through the shroud electrode to obtain the insulative coating and, being thus a non-conductor, then passes through the jet to receive a further deposition.

While the invention has been described above in considerable detail in connection with certain specific examples and embodiments thereof, the foregoing particularization has been for the purposes of illustration only and does not limit the invention as it is more precisely defined in the subjoined claims.

I claim:

1. Apparatus for the deposition, in a deposition chamber held at below atmospheric pressure, of a material from a gaseous suspension of ionized particles of the material onto a filamentary substrate moving linearly at a constant rate through said chamber, said apparatus comprising: a first electrode in the form of a very small diameter conductive tube concentric with said substrate; a second electrode in the form of a relatively large diameter conductive tube concentric with said substrate and spaced axially from the first electrode; a conduit extending from outside said chamber and joining the first electrode tube at a point intermediate its ends for introducing ionized particles of said material into said chamber through the open ends of the first electrode tube; a sliding electrical contact to said substrate at a point outside the second electrode tube near the end remote from the first electrode; and means for establishing said electrodes at different electrical potentials relative to said contact.

2. Apparatus as claimed in claim 1 in which said substrate is a nonconductor, said material is a conductor, and the direction of substrate motion is from the first to the second electrode.

3. Apparatus as claimed in claim 1 in which said substrate is a conductor, said material is a nonconductor, and the direction of substrate motion is from the second to the first electrode.

4. Apparatus for the deposition of a material from a gaseous suspension of ionized particles of the material onto a nonconductive filamentary substrate moving at a constant rate through said chamber, said apparatus comprising: a chamber adapted to be held at a low pressure, a first electrode in the form of a very small diameter conductive tube concentric with said substrate; a second electrode surrounding and concentric with said substrate, spaced axially from the first electrode, and presenting to the nearer end of the first electrode tube a much larger area than that presented by the first electrode; a conduit extending from outside said chamber and joining the first electrode tube at a point intermediate its ends for introducing ionized particles of said material into said chamber through the open ends of the first electrode tube; means for supporting and conveying said substrate axially through said electrodes; and means for establishing an electrical potential difference between said electrodes.

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