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GLOW DISCHARGE VAPOR DEPOSITION APPARATUS

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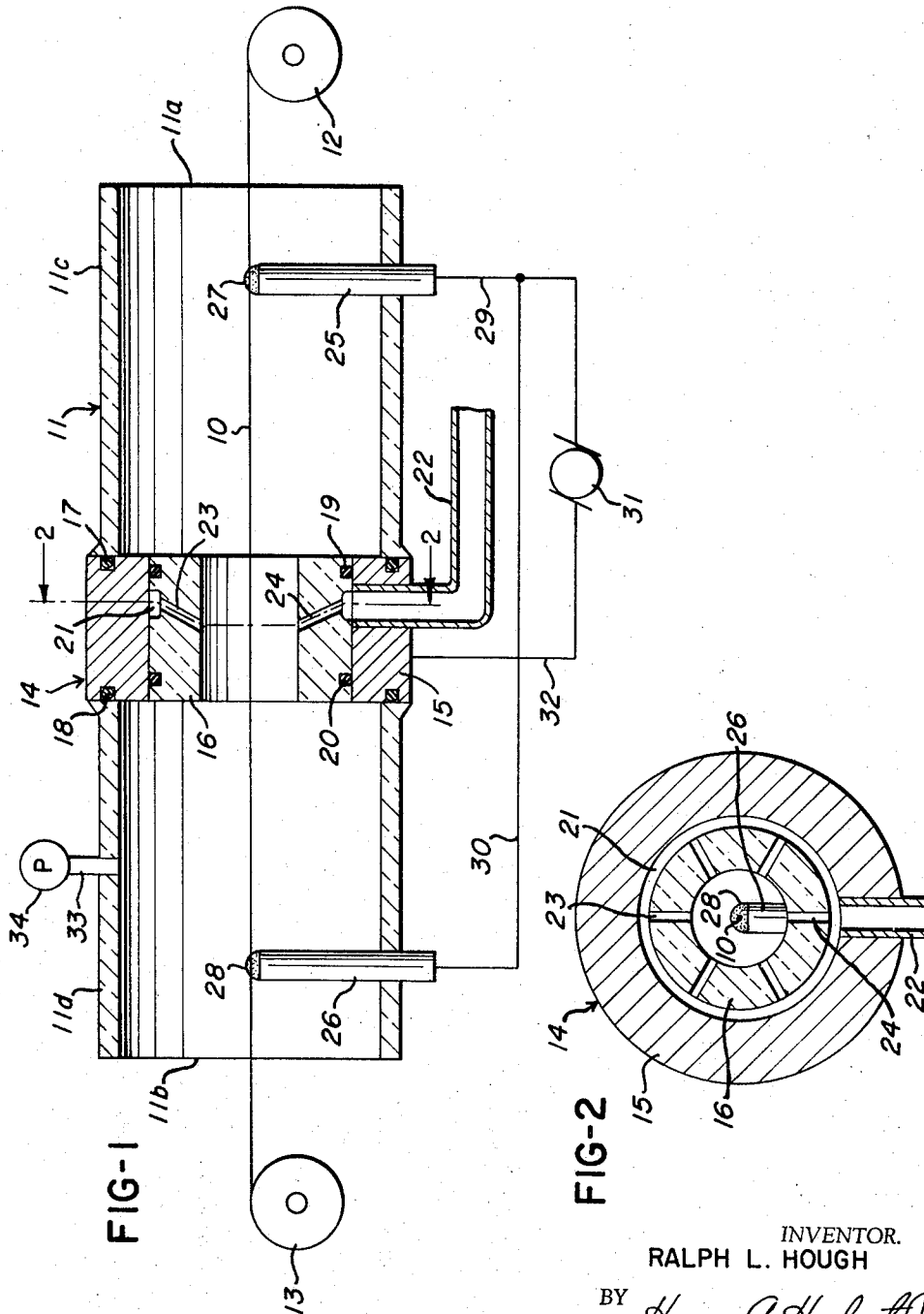


FIG-2

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GLOW DISCHARGE VAPOR DEPOSITION APPARATUS

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7 Claims. (Cl. 118—49.5)

The invention described herein may be manufactured and used by or for the United States Government for governmental purposes without payment to me of any royalty thereon.

The present invention relates to an apparatus for accomplishing the deposition of materials from gaseous substances under the influence of electronic energization. More specifically, the invention relates to such an apparatus for accomplishing the vapor deposition upon one or a series of strands or filaments which are of substantial length and are sometimes referred to as continuous substrates.

In the art of reinforced resinous or plastic composite materials intended for structural and/or ablative applications, interest has rapidly developed in a great number of reinforcing components in the form of very long strands or filaments which may be continuously wound or otherwise laid up in the plastic matrix to reinforce the same. To impart desired refractory capability or other properties such as thermal and electrical conductivity to such reinforcements, the practice has developed of applying a variety of coatings upon a filamentous substrate; and devices have been perfected through which such a substrate of substantial length may pass and be coated by pyrolytic or other refractory material in a continuous operation. In many of such devices the coating material has been derived from a gas or vapor which is contained within a zone around the moving substrate and, in response to heat or electronic energization, undergoes a gas-phase reaction at the substrate surface resulting in the formation of a film or coating of the solid material thereon.

While these prior art apparatuses have gradually been perfected to the point at which they are capable of producing reasonably uniform reinforcing strands of the type described in a continuous operation, the heat required for pyrolytic deposition on the one hand or the electrical energy required for a glow-discharge deposition on the other have resulted in a relatively high consumption of power which in itself has increased the cost and has limited the availability of these reinforcements at a time when the demand for them is rapidly rising. Beyond this however, the accommodation of this power and of the heat or electrical energy which it engenders requires complicated, expensive and cumbersome components, accessories and procedures which seriously impair the efficiency of the process. As the desire and necessity for quality control increase, the limitations of the prior art apparatus become even more keenly felt; and, although reasonable degrees of purity and uniformity of the various coatings have been achieved by the prior art, such achievement has been so costly in terms of the apparatus required and of the time spent in operating it that quality has admittedly suffered in the interests of economy.

It is accordingly an object of this invention to provide an improved apparatus for the deposition of materials from gaseous vapors in response to thermal and/or electronic energization.

Yet another object of the invention is to provide such a vapor deposition apparatus which will accomplish its deposition in a continuous and easily controlled uniform manner upon a filamentous substrate of substantial length moving continuously through the apparatus.

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Yet another object of the invention is to provide such an apparatus which will itself be relatively simple and economical to construct and will have only limited power requirements so that its components and accessories need not be cumbersome, complicated or expensive.

Still another object of the present invention is to provide a vapor deposition apparatus for the manufacture of high modulus, high density coatings of pyrolytic and related materials upon a variety of filamentous substrates.

To achieve these and other objects and advantages which will appear from the following disclosure, the present invention provides a novel electrode and jet nozzle assembly capable of establishing an atmospheric zone which, in combination with a pyrolyzing or glow-discharge tube, will support the formation of a solid coating upon a substrate moving continuously therethrough. More specifically, the electrode-nozzle component of the apparatus of the present invention represents means for pre-energizing the gaseous ingredients for the plating reaction before they are actually introduced into the plating zone and means for directing the gases while so energized onto the substrate, which, in the preferred practice of the invention, is in the form of a filament or a strand composed of multiple fibers of staple length or of one or more continuous filaments of substantial length and which moves continuously through the electrode-nozzle unit and the plating atmosphere it establishes. This electrode-nozzle component is a hollow-walled unit having a substrate passage to accommodate the movement of the substrate centrally thereof and a lateral arrangement of forwardly directed jet passages in communication with a supply of the gas, gaseous mixture or gases which are under sufficient pressure to pass through the jet nozzles and to impinge upon and form an ionized gaseous cloud around the substrate. Such a flow of gas directed against the substrate is admirably suited for increased deposition rates, particularly with such chemical vapor deposition reactions with rate limiting steps determined by diffusion through the hot zone of the stagnant gas near the substrate or for reactions wherein no chemical intermediates are involved. It has accordingly been found that the jet distribution passages mechanically assist and cooperate with the non-uniform electrical field to force diffusion by mechanical as well as electronic means. In certain preferred embodiments of the apparatus of this invention, the electrode-nozzle component is in the form of a hollow-walled cylinder, the outer portion of which is in fluid-communication contact with the gas supply and the inner portion of which is provided with a plurality of radially spaced jet openings which are themselves in fluid-communicating and fluid-transmitting relationship with the deposition gas which is introduced to the unit through the outer portion of the cylindrical wall. While the jets are radially aligned in a plane transversely of the electrode-nozzle unit, they are angularly disposed to such a plane, being directed forwardly or in the direction of travel of the substrate by an angle of within the range of from 15 to 60 degrees with such plane.

At the same time, the electrode-nozzle unit is composed of electrically conductive material and is electrically energized by a direct current power source which is also associated with the substrate which itself is composed of electrically conductive material in such a manner that a voltage or electrical potential exists between the electrode-nozzle unit and the substrate. The magnitude of such voltage is preferably at least as great as the ionization or breakdown potential of the gas or mixture of gases passing through the various laterally extending openings so that the gas, while it is within the electrode and before it is introduced into the deposition

area, becomes ionized and assumes a polarity which is the opposite of the polarity of the substrate. As a result of the simultaneous energization and direction of the gaseous ingredients thus achieved, it has been found that the plating of a uniformly dense and pure solid coating or film of at least some of the elements of the gaseous mixture will be deposited upon the substrate with the involvement of a minimum amount of electrical energy, the requirement for little or no heating of the substrate and at a remarkably high synthesis rate which allows the substrate to be fed through the plating atmosphere at a high rate of speed thereby greatly increasing the production capacity of the apparatus and consequently reducing the unit cost of manufacture.

The invention thus generally described may be more clearly understood by reference to the following detailed description of a specific embodiment thereof in connection with which reference may be had to the appended drawings wherein like reference numbers refer to like parts and:

FIGURE 1 is an elevational view, schematic in part and partially in cross section, of an ionization or glow-discharge tube embodying an electrode-nozzle component according to the present invention, and

FIGURE 2 is a cross sectional view taken on the line 2—2 of FIGURE 1 of the electrode-nozzle unit thereof.

Referring now to the drawings, the filamentous substrate 10, which may be composed of an electrically conductive metal such as a finely drawn tungsten wire or may be a filament or any material, at least the outer surface of which is electrically conductive, is caused to pass through and longitudinally of an ionization or glow discharge tube 11. The tube 11 is primarily composed of a refractory and electrically insulative material such as quartz and is usually of a generally tubular or hollow cylindrical configuration, the ends 11a and 11b of which are substantially closed so as to retain a controlled atmosphere therein. The ends 11a and 11b are however provided with openings of sufficient size to allow for the introduction and exit of the substrate 10, the movement of which is responsive to the controlled rotation of the supply roll 12 and the take-up reel 13 upon which the filament is stored after it is plated. It is to be understood that, in certain instances to improve the sealing of the tube, the openings through the ends 11a and 11b may be associated with various sealing means such as glass tubes partially filled with mercury or another liquid through which the substrate may pass on the one hand but which will be of sufficient density and intimate association with the substrate that the gas within the tube may not pass therethrough on the other hand.

At some point along the length of the tube and preferably centrally or spaced from the ends thereof, is positioned electrode-nozzle unit according to the present invention which is designated generally by the number 14. In this preferred illustrated embodiment the total hollow-walled cylindrical shape of the unit comprises the outer cylindrical shell 15 composed of an electrically conductive and structurally sound material such as steel or another ferrous alloy and the inner cylindrical sleeve 16, the outside diameter of which is substantially equal to the inside diameter of the shell 15 so that the two may be snugly associated to represent what amounts to an integral unit. The inner sleeve 16 is also preferably composed of an electrically conductive material; but in the preferred case, it is also composed of a relatively inert high temperature material. Where the sleeve is in fact composed of graphite which has these characteristics, it has been found that a high degree of purity can be achieved in the coating substrate; and it is theorized that this results from the fact that there is no tendency of the reactive deposition gases to combine in any way with the nozzle unit in a manner which might result in the formation of soot or sludge or other impurities which tend to disrupt the density and

uniformity of the deposited coating or otherwise to enhance the graininess thereof.

The unit 14 may be associated in a fluid-tight manner with the balance of the tube 11 which may comprise two separate sections 11c and 11d by joining one of the same to opposite sides of the unit 14 as illustrated; and the contact between these separate tube sections and the opposite sides of the electrode may be made fluid tight by the interposition along their joined surfaces of deformable sealing members such as the O-rings 17 and 18, for the accommodation of which grooves may be provided on the contacting surfaces of the electrode and/or the tube sections. To insure a fluid-tight relationship between the outer shell 15 and the inner sleeve 16 of the electrode, similar deformable sealing members such as the O-rings 19 and 20 are positioned in grooves provided in either or both of the shell 15 and the sleeve 16 circumferentially of their contacting cylindrical surfaces, preferably at points spaced from but near the end faces thereof. At some point along the mated cylindrical surfaces of the shell 15 and the sleeve 16 between the portions thereof which are sealed by the O-rings 19 and 20 is provided a circumferential groove or channel 21 which, in the case of the illustrated embodiment, is in the form of a groove about the exterior portion of the sleeve 16. It is to be understood however that the same groove might be provided about the inner surface of the shell 15 or it may be provided by a combination of mated grooves about the inner surface of the shell 15 and the outer surface of the sleeve 16. In communication with this groove 21 which, when the shell 15 and the sleeve 16 are joined, actually represents a channel or passage circumferentially of the unit and within the wall thereof, is the gas inlet conduit 22 which may be a suitable tubular member inserted in fluid-tight relationship into a radially extending bore through the shell 15. At its other extremity, the conduit 22 is associated with a supply reservoir or supply reservoirs for the gas or gases to be involved in the plating reaction in connection with which means may be provided for pressurizing the gas to cause a flow through the conduit, through and around the channel or passage 21 and, from it, through the radially positioned but forwardly directed jet passages 23 and 24 which may be cylindrical with a diameter ranging from .020 to .060 inch. The location of the circumferential gas distribution passage 21 and the conduit 22 communicating therewith is preferably nearer that face of the electrode unit 14 which is nearer the supply roller 12 so that the openings of the jet passages 23 and 24 may be positioned and directed to cause the gas emanating therefrom to impinge upon the substrate while it is still within and under the electrical influence of the electrode-nozzle unit 14.

As best shown in FIGURE 2, a plurality of on the order of six or so jet passages such as 23 and 24 are uniformly spaced radially about the sleeve 16 to provide a uniform distribution of the gas about the entire circumference of the substrate 10. On the other hand, as best shown in FIGURE 1, these jet passages such as 23 and 24 are angularly disposed to a vertical plane through the unit 14 so that the gas issuing from them is aimed at least partially in the direction of the movement of the substrate 10. The angular disposition of these jets is preferably within the range of from 10 to 60 degrees from the vertical plane; and, in the illustrated embodiment, such angle approximates 30 degrees from the vertical. The effect of this arrangement of conduits and passages is to create a concentrated cloud of the deposition gases at the axis of the unit 14 and moving axially therethrough in the direction of the movement of the substrate 10. To obtain the maximum benefit from this gaseous concentration, the feed and movement of the substrate is then preferably controlled so that it also moves axially through the electrode unit 14.

In cooperation with the movement of the zone of deposition gases and of the substrate thus established is the

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electrically energizing system which may, as in the preferred embodiment illustrated, be associated with the substrate 10 by the terminal units 25 and 26 which are in the form of hollow cylindrical tubes filled at least partially with mercury or another electrically conductive liquid projecting above the upper ends of the tubes in the convex menisci 27 and 28 which are so positioned that the substrate passes through them and may be electrically energized by the liquid carrying the electrical energy which it receives from the power supplied to the terminal units. These terminal units 25 and 26 are themselves associated by the conductor wires 29 and 30 respectively with a direct current power source such as the direct current generator 31 which, by the conductor wire 32, is also connected to the electrode nozzle unit 14. Since the shell 15 and the sleeve 16 of this unit are both composed of electrically conductive material, the association of the generator with only the outer surface of the outer shell 15 will cause the entire electrode to be electrically energized. As indicated above, the electromotive force or potential difference established across the space between the substrate 10 and the inner surface of the hollow electrode unit 14 must be such that it will cause the ionization of the gaseous mixture being introduced by the above described conduits and passages to the point at which the gas will also become electrically conductive. The gas thus ionized is then subject to the influence of the non-uniform electrical field created as a result of the fact that the inner surface of the opening through the electrode is of substantially greater area than the exterior surface of the equivalent length of the substrate passing through it. To keep this ionization potential at a minimum and to provide a uniform, regular, smooth and high density coating deposit, it has been found desirable to control the energization of the components so that the electrode unit is negatively charged and the substrate is positively charged. Such a practice therefore cooperates with the other features of the electrode-nozzle unit of this invention in that it acts to reduce the ionization potential thereby making production of a coated filamentous substrate possible at even lower voltages than might otherwise be required.

To provide other environmental conditions which are favorable to an efficient plating reaction, the glow-discharge device may, in a conventional manner such as via a conduit 33, be associated with a vacuum pump 34 by means of which the pressure within the tube and at the reaction zone can be reduced to a partial vacuum. In other cases, where it might be desired to raise the temperature of the tube or of the substrate at least at the point where the deposition reaction is taking place, a potential difference between the standpipe terminal units or electrodes 25 and 26 may be so regulated that a current will flow through the electrically conductive substrate at those points between its contact with the menisci 27 and 28 and thereby resistance heat the same.

As an example of the improved efficiencies obtainable by use of the above described apparatus, a carbon monoxide carrier gas has been passed through the conduit 22 and the jet passages 23 and 24 at a flow rate of 50 milliliters per minute after having been bubbled through nickel tetracarbonyl at room temperature with a substantial vacuum of on the order of from 3 to 5 milliliters of mercury maintained within the tube. Where the diameter of the inner opening through the electrode unit 14 was 0.5 inch and the substrate was a continuous boron filament approximately 100 microns in diameter, a voltage of only from 400 to 500 volts across the space between the electrode and the substrate was required to produce the relatively nominal 0.3 milliamp current flow through the ionized gaseous cloud which caused the deposition of a nickel coating upon the substrate of a uniform thickness of up to 0.4 micron at a synthesis rate allowing movement of the substrate at approximately 2 feet per minute through the electrode. By way of comparison, the prior art glow-dis-

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charge tubes not utilizing the electrode-nozzle assembly of this invention have required a voltage of up to 2100 volts to establish a current of from 40 to 60 milliamps to obtain the same degrees of thickness of similar coatings at the same synthesis rate.

While the present invention has been described in detail in connection with certain specific embodiments thereof, it is to be understood that the foregoing particularization has been for the purpose of illustration only and does not limit the scope of the invention as it is defined in the subjoined claims.

I claim:

1. In an ionization tube apparatus for the glow-discharge deposition upon a substrate of a solid coating from an ionized gas, the combination with such a tube of an electrode-nozzle unit of electrically conductive material which comprises a substrate passage therethrough, an inlet conduit in communication with a supply reservoir of the deposition gas, distribution passages within the wall of said unit in communication with said inlet conduit and with the interior surface of said substrate passage at a plurality of circumferentially spaced openings thereon, means for reducing the pressure of the atmosphere within said tube relative to the pressure of the gas in the supply reservoir, means for electrically energizing said electrode-nozzle unit and said substrate whereby an electromotive force at least equal to the ionization potential of the deposition gas is established between them, means for moving said substrate through said passage and said distribution passages being inclined from a plane transverse to the movement of said substrate at an angle within the range of from 10 to 60 degrees opening in the direction of movement of said substrate.

2. An apparatus according to claim 1 wherein at least the inner surface of said electrode-nozzle unit defining said substrate passage is composed of an electrically conductive but chemically inert material.

3. An apparatus according to claim 2 wherein said electrically conductive but chemically inert material is graphite.

4. An apparatus according to claim 1 wherein said electrical energizing means positively charge said substrate and negatively charge said electrode-nozzle unit.

5. An apparatus according to claim 1 wherein said electrical energizing means comprise at least a pair of spaced terminal units in electrical contact with said substrate, a direct current power source associated with said terminal units and means for controlling the voltage to said terminal units to the extent that a current flows through the portion of said substrate between said terminal units to electrically resistance heat the same.

6. An apparatus according to claim 5 wherein said terminal units are on opposite sides of said electrode-nozzle unit.

7. An electrode-nozzle assembly for incorporation in an ionization glow-discharge deposition device comprising an outer cylindrical shell of electrically conductive material having an opening through the wall thereof, an inner hollow cylindrical sleeve of electrically conductive material having a substrate passage axially thereof positioned within said outer shell with the outer surface of said sleeve in contact with the inner surface of said shell, grooves along the contacting surfaces of said sleeve and said shell near the end faces thereof, deformable sealing members positioned within and substantially occupying said grooves, circumferential distribution passage defined by the contacting surfaces of said sleeve and said shell between said deformable sealing members, a plurality of circumferentially spaced radially disposed jet distribution passages each inclined within the range of 10 to 60 degrees from a plane transverse to an axis common to each of said sleeve and shell and in communication with said circumferential distribution passage, a radially disposed gas inlet conduit passing through said shell and in communication with said distribution passages for sup-

plying the same with a pressurized vapor deposition gas, and means for electrically energizing said assembly and a deposition gas within said distribution passages.

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