Nov. 8, 1960 S. J. STEIN ET AL 2,958,899

APPARATUS FOR DEPOSITION OF SOLIDS FROM VAPORS

Filed Oct. 9, 1953 2 Sheets-Sheet 1

Fig. 1.

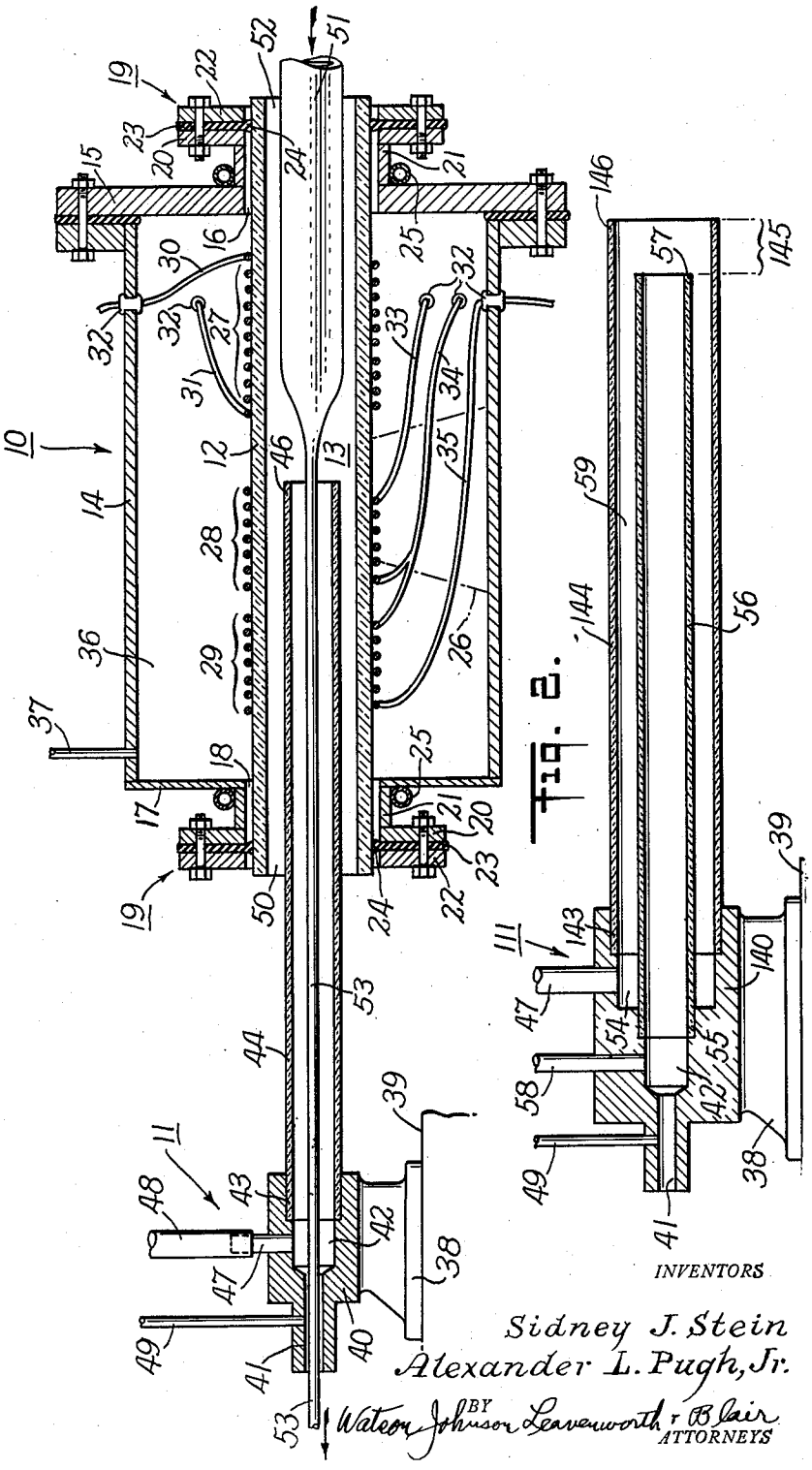


Fig. 2.

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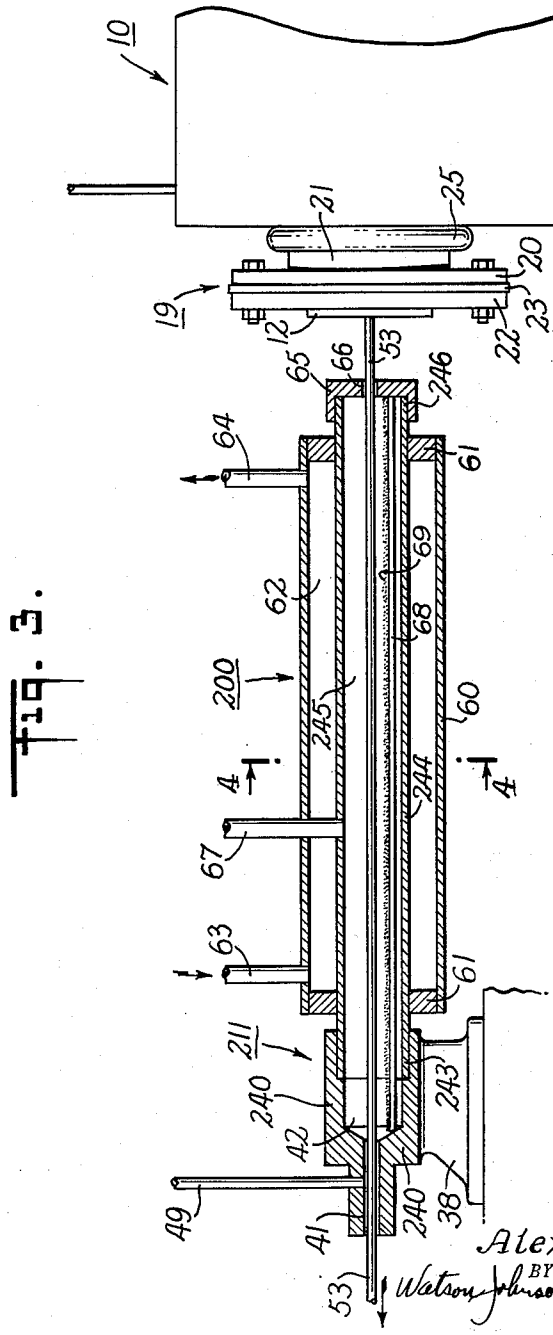


Fig. 3.

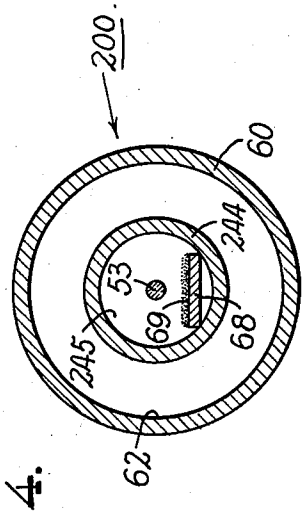


Fig. 4.

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APPARATUS FOR DEPOSITION OF SOLIDS FROM VAPORS

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4 Claims. (Cl. 18—8)

The present invention relates to apparatus for and methods of depositing upon a base material the solids resulting from pyrolytic decomposition of gaseous medium, in addition to certain types of the resulting products which may well be adapted to use as electrical resistors. Although practice of the present invention may be particularly advantageous in the production of small electrical resistors of the type wherein the substrate is in the form of a filamentary core of dielectric material and carries thereon the semi-conductor in the form of a surface film, the present invention may be employed to advantage in the production of other electrical devices, such as capacitors, etc., as well as in the manufacture of other products wherein a film of solids is to be, or may be to advantage, deposited on a base material by pyrolysis.

Prior to the present invention it was proposed in the United States patent to Pender, No. 1,771,055, to make electrical resistors by first heat drawing a filament of glass or the like dielectric material and then cooling and spooling the drawn filament. It was proposed thereafter to feed the drawn filamentary substrate from the spool through a liquid applicator where the filament was coated with a solution containing in suspension fine carbon particles, and the coated filament was then drafted through a furnace to drive off volatile constituents leaving on the filamentary substrate a carbon film or coating. After application of a protective coating, the coated filamentary substrate was severed or broken into sections or lengths to form resistor units. It has also been proposed to deposit a semi-conductive film of solids on substrates by pyrolytic decomposition of gaseous mediums in heating chambers. Unfortunately, the practice of all of such procedures is characterized by difficulties in attaining a secure bond between the films and substrates now attributable to fouling of the substrates surface between the drawing and film deposition procedures. Further, the devices for producing such resistors are complicated and are featured by complex means for correcting or minimizing such difficulties.

A general object of the present invention is to provide a unique and simple method which is readily practiced on an economical basis, and simple, readily-constructed and economical apparatus, to produce products of superior quality with avoidance of such prior art difficulties, while allowing efficient production of such devices in various forms.

A more specific object of the present invention is to provide a novel method whereby pyrolytic deposition of film solids is attained in a controlled manner on thoroughly clean filament surfaces immediately after drawing, prior to cooling of the filamentary substrate below temperatures of decomposition of film source vapors or gaseous medium with attendant economy in heat consumption, the method being adapted to practice advantageously in a continuous manner.

Another object of the present invention is to provide simple apparatus which permits ready and efficient practice of this method and in which the hot filamentary substrate, as it is drawn therein, is moved immediately through a heated atmosphere of film source vapors to receive a film of pyrolytically deposited solids.

A further object of the present invention is the provision of forms of this apparatus wherein the temperatures in successive zones are readily controlled whereby the substrate starter material effectively may be heated to and maintained at an efficient drawing temperature with rapid and accurate decrease adjustment of the temperature of the hot filament as it is drawn away from the drawing zone to below the sag softening temperature thereof and to a controlled temperature at which pyrolytic decomposition of film source vapors is most effectively attained in an immediately following deposition zone.

An additional object of the invention is to provide embodiments of the apparatus which, efficiently, may carry out the invention even with respect to deposition starter solids whose temperatures of vaporization are close to their temperatures of decomposition.

A still further object of the invention is the production of efficient electrical resistors of the indicated type having excellent quality and exceptionally good operating characteristics, due in part to the mentioned unique physical features and in part to the new and novel chemical composition of their electrically conductive resistance films.

Still another object of the present invention is to provide procedural embodiments which are practically and efficiently practicable in commercial production of fine quality electrical resistors and like products, and structural embodiments which are readily constructed and permit efficient use and operation thereof.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, the apparatus embodying features of construction, combinations and arrangement of parts which are adapted to effect such steps, and the product which possesses the characteristics, properties and relation of elements, all as exemplified in the detailed disclosure hereinafter set forth, and the scope of the invention will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings, in which:

Figure 1 is a sectional elevation taken substantially axially of an embodiment of the apparatus of the present invention, particularly designed to receive deposition starter materials in vapor form;

Figure 2 is an axial section of a modified form of the deposition assembly suitable for use with the furnace of Figure 1;

Figure 3 is a side elevational view, with parts broken away and in axial section, of another embodiment of the apparatus of the present invention, particularly designed for use with deposition starter materials in solid form to be vaporized in the pyrolysis operation of the apparatus; and

Figure 4 is a transverse sectional view taken substantially on line 4—4 of Figure 3.

Referring to the drawings, in which like numerals identify similar parts throughout, it will be seen from Figure 1 that an embodiment of the apparatus which is particularly designed for handling deposition starter material in vapor form, comprises a furnace **10** and a deposition chamber assembly **11**. The furnace **10** includes an elongated tube **12** of suitable refractory material, such as mullite or alumina, having a bore open at both ends to provide therein an elongated, through, cylindrical chamber **13**. The refractory material for the tube **12** is chosen

to have a high softening point, e.g., appreciably above 1750° C. A shell 14 of any suitable material, such as steel, surrounds the tube, 12 and includes at the entrance end of the furnace a removable, centrally-apertured, gasketed closing plate 15 having an axial hole 16 of a diameter appreciably greater than the external diameter of the tube 12 at the discharge end, and a centrally-apertured, fixed transverse wall 17 with its axial hole 18 of similar diameter. The spaces between the end walls 15 and 17 of the shell 14 and the ends of the tube 12 are respectively sealed by a pair of gasket units 19, each comprising a radial flange 20 connected to the adjacent shell end wall by a tubular section 21, an outer end ring 22, and an interposed disk or gasket ring 23 of silicon rubber, or the like. Each of the gasket rings 23 has an inner circular edge 24 snugly engaged in fluid-tight manner against the external surface of the tube 12. The gasket units 19 at opposite ends of the furnace are suitably cooled by cooling tubes 25. The tube 12 is suitably supported in the shell 14, preferably by means auxiliary to gasket units 19 such as a stool which is diagrammatically indicated in dotted lines at 26.

Within the shell 14 the chamber tube 12 is provided with a main electric heating coil 27 and two auxiliary electric heating coils 28 and 29 lapped thereabout. The main heating coil 27 has its terminal ends connected to a suitable source of electric power by leads 30 and 31 extending through ceramic insulating sleeves 32 in the shell wall. Auxiliary heating coil 28 is connected by leads 33 and 34 to a suitable power source also extending through the shell wall by similar ceramic insulating sleeves 32; and the auxiliary coil 29 is supplied with power by one of the leads of the coil 28, such as 34, and another lead 35, which is likewise led through the shell wall by another ceramic insulating sleeve 32.

The end wall 15 of the shell 14 is made removable, not only for ready access to the heating elements, but also to permit the space 36 between chamber tube 12 and the shell to be packed with insulating material. For this purpose, a mixture of charcoal and aluminum oxide is preferably employed. The body of insulating material in the space 36 supplements the supporting function of the stool 26, and the charcoal content constitutes, in heating operation of the furnace 10, a source of reducing atmosphere of carbon monoxide and carbon dioxide in the shell to prevent oxidation of the conductors of the heating units 27, 28 and 29. The shell 14 is provided with a venting duct 37 communicating with the space 36 to permit escape of the reducing gases.

The deposition assembly 11 includes a stand 38 slidably mounted upon a horizontal support 39 and carrying a head 40 which has a transverse bore 41 extending therethrough. The head bore 41 is counterbored to provide a stepped enlargement 42 in the outer end of which is fixedly supported discharge end 43 of an elongated refractory tube 44 of quartz, or the like, which provides therein a deposition chamber 45. The deposition chamber tube 44 is of an external diameter appreciably less than the internal diameter of the furnace tube 12. Thus the other free end 46 of the tube 44 is readily receivable coaxially in the furnace tube 12 to any desired extent as permitted by the sliding mount of the stand 38 upon the supporting surface 39 while permitting free exhaust of reaction or decomposition gaseous products. The counterbore 42 is communicated by any suitable means, such as a tube 47 and conduit 48, with any suitable source of deposition vapors. Since the head bore 41 constitutes the solid products discharge passage for the deposition chamber 45 through which the coated filamentary substrate is drawn, it is provided at a point beyond the deposition vapor inlet 47 with a communicating duct 49 to admit inert gas, such as nitrogen, to serve as a fluid seal, preventing escape loss of deposition vapors from the discharge end of the deposition chamber head and preventing oxidation of film solids by barring entrance of air.

By way of illustration, operation of the embodiment of the apparatus, shown by way of example in Figure 1, will be here described in connection with simple starter materials well known to prior art practices. For example, the stand 38 may be slidably manipulated on the supporting surface 39 so that the free end 46 of the deposition chamber tube 44 is axially received by the discharge end 50 of the bore of the furnace tube 12 constituting chamber 13, up to a point short of the main heating unit 27 but preferably past the auxiliary heating units 28 and 29, as shown in Figure 1. A rod or tube 51 of substrate starter material, such as Vycor glass (about 96% silica with the remainder being chiefly boric oxide) is inserted into the receiving end 52 of the furnace chamber 13, and is there supported for relatively slow feed in a suitable manner by means well known and thus not shown.

In order to start the drawing operation, the Vycor tube 51 preferably initially is heated at one end before insertion to a softening temperature, and a length of relatively fine filament 53 of about 1/16" in diameter is drawn therefrom and extended through deposition chamber 45 and discharge bore 41 with insertion of the Vycor tube in the furnace chamber 13. Means for pulling the filament 53 beyond the deposition tube head 40 also is known in the prior art and is thus not shown. The main heating coil 27 heats the Vycor tube 51 at its drawn end inserted therein and maintains it at a suitable drawing temperature as for example 1750° C. With pull applied to the filament 53, the latter is continuously drawn through the deposition chamber 45. Methane gas (with or without an inert carrier gas, such as nitrogen) is supplied through the conduit 48 to the deposition chamber 45 with fluid seal of nitrogen gas supplied to the discharge bore 41 by the duct 49.

It will be noted that the main heating unit 27 is appreciably spaced from the entrance end of the deposition chamber 45 so as to permit a sharp drop in the temperature of the filament preferably to below the softening temperature of the substrate starter material, thereby allowing hardening of the filament at least to a sufficient degree to prevent sagging during drawing and further drawing of the filament. The filament 53, however, enters the deposition chamber 45 immediately after the drawing operation so as to present to the deposition starter gaseous medium, in this case methane, a chemically-clean surface for effectively bonding reception of pyrolytically deposited film solids. Residual heat in the filament 53, remaining from the drawing operation in the vicinity of the main heating coil 27 which defines a drawing zone in the furnace chamber 13, is relied upon for the source of heat at a suitably high temperature to effect decomposition of the methane gas, the deposition temperature of which may be approximately 900° C. The auxiliary heating units 28 and 29 are employed and controlled only to regulate the cooling after the drawing operation to maintain the filament 53 at such a decomposition temperature for efficient deposition in the chamber 45, and consequently, the deposition chamber tube 44 can be and preferably is maintained at a sufficiently low temperature which avoids excessive deposition upon the deposition chamber tube walls, thereby minimizing fouling. Such lengths and characteristics of the heating units 28 and 29 and the heating are selected as may be dictated by the deposition time required and by vaporization temperatures of starter materials and the particular structural features of the apparatus. However, the heat supplied thereby is sufficiently low as to avoid heating the deposition chamber walls to the decomposition temperature of the deposition starter material. With increased lengths of the heating units 28 and 29 and with the use of both rather than only one, thickness of the deposited film of decomposition solids, such as carbon

which is pyrolytically deposited from the methane gas, is increased; this lowers the resistivity thereof when the filament is drawn through the deposition chamber **45** at the same relative rate of speed. The use of the two auxilary heating units **28** and **29** is advantageous, since the end of the deposition tube **46** is hotter than portions more remote from the main heating unit **27**. Thus, auxiliary heating unit **29** may be relied upon to supply more heat than auxiliary heating unit **28** so as to maintain the entire portion of the deposition tube **44** in the furnace chamber **13** at substantially the same temperature to avoid undue cooling of filament **53** while therein. It is to be understood that, of course, even though there is no external source of heat for that portion of the deposition tube **44** extending beyond the furnace chamber **13**, pyrolysis takes place therein with a degree of deposition of solids on the surface of the filament **53** due to its maintenance at a temperature at or above the decomposition temperature.

The modified deposition assembly **111** of Fig. 2 provides on the stand **38** a head **140** traversed by bore **41**. The head bore **41** is counterbored to provide a stepped enlargement having two sections **42** and **54**, with the latter of a diameter larger than that of the former. One end **55** of an elongated refractory tube **56** of quartz, or the like, is fixedly supported in the entrance end of counterbore section **42**, and with the entrance end of this tube located at a point **57**. A duct **58** communicates with the section **42**, as shown, to admit inert gas, such as nitrogen, as does duct **49**, communicating with the bore **41** beyond the section **42**. The discharge end **143** of an elongated refractory tube **144**, also of quartz or the like, is fixedly supported in the entrance end of counterbore section **54** and, as shown, this tube is of a diameter larger than the diameter of the tube **56** to provide elongated annular space **59** therebetween, which is in communication with tube **47** connected to the section **54** to supply thereto the deposition vapors. Entrance end **146** of tube **144** extends beyond the entrance end **57** of tube **56**, as shown, to provide a deposition zone **145** therebetween.

In use of the deposition assembly illustrated in Fig. 2, the entrance ends **146** and **57** of the respective tubes **144** and **56** are inserted in the bore **13** of furnace tube **12** in the manner taught with respect to the deposition tube **44** of the deposition assembly **11** of the Fig. 1 embodiment, so as to receive from the furnace chamber the relatively fine, drawn filament to be pulled out through bore **41**. The inert sealing gas supplied by duct **49** to the bore **41** prevents entrance of oxidizing air and the inert sealing gas supplied by the duct **58** to the counterbore section **42** flows through the inner tube **56** toward its entrance end **57** to prevent entrance thereinto of the deposition vapors. The deposition vapors are supplied from any suitable source through duct **47** to the counterbore section **54** and the space **59** between the tubes **56** and **144** for contact of the hot filament in the deposition zone **145**.

Thus, the deposition vapors are confined to contact of the hot filament in the relatively short zone **145** so as effectively to limit the temperature range in the zone where deposition of a film on the hot filament may take place. So limiting the range of temperature variations in the deposition zone is advantageous in certain operations, for example, in the deposition of carbon. Carbon film solids which are pyrolytically deposited at lower temperatures, such as those which may exist at the discharge end **43** of the deposition tube **44** of the Fig. 1 apparatus, may tend to be soft and of a sooty character. At the higher temperatures, which exist in the vicinity of the entrance end **46** of the deposition tube **44**, the carbon film solids which are pyrolytically deposited there first upon the hot filament are appreciably harder. As a result, in the pyrolytic deposition of carbon film solids upon the hot filament with the use of certain embodiments of the form of the apparatus illustrated in Fig. 1, a film of hard solids may first be deposited upon the hot filament and then overlaid with a softer, somewhat sooty deposit effected in the cooler end of the deposition chamber **45**. With the use of the deposition assembly of Fig. 2, pyrolytic deposition of solids, such as carbon, from the deposition starter gaseous medium, such as methane, is effected in the relatively narrow zone **145** to which contact between the deposition gas and the hot filament is substantially limited, and where there can be only a limited range of temperatures, with the latter being subject to ready control. As a result, it is practically possible pyrolytically to deposit on the filament in that relatively narrow controlled zone **145** only hard films of deposition solids.

Practice of the present method features use of residual heat in the base material which remains after an initial heat treatment, e.g., during drawing of a filamentary substrate, to effect pyrolytic decomposition of the deposition gaseous medium with attendant effective deposition of decomposition solids on base material surfaces while such deposition on deposition chamber walls and other parts of the apparatus is minimized. This is attained by the presence of a temperature gradient between the base material surface and the deposition chamber walls with the latter at temperatures appreciably below the decomposition temperature of the particular film source gaseous medium employed, while the surface of the base material is at or above this temperature. The auxiliary heat sources about the deposition chamber are employed not to heat up the base material after cooling following the initial heat treatment but to control the rate and degree of such cooling whereby the surface of the base material is held up to and maintained at or above the decomposition temperature while in the decomposition chamber, and to provide, where necessary, heat for vaporization of the decomposition medium. It will be noted that pyrolytic deposition begins immediately after the filamentary substrate is drawn with decomposition of deposition gaseous medium by the temperature of residual drawing heat; thus at the time when the substrate surface is clean and in an active state from both physical and chemical standpoints. The pyrolytic decomposition of the gaseous deposition medium appears largely to be a surface phenomenon, taking place largely at the surface of the hot, freshly-drawn filament. It is believed that the hot, clean surface of the freshly-drawn filament exerts a catalytic effect with respect to the pyrolytic decomposition of the deposition medium and that the observed unusually effective bonding of the film to the substrate may be due to initial "wetting" of the substrate surface by fresh decomposition solids produced at or directly adjacent the cleansed substrate surface. It is also possible that there is some chemical reaction between components of the filamentary substrate and the components of the deposition gaseous medium.

As will be hereinafter more fully explained, some of the deposition starter materials may have relatively high decomposition temperatures which may closely approach the softening and drawing temperatures of certain substrates starter materials. It is to be understood that the present procedure may be efficiently practiced with apparatus where the filament, as it passes through the initial zone of the deposition chamber, may be substantially at the softening temperature of the substrates material so that the pyrolytic decomposition of the deposition vapors may take place substantially at that softening temperature. In such cases, a tacky or sticky condition of the filament surface will be noted. However, effective operation and practice of the present invention makes it highly desirable that the substrates material or drawn filament be in or drawn through the deposition chamber at a temperature below the sag softening temperature of the substrates member. The sag softening temperature of any particular rod-like or filamentary base or substrate member of any certain material is that temperature at which it will sag, i.e., is non-self-supporting; and is

determinably governed by the softening point of this material; the distance between the points of successive support; speed of any linear travel; and rate of heat dissipation from the deposition zone of any particular deposition apparatus. It will thus be understood that the temperature at the surface of the base material or filamentary substrate in the deposition zone may be at the softening temperature of the base or substrate material or a temperature which causes this surface to be soft while the base member or filamentary substrate as a whole is of such rigidity that it is relatively non-sagging under the conditions of handling in this particular apparatus. As will appear more fully hereinafter, it is desirable and of practical importance to practice the present method where possible at temperatures appreciably below the oxidation temperatures of the deposit material when the latter are of the type which oxidize at elevated temperatures.

Numerous deposition starter materials may be employed within the scope of this invention with the satisfaction of the above criteria. Classes of compounds which may be thus employed include aliphatic, aromatic and alicyclic compounds, particularly hydrocarbons and halogen derivatives thereof, silanes, hydrocarbon-substituted silanes, halosilanes, alkyl aryl halosilanes, as well as other substituted silanes; and also metal halides, oxyhalides, hydrides, chelates, and carbonyls. Moreover, various mixtures of such compounds may be employed.

Among specific compounds which may be so employed are alkanes, as, for example, methane, ethane, propane and butane; alkenes as, for example, ethylene and propylene; and alkines as, for example, acetylene, and their halogen derivatives. The aliphatic, aromatic and alicyclic hydrocarbons may, upon pyrolytic decomposition according to this invention, result in deposition of carbon on the base starter material. Silanes, as for example, mono-, di-, tri- and tetrasilanes, and halosilanes as, for example, mono-, di-, tri- or tetrachlorosilane; siloxane; hydrocarbon-substituted silanes, as for example, methyl silane, tetramethyl silane, hexamethyl disilane, trimethyl chlorosilane and triethyl chlorosilane; and silicon halides and oxyhalides as, for example, silicon chloride or silicon oxychloride result in deposition on one base starter material of silicon and, in the case of hydrocarbon-substituted silanes, in deposition of carbon as well. Metal compounds including metal halides as, for example, chlorides and oxychlorides and metal hydrides result in deposition of the metal on the base starter material. Metal chelates and metal carbonyls as, for example, nickel, molybdenum, tungsten or chromium carbonyl also result in deposition of the metal on the base starter material. For example, boron and garmanium halides and hydrides result in deposition of the respective metal on the base starter material. Thus, BCl_3 and diborane, B_2H_6, result in deposition of boron. Hydrocarbon-substituted boron hydrides and boron chlorides result in deposition of both boron and carbon. Various mixtures of the different classes of materials may be employed, one particularly useful material being mixtures of hydrocarbons and a silane or silicon halide, which result in deposition on the base starter material of both carbon and silicon in the form of elementary mixtures and/or compounds of the elements present.

It will thus be understood that any compound or compatible mixtures of compounds pyrolytically decomposible in vapor phase at atmospheric pressure and at temperatures preferably below the sag softening temperature of the selected base material to produce a deposit of a solid decomposition product or products on the base material may be employed in practice of the method of the present invention. It is also to be understood that the deposition starter materials may normally be in solid, liquid or gaseous phase.

The silicon and hydrocarbon compounds and compounds of similar semi-conductors pyrolytically deposit solids in a temperature range between about 800° C. and 1600° C., while those metal carbonyls suitable as deposition starter materials for the production of resistors and the like will pyrolytically decompose at a considerably lower temperature, such as about 100° C. and 300° C. Thus, for efficient practice of the present invention with the use of metal compounds as deposition starter materials, it may be advisable to employ base or substrates starter material having an appreciably lower softening temperature than those desired for use with other deposition starter materials which pyrolytically decompose at appreciably higher temperatures, so as to reduce the residual heat in the drawn filamentary substrate and to avoid complicating the apparatus.

Further, when the temperatures of volatilization and the temperatures of decomposition are relatively close, as may be the case with the metal carbonyls, and although it is possible to volatilize such solids as starter materials and feed the vapors to the deposition chamber of apparatus of the type depicted by way of example in Figure 1, it is often simpler to feed the solids directly to the deposition chamber or charge the latter therewith so that they are volatilized in the chamber and pyrolytically decomposed at the base material or filamentary substrate surfaces to deposit a film thereon. Such procedure avoids the possibility of excessive fouling of a separate vaporization chamber and feed lines between it and the deposition chamber with pyrolytic decomposition depositions, a problem difficult to avoid since the decomposition temperature may be so close to the vaporization temperature as to demand very close temperature control of evolved vapors during vaporization of the solids and feed of these vapors to the deposition chamber. However, the present invention contemplates within the scope thereof use of such apparatus as illustrated in Figure 1 for deposition of solids from vaporized solid deposition starter material fed from a separate source to the deposition chamber, with the necessary precautions being suitably accommodated.

By way of example, an embodiment of the apparatus of the present invention suitable for use in practicing the present method for pyrolytic deposition of solids from metal compounds and the like, such as metal carbonyls, is illustrated in Figs. 3 and 4. As base starter material Pyrex glass may be employed in the form of a rod for drawing a filamentary substrate in the production of particular products of the electrical resistor type. Such Pyrex glass may be of the No. 1720 formula containing approximately 58% silica, 19% aluminum oxide, 12% magnesium oxide, 5% boron oxide, and small amounts of calcium and alkali oxides; and having a softening point of about 915° C. This permits the use of much lower drawing temperatures in the drawing furnace 10. Other Pyrex glass formulas Nos. 7740, 7720 and 7070 respectively have softening points of 820° C., 755° C. and 715° C. However, considerable immediate cooling of the drawn filamentary substrate, prior to pyrolytic deposition of a metal film thereon from metal carbonyls and like relatively low decomposition point deposition starter materials, is advisable if not imperative to avoid oxidation of deposited metal. As proposed in Fig. 3, the deposition tube or the deposition zone provided thereby is, for the purpose of attaining such rapid and appreciable cooling of filament 53, located remote from the discharge end of the drawing chamber of furnace 10, such as a distance of about 3" or greater. With such physical separation of the deposition chamber or zone from the drawing chamber provided in the deposition assembly 211, a separate source of heat may be employed to advantage in association with deposition tube 244, such as is proposed at 200, accurately to control the much lower temperature of the filamentary substrate in the deposition chamber 245.

Since in practice of the present invention, pyrolytic deposition of solids from metal compounds may be efficiently effected, at relatively low temperatures, such

as, for example, about 100° C., the deposition tube **244** may be made from materials more economical than quartz, such as copper. The copper deposition tube **244** is supported in head **240** of the stand **38** in a manner similar to the support of the quartz deposition tube **44** in the head **40** of the Fig. 1 apparatus. The copper deposition tube **244** is surrounded by a copper jacket sleeve **60** and spaced therefrom by closing end rings **61, 61,** which may be of copper suitably soldered to the deposition tube and the sleeve, so as to define therebetween a closed jacket space **62**. Inlet and outlet tubes **63** and **64** communicate with the jacket space **62** preferably through opposite ends of the jacket sleeve **60** for circulation through this space for any suitable heat supplying medium, such as hot water, ethylene glycol, or oil, for transfer of heat to deposition chamber **245** and the filamentary substrate **53** passing therethrough. Thus, the deposition tube **244**, jacket sleeve **60**, closing rings **61, 61** and inlet and outlet tubes **63** and **64** together constitute a heat exchanger.

The entrance end **246** of the deposition tube **244**, which extends beyond the jacket provided by the sleeve **60** and the rings **61, 61**, is closely fitted with a slidable cap **65**, which is removable and which also may be of copper. The cap **65** is provided axially with an aperture **66** through which the filamentary substrate **53** is drawn with minimum spacing, e.g., 0.010" to 0.025", between the filament surface and the edge of the aperture, and this spacing is of the order of the spacing between the filament and the wall of the bore **41** for the like purpose of minimizing entrance of air and leakage from the deposition chamber **245**. Communication to the deposition chamber is effected by a tube **67** extending through both the deposition tube **244** and the jacket sleeve **60** for supply of various vapors or gases, as will appear hereinafter.

As will be seen from Figs. 3 and 4, the deposition starter material may be fed directly to the deposition chamber **245** in the form of particulated solids, such as metal carbonyl powder. A charge of such solids may be provided in the deposition chamber **245** by loading a relatively long, thin metal plate or strip **68** with the powder, which after loading is inserted in the deposition tube **244** from its entrance end **246** with the closing cap **65** removed and, as shown, to rest beneath the moving filamentary substrate **53** with the powder out of contact with the latter. This load of metal carbonyl powder on the long, thin metal strip **68** is indicated at **69** in Figs. 3 and 4. Strip **68** is capable of supporting thereon, out of contact with the lower side of the moving filament **53**, a sufficient quantity of the metal carbonyl powder **69** to accommodate continuous runs of filament through the apparatus for periods of at least an hour. Since the usual base material starter rod unit is generally of such dimensions as to provide a run of approximately one hour, sufficient metal carbonyl powder may be provided in the load **69** upon strip **68** to assure a supply of metal deposit film for coating all of the filament **53** which is drawn from one base starter rod unit. Accordingly, while a new base starter rod unit is being set up in the drawing furnace **10**, a new charge of metal carbonyl powder may be placed upon the supporting strip **68** by simple removal of cap **65**, withdrawal, reloading, and reinsertion of the strip **68**, and replacement of the cap.

In use of the apparatus depicted in Figs. 3 and 4 for the purpose of pyrolytically depositing film solids from metal carbonyls, the filamentary substrate **53** may have a temperature of about 1500° C. at the time of drawing, while the pyrolytic deposition might desirably be accomplished in the deposition chamber **245** at a temperature of about 100° C. Thus, in order to allow considerable cooling of the filamentary substrate **53** after it passes from the furnace **10**, before entering the deposition chamber **245**, the entrance end of the latter is placed an appreciable distance from the discharge end of the furnace, such as about three or more inches. The temperatures of the hot drawn filamentary substrates **53** and the vapors surrounding them in the deposition chamber **245** are adjusted and closely controlled by the heat exchanger with transfer of heat to or from the hot fluid circulated through the jacket space **62** via the inlet and outlet tubes **63** and **64**. The pyrolytic decomposition with deposition of film solids on the moving filamentary substrates **53** results. Since the entrance end of the deposition chamber **245** is out of the atmosphere in the furnace chamber, some precaution should be taken to prevent undue entrance of oxidizing air. Such is accomplished by the closing cap **65**, the minimizing of the spacing between the edge of the cap aperture **66** and the moving filamentary substrates **53**, in addition to the similar spacing between the latter and the wall of discharge bore **41**, the supply of inert gas by duct **49** and the production in the deposition chamber of waste gases. Additional inert gas may be supplied to the deposition chamber **245** via duct **67** further to assure that no air will enter the deposition chamber. Also, if it is desired pyrolytically to deposit film solids of a plurality of metals simultaneously, vapors of one may be supplied from the load of carbonyl powder **69** on the strip **68**, and another may be supplied in a gaseous state through the duct **67**. Also, the duct **67** may be employed for supply of the deposition starter gaseous medium when all of the pyrolytic deposition is to be effected therefrom without hte provision in the deposition chamber of a charge of solids, such as that at **69**.

It has been found in electrical resistors that a film of a mixture or alloy of a plurality of metals may be of superior quality to a film of similar thickness of a single metal, in that the first-mentioned film has a higher resistance, lower temperature coefficient of resistance, and is more stable. When metals are pyrolytically deposited as a film, they are initially in an amorphous state, while the more stable state of the metals is the crystalline state. Accordingly, there is tendency for conversion of the metals in the amorphous state to the more stable crystalline state with attendant increase in resistance of the metal film due to movement of the atoms closer together to form the crystals thereby leaving intervening spaces. In order to avoid this material changing of the resistance, impurities may be added to the metal films in the form of so-called "doping agents." Such "doping agents" change the resistance of the metal film and lower the temperature coefficient of resistance. It has been found in production of electrical resistors according to this invention that incorporation of a small amount of tetraethyl lead in the decomposition starter material employed will materially and uniquely increase the load life of the resistors. Incorporation of tetraethyl lead also unexpectedly increased the resistance obtained with a given deposition coating to a substantial degree.

In advantageous practice of the present invention in connection with the production of electrical resistors, the addition of silicon to the pyrolytically deposited carbon films is found to improve the humidity properties of the latter and appears to lower the temperature coefficient of resistance. Although the source of silicon may be a non-hydrocarbon silicon compound, as, for example, silicon tetrahalide, a silane, or halosilane vapors of which are mixed with a hydrocarbon gas (as the source of the carbon), it has been found in the development of the present invention that vapors from a single compound including both carbon and silicon components may be employed to advantage. Such common source of both the carbon and silicon is particularly advantageous since differences of decomposition temperatures, often characteristics of a mixture, are avoided and precise control is easily attainable. It has been found to be particularly advantageous to employ for this purpose trimethylchlorosilane. It appears that pyrolytic decomposition of trimethylchlorosilane yields, in addition to carbon and silicon, silicon

carbide, hydrogen, chlorine, and possibly hydrogen chloride. In any event, the desirable carbon and silicon solids are deposited together in the form of a film on the substrates with escape of the gaseous decomposition products from the open end of the deposition chamber and the open ends of the furnace tube. It should also be noted that where a mixture is employed as the deposition source material, the surface of the base material should be at or above the highest of the decomposition temperatures of the components of the mixture.

Practice of the present invention to produce electrical resistors characterized by metal films obtainable with pyrolytic decomposition of metal carbonyls has been found to be efficiently possible at unusual speeds and pressures. For example, with the use of nickel carbonyl, the metal is found to be depositable by pyrolytic decomposition at atmospheric pressures and at relatively high speeds of subtrates travel, e.g., where any particular section of the filamentary substrate remains in the deposition chamber for an overall period of only a few seconds. These unusual results have ben attained by temperature gradient between the hot base material and the cooler walls of the deposition chamber, removal of the metal as a deposit upon the travelling filamentary substrate from the reaction chamber, and by permitting the decomposition gaseous products, including carbon monoxide, readily to diffuse out of openings in the ends of the reaction chamber.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above process, in the described product and in the constructions set forth without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Particularly it is to be understood that in said claims, ingredients or compounds recited in the singular are intended to include compatible mixtures of such ingredients wherever the sense permits.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. Apparatus for depositing on base material a film of the solid products of pyrolytic decomposition of a gaseous medium comprising, in combination, a main heat source furnace having a tubular heating chamber open at both ends to receive through one end a body of starter base material and to permit withdrawal from the other end of a filamentary substrate drawn from the starter body as the latter is heated to its softening point in said furnace, a deposition chamber in the form of a tube to permit the drawn filament to pass therethrough, and having a filament entrance end adjacent the other end of the furnace said deposition chamber being supported for movement axially of said furnace, and being of a diameter relative to the diameter of the heating chamber of said furnace as to be slidably receivable in the heating chamber, and means to supply deposition gaseous medium to the interior of said deposition chamber tube.

2. The apparatus as defined in claim 1 characterized by the provision of auxiliary heat source means to be located in the vicinity of a zone of said deposition chamber tube to control cooling therein of the hot filament.

3. The apparatus as defined in claim 1 characterized by said tube being supported at its filament-withdrawal end with a head having a filament outlet passage extending laterally therethrough, duct means to supply inert gas to said passages at a certain point with said passage being restricted beyond this point to a diameter approaching the diameter of filamentary substrates to be drawn therethrough, and means to supply deposition gaseous medium to said deposition tube chamber ahead of the duct means communicating point.

4. The apparatus as defined in claim 1 characterized by the provision of a second tube arranged concentrically within said deposition chamber tube through which the drawn filament also is to be moved, both tubes having open entrance ends for reception of the moving drawn filament with that of the inner tube being set back appreciably beyond the entrance end of the outer tube to define a deposition zone therebetween, said deposition gaseous medium supply means communicating with the space between said tubes for flow of said medium to said zone, and means to supply an inert gaseous medium to the interior of said inner tube for flow toward its entrance end to bar entrance of said medium for substantially confining contact between the latter and said filament to said zone.

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