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FILAMENT FOR VACUUM DEPOSITION APPARATUS AND METHOD OF MAKING IT

Filed Jan. 11, 1962

Fig. 1

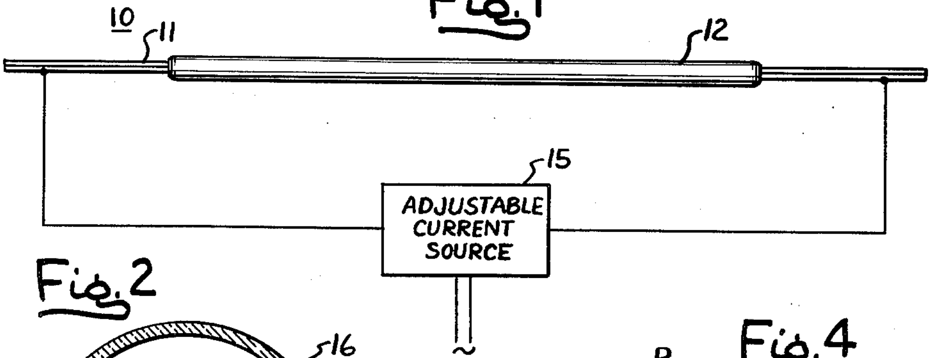


Fig. 2

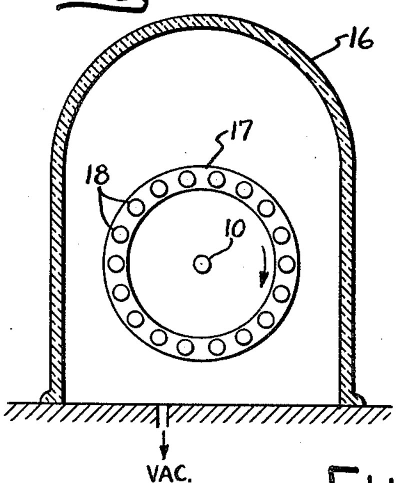


Fig. 4

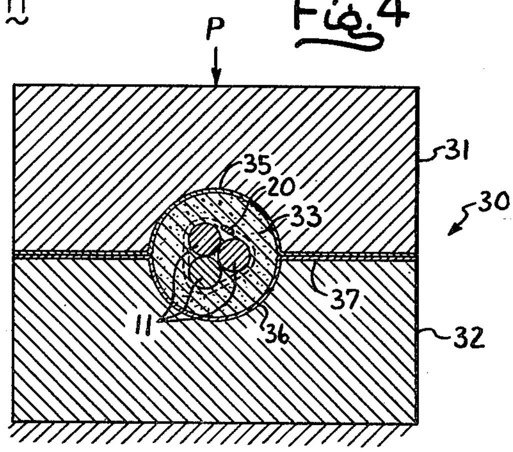


Fig. 5

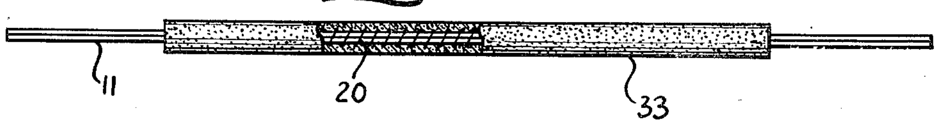


Fig. 6

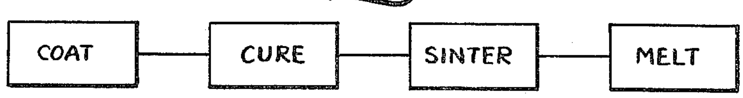
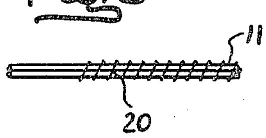


Fig. 3



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3,190,771

FILAMENT FOR VACUUM DEPOSITION APPARATUS AND METHOD OF MAKING IT

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9 Claims. (Cl. 117—227)

The present invention relates to an improved filament for vacuum deposition apparatus and which is particularly suitable for the depositing of conductive films on resistor blanks.

It is an object of the present invention to provide an improved filament for vacuum deposition apparatus which is capable of vaporizing metal for uniform deposition on resistor blanks or substrates arranged in the neighborhood of the filament.

It is another object of the invention to provide a filament for vacuum deposition apparatus and a procedure for making it which is especially suited for deposition of alloy films and which is capable of producing a resistive film in which the alloy constituents are maintained in a substantially predetermined proportion during the period of vaporization.

It is another object to provide a procedure for producing a filament which is wetted with metal alloy and where the nature of the materials is such that wetting is normally difficult to achieve. Specifically it is an object to provide a procedure for producing a tungsten filament wetted with an alloy of chromium and titanium.

It is still another object to provide a filament coated with an alloy having a relatively low melting point for vaporization of the alloy when the filament is electrically heated and which includes novel provision for maintaining the alloy evenly distributed over the length of the filament even though in molten state.

It is another object related to the foregoing to provide a filament for vacuum deposition apparatus which permits the rate of deposition to be easily and precisely controlled.

Finally it is an object to provide a filament for vacuum deposition apparatus which enables production of precision resistors which are more stable and consistent from unit to unit than has been possible in the past.

Other objects and advantages of the invention will become apparent upon reading the attached description and upon reference to the drawings in which:

FIGURE 1 shows a vaporizing filament constructed in accordance with the present invention and with the current source diagrammatically indicated.

FIG. 2 is a diagram illustrating a vertical section of a vacuum deposition apparatus in which the invention is preferably used.

FIG. 3 is a fragmentary view showing the conductive core made up of a bundle of conductors and having a wire helically wound thereon.

FIG. 4 is a cross section of a mold employed in forming a filament using powdered alloy.

FIG. 5 shows a filament after the molding process with a portion broken away to reveal the internal helical winding.

FIG. 6 is a diagram showing the series of steps employed in producing the filament illustrated in FIG. 1.

While the invention has been described in connection with a preferred procedure and embodiment, it will be understood that the invention is not necessarily limited to the procedure and embodiment shown but we intend,

on the contrary, to include within the scope of the invention the various alternative or equivalent constructions or procedures included within the spirit and scope of the appended claims.

Turning now to the drawing there is disclosed in FIG. 1 a filament **10** constructed in accordance with the present invention having a heater **11** in the form of a bundle of electrical conductors and an adherent layer **12** in the form of a metal alloy capable of being vaporized when the temperature of the heater is raised. Current is supplied to the ends of the heater **11** by means of a current controlling device **15** having provision for manual or automatic current control and deriving current from the regular A.-C. supply lines.

The vacuum deposition device in which the filament **10** is employed does not per se come within the scope of the present invention and it will suffice to describe it briefly. The filament is mounted to extend axially within a vacuum chamber **16**. Surrounding the filament **10** and concentric with it is a cylindrical carrier **17** for a plurality of resistor blanks **18**. Such resistor blanks are arranged in groups with the resistor blanks in each group end to end and with each group being spaced the same distance from the filament **10** and parallel to it. Means are preferably provided for rotating the groups of blanks around the filament and simultaneously around their own axes so that substantially the same amount of vaporized alloy is deposited over each unit area. Thus at the completion of the film deposition process all of the blanks will be found to lie within a narrow range of resistance. Following nitriding, the resistor elements may be brought to the final value of resistance in an automatic "spiraling lathe" which is well known to those skilled in the art.

In accordance with one of the aspects of the present invention a novel procedure is employed for making filaments as disclosed in FIG. 1. Preferably the heater **11** is in the form of a group of conducting wires, for example, three in number, arranged parallel to one another. Means are provided for binding the conducting wires together and for providing anchorage for the vaporizable alloy. In the present instance this function is accomplished by a relatively thin wrapping wire **20** (FIGS. 3 and 4) having convolutions which are equally spaced from one another. The heater **11** and wrapping wire **20** are preferably formed of a high melting point metal which may be heated to high temperature without substantial vaporization even in partial vacuum and which is capable of being wetted by the vapor-producing alloy to be employed. In the present instance tungsten is preferred although molybdenum is a satisfactory alternate.

For the purpose of coating the heater it is placed in a mold **30** of the flash type having cooperating mold sections **31, 32** along with a quantity of finely divided alloy powder **33** and a binding agent. The composition of the alloy powder depends upon the desired composition of the resistive film. In a practical case we prefer to employ powdered metal in the form of an alloy of chromium and titanium having particle size capable of passing a 100-mesh screen. Preferably an alloy of 35% chromium and 65% titanium is used, although the amount of chromium in the alloy may be as much as 65% (remainder titanium) if desired. In order to bind together the particles a minor proportion of resin is intimately mixed with the alloy. Preferably the resin is one which may be cured by heating and which may be driven off by elevation of temperature with a low ash residue. We prefer to use urea resin for this purpose, for example Rohm & Haas F200E which is a polymer formed by the reaction of urea with formaldehyde and characterized by the following properties:

Percent solids	±2%–50.
Solvent	Xylol-butanol (1:1).
Acid No., solids basis	6–10.
Specific gravity	1.01.
Pounds per gallon	8.4.
Color	Colorless and clear.
Viscosity, Gardner-Holdt at 25° C.	W–Z.
Mineral thinner tolerance	11–18.

A proportion of four parts of metal to one part of resin has been found to be optimum although a 5:1 ratio between these components may also be successfully used. If desired, where the alloy powder is deposited by means other than molding, as covered below, the proportionate amount of resin may be increased.

In order to free the molded filament from the mold sections and to eliminate the need for a mold release agent, we prefer to line the mold halves with a layer of aluminum foil. The layers indicated at **35**, **36** have an outward extension or flash **37**. After the heater **11** has been centered within the mold surrounded by the alloy-resin mix, indicated at **30**, pressure P is applied to produce the desired degree of compaction. When the molding pressure is released, the mold halves are separated and the molded filament, encased in the aluminum foil, is removed. The foil, in addition to facilitating release, serves to hold the powdered elements temporarily in contact with the heater prior to the curing operation. A plurality of such molded filaments are then placed in a suitable oven and baked to the degree necessary to cure the resin and to rigidify the powdered layer. Where urea resin is employed, baking for one half hour at 150° C. is adequate. After baking, the foil is peeled away and the coated filament is ready for the next procedural step.

In accordance with the present invention the completed filament is produced by subjecting the filament assembly to progressively increased temperatures, in the presence of vacuum, first for the purpose of driving off the resin binder and secondly for the purpose of melting the sintered mass so that it becomes liquid for wetted contact with the conductors **11** of which the heater is formed and with the wrapping wire **20**. The sintering procedure is carried out at a temperature on the order of 1000° C. with the vacuum serving to remove the decomposition products of the urea resin. In practice we prefer to place the cured but unsintered filament assemblies in a vacuum chamber and with each connected to a power supply **15**. A vacuum is drawn and the temperature of the filament assembly is gradually increased by increasing the current. Preferably the vacuum is high enough so that there is substantially no oxidation of the heater conductors or the alloy powder, the pressure not exceeding about 20 microns Hg. On the other hand, since considerable outgassing occurs during burn-out of the resin, higher degrees of vacuum are not necessary and may result in action which is too violent. The sintering step is preferably carried on for a period of time on the order of 30 minutes. Upon completion of this step, the layer of powder occupies substantially the same volume as the powder-binder mix but the structure has the usual porous construction of a sintered product.

In order to change the form of the vaporizable layer from the porous to the solid condition, the temperature is further increased by increasing the current from the power supply **15** until the melting point of the alloy is reached. In the case of a chromium-titanium alloy having a ratio of, say 35% chromium and 65% titanium, the melting point is achieved at 1800–1900° C. At this point it is found that the porous structure is progressively converted, with the adjacent particles wetting the heater

conductors and the wrapping wire **20**, filling all of the interstices between them to form a molten "pool" into which the outer portion of the sintered layer gradually settles. The melting temperature is maintained until all of the powder has been changed to the molten form. Care is taken to prevent the molten alloy from becoming so thin that there is danger of dripping or running from one end to the other of the conductor wires. The wrapping wire acts in dual capacity in this respect. It provides sufficient wetted area so that a substantial amount of molten alloy may be held in place upon the surface of the heater and, in addition, it tends to inhibit any endwise flow of the molten material which may take place under the action of gravity if the filament is not perfectly level.

After all the alloy has melted and the filament has the appearance shown in FIG. 1, the flow of current is immediately cut off in order to prevent unnecessary evaporation of the alloy. Subsequently, when the filament is positioned in a vacuum deposition device and electrical contact is made, the current from the powder supply **15** is adjusted to produce a heating effect which will result in the desired rate of vaporization of the alloy under the existing condition of partial vacuum. A temperature of 2000° C. may be used. Response to adjustment of current is precise and immediate in effect.

Because of the fact that vaporization may take place in all radial directions from the filament, deposition is more uniform than where conventional vaporization means, for example, a boat type source, is employed.

Each step of the above procedure is not limited to treatment of a single filament and, if desired, filaments may be fabricated in quantity production runs and at low unit cost.

While the invention has been described above in connection with a heater element comprising a bundle of parallel wires, it will be apparent that the heater may, instead, be in the form of a hollow tube to provide a large surface area combined with limited cross section of metal. Moreover, if desired, such tube may be wound with a wrapping wire or the surface area increased in some equivalent way as, for example, by the use of spaced rings without departing from the present invention. Moreover, instead of sintering and melting as separate fabrication steps, the sintering and melting operations may be performed in situ in the deposition apparatus **16** (FIG. 2) ahead of the regular evaporation cycle, but if this is done shielding should be provided between the filament and resistor blanks to prevent contamination of the blanks during the period that the resin is being driven off.

While the invention has been described above including the step of molding the alloy powder about the heater, it will be understood that the invention in certain of its aspects is not limited thereto but contemplates the application of powder in other ways. For example, the powder may be formed with a minor proportion of urea resin and a vaporizable vehicle into a slurry which is painted upon the heater in successive coats to a desired depth. Or, if desired, the slurry may be applied to the heater by dipping, with evaporation of the vehicle between successive dipping operations. In such event it will be apparent that the filament may be sintered without necessity for using metal foil for interim support.

It is found that a filament made in accordance with the present teachings is capable of depositing an alloy film in which the proportion of the metals in the alloy may be established with precision and in which such proportion remains constant during the entire period of vacuum deposition. Thus it is possible, using the present filament, to produce precision film type resistors having a higher degree of stability and a higher degree of consistency from unit to unit than has been possible with a conventional vapor source. After the filament has undergone one "run" in a vacuum chamber, it is removed and may be subsequently used for the production of film type resistors having characteristics which are less exacting.

While the procedure for producing filaments wetted with chromium-titanium alloy has been employed on a commercial scale, the reasons for the complete and immediate wetting, achieved using materials normally difficult to wet, are not fully understood. It is likely that the urea resin is driven off so completely during the course of sintering that the metal powder constituents and tungsten wire are left in a clean state in condition for incipient fusion and wetting by the alloy. It is moreover possible that the urea resin acts in some way as a flux to positively promote the wetting which has been achieved.

The term "alloy" has been employed in the following claims since we prefer to use a vaporizable metal layer having more than one constituent. However, a single metal may be used without departing from the invention and consequently the term "alloy" shall be understood to apply to and cover use of one or more metals in the vaporizable layer.

We claim as our invention:

1. The method of making a filament for a vacuum deposition apparatus which comprises the steps of forming in along the length of a conductor a substantially uniform layer of vaporizable metal powder including chromium and titanium in desired proportions having mixed therewith a minor portion of thermosettable resin, which is thermally decomposable to produce vaporizable decomposition products maintaining a vacuum about the filament thus formed, passing current through the conductor to produce a temperature which is sufficently high as to decompose the resin and vaporize the decomposition products and to produce a sintered layer of alloy powder, and then increasing the current to produce a temperature sufficiently high as to melt the sintered layer so that it becomes wettingly adherent to the conductor and distributed substantially uniformly along the length thereof.

2. The method of forming an adherent coating of alloy on a base of high melting point metal which comprises the steps of forming on the base a substantially uniform layer of a vaporizable metal alloy powder having mixed therewith a minor portion of a thermosettable which is thermally decomposable to produce vaporizable decomposition products and a low ash residue subjecting the base in the presence of vacuum to a temperature which is sufficiently high as to decompose the resin and vaporize the decomposition products and to produce a sintered layer of metal powder, and then increasing the temperature while maintaining the vacuum to melt the sintered layer so that the alloy becomes wettingly adherent to the base and distributed substantially uniformly over the surface thereof.

3. The method of making a filament for a vacuum deposition apparatus which comprises the steps of molding in a uniform layer along the length of a conductor a vaporizable metal powder having mixed therewith a minor portion of a thermosettable resin which is thermally decomposable to produce vaporizable reaction products curing said resin by heating so that the layer of powder is durable and self-supporting, sintering the filament in the presence of vacuum at a temperature which is sufficiently high as to decompose the resin accompanied by outgassing of the decomposition products, and then increasing the temperature to melt the layer of sintered metal powder so that it becomes wettingly adherent to the conductor and distributed substantially uniformly along the length thereof.

4. The method of making a filament for a vacuum deposition apparatus which comprises the steps of forming in along the length of a conductor a uniform layer of vaporizable metal powder having mixed therewith a minor portion of a thermosettable resin which is thermally decomposable to produce vaporizable decomposition products, sintering the filament thus formed in the presence of vacuum at a temperature which is sufficiently high as to decompose the resin accompanied by outgassing of the decomposition products, and then increasing the temperature to melt the layer of sintered metal powder so that it becomes wettingly adherent to the conductor and distributed substantially uniformly along the length thereof.

5. In a filament for vacuum deposition apparatus the combination comprising a central heater formed of a bundle of conductive wires, an anchoring wire helically wound about said bundle with relatively wide spacing between the successive convolutions thereof, said wires being made of a resistive material having a high melting point, the bundle of conductive wires being surrounded by a uniform layer of vaporizable metal alloy which is wettingly adherent thereto with the alloy filling the interstices between the wires so that the alloy is maintained substantially uniformly distributed along the length of the conductors when heated to a temperature above the melting point, said alloy being of the type capable of vaporization in a partial vacuum for deposition of alloy in the form of a film upon substrates in the neighborhood of the filament.

6. The method of making a vaporizing filament for vacuum deposition apparatus which comprises the steps of winding a strand of conductive wire about a bundle of conductors so that the conductors are held compactly together and with the successive convolutions of the winding being spaced from one another, forming a layer of vaporizable metal alloy powder mixed with a vaporizable binder over the bundle of conductors and of substantially uniform thickness, maintaining a vacuum about the filament thus formed, heating the conductors to successively higher temperatures so that the binder is driven off to produce a sintered layer of alloy powder followed by melting of the layer so that it becomes wettingly adherent to the conductors and to the wire which is wound about such conductors, and then allowing the filament to cool so that the alloy solidifies.

7. In a procedure for making precision film type resistors the steps which comprise forming on a high melting point conductor a layer of vaporizable alloy powder having a minor proportion of vaporizable binder material mixed therewith, placing the filament thus formed in a vacuum deposition device with uncoated resistor blanks in the neighborhood thereof, passing a current through the conductor which is sufficiently high as to produce a temperature capable of driving off the binder material and sintering the mass of alloy powder, increasing the current through the conductor to produce a temperature which is sufficiently high as to melt the sintered mass so that the conductor is wettingly coated with a layer of molten alloy and to vaporize the same for deposition of a film on said blanks.

8. In a filament for a vacuum deposition apparatus having means for conducting current to the ends of the filament, the combination comprising a central conductor having a high melting point, a layer of vaporizable metal alloy powder surrounding said conductor and having mixed therewith a cured resin which is thermally decomposable to produce vaporizable decomposition products and a low ash residue, said alloy being of the type capable of vaporization in a partial vacuum for deposition of alloy in the form of a film upon substrates in the neighborhood of the filament.

9. In a filament for a vacuum deposition apparatus having means for conducting current to the ends of the filament, the combination comprising a central conductor having a high melting point, a substantially uniform layer of vaporizable metal alloy comprising chromium in the range of about 65 to 35% and titanium in the range of about 35 to 65% readily adherent to said conductor for vaporization when said conductor is heated to a temperature above the melting point of the alloy, said alloy having

mixed therewith a cured resin which is thermally decomposable to produce vaporizable decomposition products and a low ash residue.

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RICHARD D. NEVIUS, *Primary Examiner.*

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