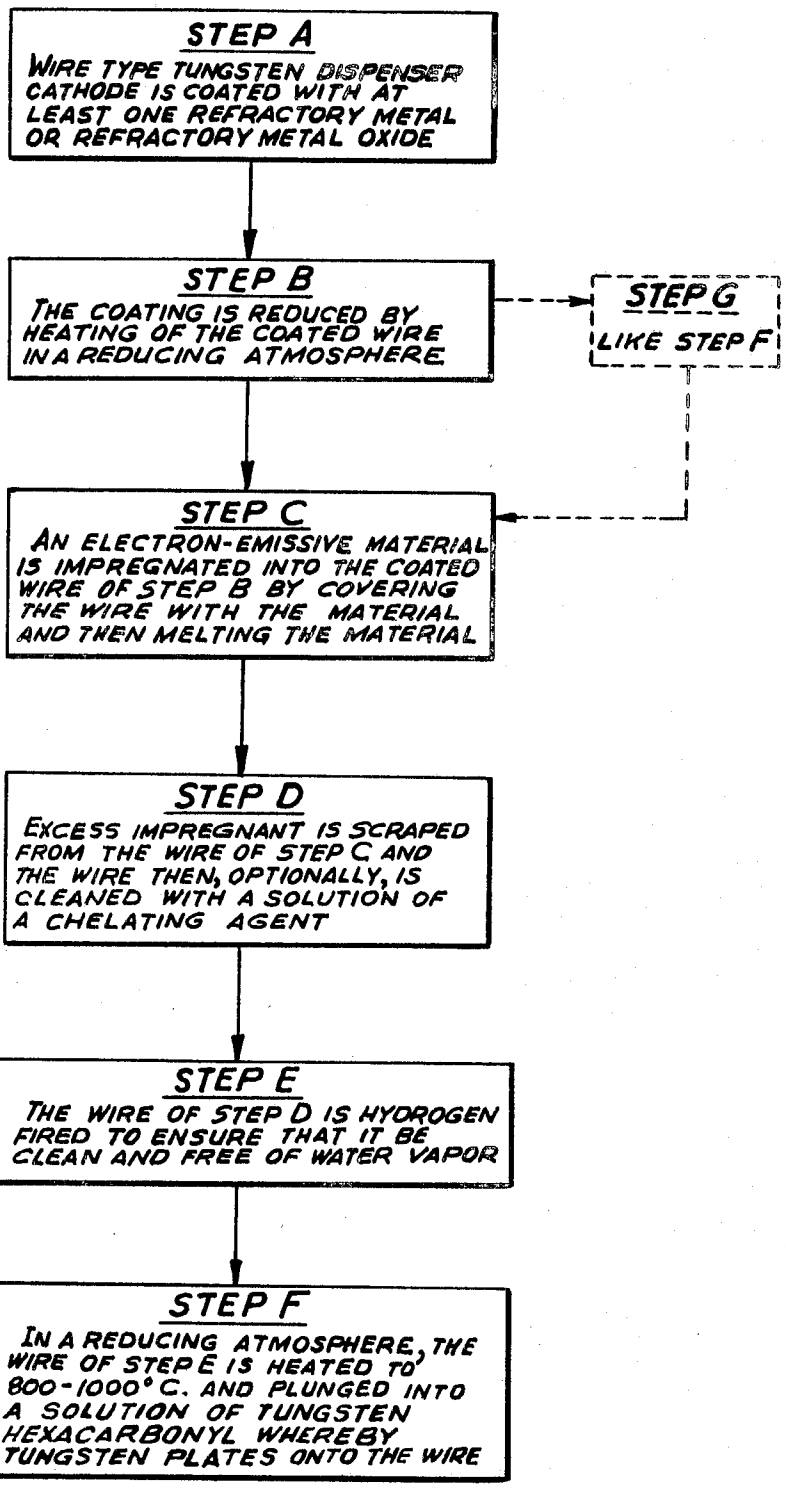
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TUNGSTEN COATING OF DISPENSER CATHODE

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TUNGSTEN COATING OF DISPENSER CATHODE

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ABSTRACT OF THE DISCLOSURE

A coating of tungsten is formed on a dispenser cathode by decomposing tungsten hexacarbonyl in the presence of the dispenser cathode.

This invention relates to the production of wire type dispenser cathodes and to a procedure for sealing off a portion of the total surfaces of a cathode to stop emission and evaporation.

Wire dispenser cathodes are useful for magnetrons designed to produce high frequency energy for cooking and industrial use. Such applications are particularly severe on the cathode since the electron back bombardment of the cathode can vary over a wide range due to a changing work load which produces an impedance mismatch. For example, the worst condition occurs for a cooking type magnetron when a housewife runs her microwave oven with a full load and then with it empty. This causes the cathode temperature to change over wide limits and as a result, the life of the cathode is limited. Moreover, wire type dispenser cathodes have a higher porosity than those made by the methods described in U.S. Pats. No. 2,700,000 and 3,076,916, because the refractory metal powder, typically tungsten, is not compacted to form the cathodes and, as a consequence, the alkaline earth metal, typically barium, of which the electron-emissive material of the cathodes is comprised, evaporates at a high rate, resulting in a short life for the cathodes, even at normal operating temperatures. Hereinafter, the prior art and the present invention insofar as they relate to cathodes constituted of porous refractory metal matrix bodies containing alkaline earth metal compounds, will be described by reference to tungsten as the refractory metal and barium as the only, or major alkaline earth metal; however, what is stated herein is also generally applicable to the art-recognized equivalents of barium, such as calcium and strontium, and the art-recognized equivalents of tungsten, such as molybdenum, tantalum, noibium and hafnium.

At the present time thoriated tungsten wire is used as the cathode for cooking type magnetrons. A thoriated tungsten wire cathode gives satisfactory life and performance, but due to its high operating temperature, which is on the order of 1600° C., it is very inefficient. Furthermore, this cathode is very susceptible to gas poisoning agents and, as a consequence, the cathode and the tube in which the cathode is disposed bust be processed in a very exacting manner, all of which adds to the cost of the tube.

A tungsten dispenser wire cathode has a number of distinct advantages over a thoriated tungsten cathode. The operating temperature is almost 600° C. lower and as a result the amount of electric power needed to heat the cathode is drastically reduced. It is easier to activate than a thoriated cathode and the cost of processing tubes containing this cathode is thereby reduced.

In order for a tungstetn dispenser wire cathode to operate satisfactorily in a cooking type magnetron, it must satisfy one rather drastic specification. It must be able to stand severe secondary electron back bombardment which will change its operating temperature from

900° C. to about 1400° C. depending upon the loading of the cooking oven. The life of a dispenser cathode at 900° C. is many thousand hours; however, the life rapidly decreases as the temperature is increased. At 1400° C. the life is only a few hours. The life of a dispenser cathode is determined by the amount of barium oxide available for reaction, the rate at which the barium oxide is reduced to free barium, and the rate at which the free barium is evaporated. A rather porous cathode contains proportionately more barium oxide than a less porous cathode, but the life of such cathodes, assuming like geometry, is about the same for any given temperature. The barium simply evaporates more rapidly from the porous one than from the less porous one.

According to the teachings of U.S. Pats. No. 2,699,008, 2,700,000 and 3,076,916, the optimum density range for the tungsten matrix should be within 80 to 86% of theoretical. According to the prior art, the barium is generally incorporated into the porous tungsten matrix as an aluminate; above a density of 86% of theoretical the porous tungsten accepts the molten barium aluminate with difficulty whereas below 80% density the total amount of evaporation products from the cathode becomes more and more excessive as the density is lowered. The optimum theoretical density is about 83%. All wire type tungsten dispenser cathodes have a theoretical density below 80% because they are not compacted before sintering and as a consequence they suffer from excessive evaporation.

The theoretical solution to the problem is to provide the structure with very porous internal portion in order for it to contain a maximum amount of barium and a low porosity outer layer. Such a cathode structure is an idealized one that would give a maximum life with a minimum amount of barium evaporation. In practice this is a difficult structure to fabricate.

As attempts to achieve the foregoing idealized structure, a number of different types of vapor deposition methods have been employed to coat tungsten dispenser wire cathodes with tungsten but with no success. These include the chloride and the fluoride procedures. Either all the pores of the tungsten matrix are closed or a reaction product is produced that is detrimental to the emission. According to one aspect of the invention, there is provided a method of depositing tungsten on wire dispenser cathodes to successfully produce the aforementioned idealized structure.

A serious fault of planar dispenser cathodes made by the procedures of U.S. Pats. Nos. 2,700,000 and 3,076,916 is the cathode-to-heater leakage. At the present time there is no satisfactory way of sealing one side of an impregnated tungsten emitting disc, and as a consequence the disc emits electrons and barium products from both sides.

According to another aspect of the invention, there is provided a method of depositing tungsten on the backside (i.e., the surface opposite the surface intended for emission) of a planar cathode which reduces the cathode-to-heater leakage to an acceptable level.

It has now been found according to the present invention, that tungsten may be deposited on a dispenser cathode consistuted of a porous refractory metal matrix impregnated with an electron-emissive material by heating tungsten hexacarbonyl in the presence of the dispenser cathode to a temperature sufficiently high a decompose the tungsten hexacarbonyl. It has further been found that this operation may particularly conveniently be accomplished by heating the dispenser cathode to the temperature sufficiently high to decompose the tungsten hexacarbonyl and then bringing the tugnsten hexacarbonyl into contact with the so heated cathode. Conveniently, the tungsten hexacarbonyl may be employed as a solution,

for example, in a hydrocarbon solvent, or carried by a gas. However, alternatively, the tungsten hexacarbonyl may be employed directly as an undiluted vapor. In one preferred embodiment, a solution of tungsten hexacarbonyl is squirted against the heated cathode. Since the heat causes the relatively small quantity of tungsten hydracarbonyl employed to vaporize, this may conveniently be referred to as a "vapor plating" technique. Direct employment of vapor is also, of course, vapor plating. In another preferred embodiment, the heated cathode is immersed in a solution of tungsten hexacarbonyl of substantially greater quantity than in the aforementioned embodiment. This last mentioned embodiment may conveniently be referred to as "immersion plating." When a vapor plating technique is utilized, a reducing atmosphere, of hydrogen, for example, facilitates the operation.

According to the first mentioned aspect of the invention a rather porous cathode can be made to function as though the density were within the range of 80 to 86% of theoretical. The method consists of vapor plating a thin layer of tungsten over the emitting surface of the wire type of tungsten dispenser cathode whereby the thus treated cathode gives most satisfactory results in magnetrons. According to the second aspect, there is provided an immersion plating technique whereby a tungsten dispenser cathode surface can be sealed selectively to effectively stop cathode-to-heater leakage.

In one specific method, according to the first aspect, the wire dispenser cathode, after it has been impregnated and cleaned in a hydrogen atmosphere is heated to about 800° C. and then plunged into a solution of tungsten hexacarbonyl; preferably, the solvent is lead-free gasoline and the concentration of the solution is about 2%. This procedure decreases the porosity of the cathode structure which results in a lower rate of barium evaporation. Another method which functions equally as well for plating tungsten on the wire cathode is to thermally decompose the tungsten hexacarbonyl at high temperature without a carrier gas or a solvent.

In a specific embodiment of the second aspect of the invention, the planar cathode is heated in a solution of the tungsten hexacarbonyl, preferably about 2% by weight in lead-free gasoline, whereby a thick coating of tungsten is deposited on the backside. Typically, after four such applications, the coating is sufficiently thick that barium will not diffuse through it. Thus, the backside of the planar cathode is coated without disturbing the emitting surface, and the coating reduces cathode-to-heater leakage to an acceptable level.

Drawing is a flow sheet, illustrative of a method according to the first aspect of the invention.

In a specific preferred procedure for treating a wire type tungsten dispenser cathode according to the invention, a small tungsten or preferably tungsten-rhenium wire about 0.005" in diameter is coated with particles of pure tungsten or a 50/50, by weight, alloy of tungsten and molybdenum, the particles having an average size of 4 microns, the thickness of the coating being 0.010" and total coated wire thickness therefore being about 0.025", or with particles of pure tungsten oxide or a 50/50, by weight, mixture of tungsten oxide and molybdenum oxide particles, the particles again having an average size of 4 microns, the thickness of the coating being 0.015" and total coated wire thickness therefore being about 0.035" (step A). The coating may be applied by dipping the wire in a slurry of the particles in a solution of 5% nitrocellulose in methyl ethyl ketone, or the slurry of particles may be sprayed on the wire by any conventional air spray gun.

The coated wires resulting from step A are placed in a hydrogen sintering furnace; the temperature of the furnace is slowly increased to about 1000° C. for ten minutes to reduce any oxide layer on the particles consistuting the coating or the entire particles if the particles are of the aforementioned oxides; after this initial reducing period, the temperature is increased to 2000° C. for twenty minutes, after which the furnace power is turned off and the coated wires are allowed to cool to room temperature in the hydrogen (step B).

The coated wires of step B are then placed on a thin molybdenum sheet or tray ("boat"). They are then covered with an electron-emissive material consisting of barium oxide, calcium oxide and aluminum oxide, preferably in the molar ratio 4:1:1 in the order named, as described in U.S. Pat. No. 3,076,916 or the molar ratio 5:3:2 in the order named; the boat holding the wire and the emissive material is then inserted into a hydrogen furnace; the temperature is increased until the emissive material is melted, at which point, it is held for a period of ten seconds. Under these conditions, the pores of the tungsten matrix of the wire are filled with the emissive material; after ten seconds the furnace is turned off and the wires are allowed to cool in the hydrogen atmosphere to room temperature (step C).

The impregnated wires of step C usually have an excess amount of the emissive impregnant clinging to the surface, and this is now removed mechanically; a final cleaning is accomplished by dipping the impregnated wires in a water solution containing a chelating agent, this cleaning being convenient but not absolutely essential (step D).

The cleaned impregnated wires of step D are then hydrogen fired at 1600° C., which temperature is just below the melting point of the impregnant (step E). This step insures that the impergnated wires of step D are clean and free of water vapor.

The cleaned impregnated wires of step E are placed in a bell jar, containing a reducing atmosphere of hydrogen, in such a way that they can be heated in the reducing atmosphere to a temperature of between 800 and 1000° C.; the wires are heated to within this temperature range and preferably to about 900° C. and plunged into a 2%, by weight, solution of tungsten hexacarbonyl in lead-free gasoline, which has been kept at 60° C., and maintained there for a period of 5 seconds, whereby a thin film of pure tungsten is deposited on the surface of the wire (step F). This vapor deposition technique as well as an equally effective alternate technique are described in greater detail below.

A step just like step F (step G) may be inserted in the procedure after step B to reduce the porosity of the tungsten initially; this step augments rather than takes the place of step F.

Wire type tungsten dispenser cathodes made according to the foregoing procedure are now ready to be inserted in cooking type magnetrons. In tests conducted a thoriated tungsten wire cathode required about 100 watts of heater power whereas approximately 40 watts of power were required for the new cathode according to the invention. This represents an appreciable saving in operational cost of the device. The two outstanding advantages of the new wier cathode are the increased life and the reduced evaporation of barium. Cathodes made by the procedure described but without step F or steps F and G will function correctly in a magnetron for a period of several hundred hours. However, the evaporation of barium is so excessive that either the electrical characteristics of the magnetron tube change so drastically that it becomes useless or the emission of the cathode drops to such a low level that the tube must be replaced. Making cathodes by the foregoing procedure has been found to increase the operational life of magnetron tubes incorporating the cathodes to more than 1,000 hours.

In step A the preferred core material of the wire type cathode is a tungsten-rhenium wire containing at least 3% rhenium and preferably one containing 10%. Such wires remain moderately ductile after they have been hydrogen fired to 2000° C., and they can be bent into various shapes. Tungsten wires containing no rhenium are very brittle when fired under the same conditions.

In step A the preferred particle material which serves as a matrix for the emitting surface of the cathode is a 50/50 alloy of tungsten and molybdenum. However, a 50/50 mixture of tungsten and molybdenum oxides functions equivalently and the choice between the two depends on their availability. This alloy and matrix are preferred to pure tungsten or tungsten oxide because a pure tungsten matrix is so brittle that it cannot be bent. The addition of molybdenum permits the matrix to be shaped.

Step D relates to a chemical cleaning procedure for removing excess impregnant from the wire cathode. A water solution of a chelating agent is employed. Such an agent forms a complex with normally insoluble compounds in such a way that the resulting combination is soluble. The chelating agent works particularly well on the alkaline earth metal oxides. For example, impregnants containing barium oxide, calcium oxide, and aluminum oxide can be chelated. Apparently, what happens is that both barium oxide and calcium oxide go into solution leaving aluminum oxide as a powder residue which then readily falls from the cathode structure. From tests made it has been found that at least a 0.1 mol of calcium oxide must be present per mol of the impregnant. Impregnants containing no calcium oxide as well as those containing yttria and silica in place of aluminum oxide cannot be cleaned by a chelating agent. A preferred composition of the chelating solution is 20 cc. of water, 4 cc. of concentrated ammonium hydroxide and one gram of ethylene diamine tetraacetic acid. The solution preferably is heated to 170° F., for example on a water bath. The impregnated wire is soaked in this solution for periods from 15 seconds up to 3 minutes. For the particular wire cathodes discussed in this application, an immersion time of 30 seconds was found to be convenient.

The chelating procedure is a rather risky means of removing excess impregnant from dispenser cathodes since the life of a cathode can be impaired if it is left too long in the solution. The length of time the cathode is left in the solution, the temperature of the solution, and the concentration must be carefully controlled. Apparently, the chelating solution can remove an excessive amount of barium oxide from the porous matrix structure.

The procedure constituting step F is not restricted to coating dispenser cathodes treated with the above-named impregnants as it has been found that dispenser cathodes treated with other conventional impregnants coat equally as well. These other impregnants include barium tungstate, barium calcium zirconate, and the like. A metallurgical microscopic examination of the cathode reveals that the tungsten deposited by means of step F penetrates the small remaining pores of the impregnated tungsten matrix and decreases the porosity of the cathode to a depth of about .005".

A convenient technique for carrying out step F is to place the container holding the solution of tungsten hexacarbonyl on a moveable pedestal directly below the heated wire. Once the wire has reached the desired temperature, the pedestal carrying the solution is raised quickly to a height that plunges the heated wire into the solution. The pedestal is held in this position for the desired interval and then it is lowered. When the temperature of the wire at the time of the immersion in the tungsten hexacarbonyl solution is about 900° C. and the immersion interval is 5 seconds; one such operation is usually sufficient to coat a wire having an original actual density of about 70% of theoretical to a degree such that it appears to have a density about 83% of theoretical, viz, the rate of evaporation of the electron-emissive material is the same as for an uncoated wire dispenser cathode having an actual density of 83% of theoretical. One can repeat the coating process many times until a very bright silvery deposit is observed. However, all pores of the tungsten matrix appears to be closed after four coating applications. Such a wire cathode exhibits little or no emission.

Wire type tungsten dispenser cathodes can be tungsten coated equally as effectively by the direct thermal decomposition of tungten hexacarbonyl vapor without hydrogen or without the use of an organic compound as a solvent for the tungsten hexacarbonyl. Tungsten hexacarbonyl has a vapor pressure of about 20 microns at room temperature. The wire cathodes are placed in a vacuum bell jar in such a way that they can be electrically heated to a temperature between 1000° C. and 1300° C. by the sudden application of electrical power. A tray of tungsten hexacarbonyl crystals is placed in the vacuum bell jar with the wire cathodes. The vacuum pumping system is arranged so that it can pump all of the air out of the bell jar and then be shut off by means of a valve. The bell jar is then allowed to rest closed off from the pump for about 10 minutes or until a standard thermocouple gauge indicates that an equilibrium pressure of at least 20 microns has been established. The wire cathodes are then heated suddenly to 1200° C. and left at this temperature until the gas pressure in the bell jar has increased to about 200 microns. The increase in pressure is due to the formation of 6 mols of carbon monoxide for each mol of tungsten deposited and the pressure is a direct measure of the amount of the tungsten hexacarbonyl reacted. Once a pressure of 200 microns has been reached the pump valve is opened and the power to the wire cathodes is shut off. After a brief wait of about five minutes the plating process is repeated a second time. Two of such coating applications is enough to reduce the porosity sufficiently so that the cathodes exhibit an apparent density of 83% of theoretical density.

Although not related directly to the production of wire type tungsten dispenser cathodes, the immersion tungsten plating technique permits the effective reduction of heater-to-cathode leakage of planar dispenser cathodes. Such cathodes conventionally consist of an impregnated tungsten planar member, typically a disc, mounted on one end of a refractory metal hollow member, typically a molybdenum hollow cylinder. In the cavity is inserted a coated coiled tungsten wire which serves as an electrical heater of the molybdenum shell and the impregnated disc. At a temperature of about 1000° C. the disc emits electrons and at the same time it gives off evaporation products. Unfortunately, this happens from both the front and back sides of the disc. The electron flow from the backside of the disc to the heater constitutes a cathode-to-heater leakage, which is very objectionable in many microwave tubes. The evaporation products cause the coating of the tungsten heater coil to deteriorate and the heater coil eventually becomes conducting.

The tungsten plating method of the invention can be modified in such a way that the backside of the disc can be coated to such a thickness that it is effectively sealed tight. In a specific preferred embodiment, a 2% solution of tungsten hexacarbonyl is prepared in the same way as was discussed previously. The planar tungsten dispenser cathode is mounted in a bell jar with the disc facing upwards. A heater coil is mounted around the planar cathode. The air in the bell jar is replaced by hydrogen and the power source for the heater coil is turned on and adjusted so that the planar cathode is heated to 900° C. About 0.1 cc. of the tungsten hexacarbonyl solution is squirted against the backside of the cathode at this temperature by means of a hypodermic needle inserted into the bell jar. The flow of hydrogen into the bell jar is maintained while the same time the planar cathode is kept at 900° C. until all of the carbon monoxide generated by the decomposition of the tungsten hexacarbonyl has been flushed out of the bell jar. The plating procedure is repeated in this manner five times. There is thus obtained on the backside of the cathode a continuous tungsten coating that is impervious to barium and the evaporation products, whereby cathode-to-heater leakage and deterioration of the heater of a tube employing the cathode are minimized.

While there has herein been disclosed preferred embodiments of our invention, it is to be understood that many changes and modifications may be made therein without departing from the essential spirit of our invention as defined in the annexed claims.

Having thus described certain forms of the invention in some detail, what is claimed is:

1. A method of depositing tungsten on a wire type dispenser cathode constituted of a porous refractory metal matrix impregnated with an electron-emissive material, comprising heating tungsten hexacarbonyl in the presence of a wire type dispenser cathode to a temperature sufficiently high to decompose the tungsten hexacarbonyl and at a temperature below the melting point of said impregnant annd regulating the deposit of tungsten on the wire dispenser cathode to decrease the porosity of said cathode without completely sealing the surface of said cathode.

2. A method according to claim 7, in which the dispenser cathode is heated to said temperature and the tungsten hexacarbonyl is brought into contact with the heated dispenser cathode whereby the tungsten hexacarbonyl is heated to said temperature and decomposes and tungsten is deposited on the dispenser cathode.

3. A method according to claim 1, in which the deposition is terminated when the porosity of the cathode is such that during operation of the cathode the electron-emissive material will evaporate from the surface of the cathode at the same rate as if the refractory metal matrix of the cathode had an actual density in the range of 80 to 86% of theoretical.

4. A method according to claim 3, in which the refractory metal is tungsten and the electron-emissive material is comprised of barium.

5. A method of depositing tungsten on one side of two sides of a planar type dispenser cathode, said cathode constituted of a porous refractory metal matrix impregnated with an electron-emissive material, said method comprising heating tungsten hexacarbonyl in the presence of said cathode side adapted to be operated by being

heated by a heater facing said side opposite said electron-emissive material-impregnated side said cathode heated to a temperature sufficiently high to decompose the tungsten hexacarbonyl and below the melting point of said impregnant, and regulating the amount of the tungsten deposited on said opposite side to seal said cathode opposite side sufficiently to prevent significant leakage of electrons and of evaporation products of said electron-emissive material to said heater.

6. A method according to claim 5, in which the refractory metal is tungsten and the electron-emissive material is comprised of barium.

7. A method according to claim 5, in which the planar dispenser cathode is heated to said temperature and the tungsten hexacarbonyl is brought into contact with the heater dispenser cathode whereby the tungsten hexacarbonyl is heated to said temperature and decomposes and the tungsten is deposited on the planar dispenser cathode.

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