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ELECTRON DISCHARGE DEVICE AND
METHOD OF MANUFACTURE

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This invention relates to electron discharge devices comprising evacuated or gas-filled envelopes containing elements of the devices and which have, in their element-enclosing envelopes, surfaces having highly advantageous properties, and to methods of forming such surfaces. More particularly, the invention relates to such a device containing in its envelope a surface of the above type comprising a finely divided material and a silica binding material which provides unusual advantages, and to methods of forming such a surface.

Although the surfaces of the present invention may be provided on various portions of electron discharge devices within their element-enclosing envelopes, for the purposes of illustration the advantages of such a surface on the anode or control grid of such a device will be discussed hereinafter. Electron discharge devices, of which amplifying and rectifying tubes are examples, usually contain in an evacuated or gas-filled envelope electron emissive means and an anode to which the electrons migrate. The electron emissive means usually comprises a cathode which is adapted to be heated and which is formed of or coated with a thermionically active material capable of emitting electrons when heated. Usually one or more grids or control electrodes are also disposed in the envelope of the device.

In most electron discharge devices of this type electron emission from the grid or anode is undesired and should be avoided to as great an extent as possible. When an electrode from which electronic emission is undesired emits electrons in sufficient quantities the operation of the electron discharge device is deleteriously affected.

The present invention provides in the element enclosing envelope of an electron discharge device an anode, grid, or other element having a surface formed of one or more finely divided electron emission inhibiting materials firmly held in place by a binder of silica derived from a colloidal silica solution. Such electron emission inhibiting material may be of a type which reacts with electron emissive material deposited from the cathode on the surface embodying the invention to form non-emissive material; or which otherwise neutralizes such deposited emissive material; or which, because of its dark or black color has a high heat radiation capacity and thus lowers the temperature of the surface and hence its electron emissivity; or which inhibits electronic emission because of its high work function or for other reasons; or which operates in a plurality of these ways. The invention also

provides methods of forming such surfaces. Outstanding advantages are provided by the present invention when the finely divided electron emission inhibiting material and the silica binder are in the form of a surface coating on the desired element, particularly on the anode or grid. The present invention, however, also contemplates that an anode or grid or other element in the envelope of the electron discharge device may be formed substantially entirely of a finely divided electron emission inhibiting material and a silica binder. The invention affords particular advantages by providing in an electron discharge device an anode or grid, or both, formed of a metal body having at least part of its surface coated with a layer of finely divided electron emission inhibiting material held in place by a binder of silica. In such case the metal body provides strength and good heat conductivity, and if formed of the refractory metals usually employed, such as molybdenum or tungsten, good heat resistance also.

The silica binder, surprisingly, has little or no deleterious effect on the electron emission inhibiting properties of the finely divided material; indeed, in some cases it appears to aid in the electron emission inhibiting properties. Moreover, when the silica binder is employed in the proportions deemed most advantageous according to the invention in a coating on a conductive electrode of a device the conductivity of the electrode is not harmfully reduced. The silica binder has great resistance to decomposition and firmly holds in place the finely divided particles of the electron emission inhibiting material even when subjected to the high temperatures usually reached in the outgassing of the electron discharge device and often reached in operation of the electron discharge device. The silica binder, moreover, does not emit electrons even at high temperatures. Moreover, it is non-gas occluding and hence does not discharge gases to the electron discharge device during operation of the device.

These and other advantages of the invention will be apparent from the following discussion.

As examples of finely divided electron emission inhibiting materials which may be employed with a binder of silica according to the invention are the oxides of certain metals, such as the oxides of chromium (particularly Cr_2O_3), tantalum (particularly Ta_2O_5), zirconium (particularly ZrO_2), tungsten (particularly WO_3), platinum, titanium, and nickel. Most, if not all, of such oxides inhibit electron emission by reacting with

the electron emissive material such as barium or barium oxide vaporized or thrown off from the cathode and deposited on the surface of the invention, to form a stable material which has little or no electron emission capacity even at the temperatures reached in outgassing or operation of the electron discharge device. Most, if not all, of such electron emission inhibiting oxides also have high work functions and hence inhibit secondary emission for this reason also.

Oxides of the above type are black or in any event darker in color than bare metals. Therefore such oxides also may act to inhibit electron emission by reducing the temperature of the anode, grid or other part of which they form the surface, due to the higher black body heat radiation constants of such oxides as compared with bare metal surfaces. The silica binder does not deleteriously affect the electron emission inhibition properties of the oxides or affect their darker colors.

According to the present invention, moreover, finely divided carbon, either in the amorphous or graphitic form, and a binder of silica, may also be employed on the surfaces of grids, anodes or other parts in the envelopes of electron discharge devices from which electronic emission is undesired. In such case, carbon appears to reduce electronic emission primarily by reducing the temperature of the surface due to the high black body heat radiation constant, although carbon also appears to react, in at least some cases, with electron emitting material vaporized or thrown off from the cathode to form non-emitting substances and in this way also inhibit electronic emission.

The present invention also provides on anodes, grids or other parts in the envelopes of electron discharge devices surfaces formed of a silica binder firmly holding in place finely divided particles of metals having the property of inhibiting electronic emission. These metals may be the noble metals, such as gold, platinum, iridium, palladium, osmium, ruthenium and rhodium, which appear to operate, by reaction or otherwise, to neutralize electronic emission effects of electron emitting material deposited on such surface on the cathode. Such metals also have high work functions which inhibit secondary emission. A metal, such as zirconium, which in its finely divided state is black or dark in color and hence has a high black body heat radiation constant, may also be held in place by a binder of silica according to the invention to form a surface of an anode, grid or other part from which electron emission is undesired. Metals such as zirconium appear also to inhibit electronic emission by reaction or similar means with electron emitting materials deposited on the surface from the cathode. Zirconium and similar metals also have gas absorption properties which are advantageous in electron discharge devices for removing traces of undesired gases from the interior of such devices. Electron discharge devices having surfaces formed of finely divided zirconium or similar gas absorbing metals and a silica binder are described and claimed in copending application Serial No. 425,377, filed January 1, 1942, by the present inventor.

The present invention offers particular advantages in connection with the formation of surfaces of such electron emission inhibiting metals, since it obviates the necessity of heating such metals to a high sintering temperature and since it eliminates the necessity of plating such metals,

both of which processes result in some alloying of the metal with the base metal of the coated electrode, with a consequent loss of electron emission inhibiting or other desired properties.

According to the present invention electron emission inhibiting surfaces may be formed of more than one finely divided electron emission inhibiting material and a silica binder. Thus, coatings employing more than one electron emission inhibiting oxide may be employed. If it is desired to increase the conductivity of the surface coating, carbon may be mixed with one of the metal oxides useful for inhibiting electronic emission and both held in place by a silica binder. Combinations of carbon and zirconium oxide and carbon and molybdenum oxide in a silica binder may be employed to advantage. Similarly, mixtures of carbon and finely divided metal, or of a finely divided metal oxide and a finely divided metal, with or without finely divided carbon, in a silica binder may be employed.

When a surface coating of the material of the invention is applied to an anode, grid or other part of an electron discharge device, a coating material is made of a suspension of the finely divided electron emission inhibiting material in a liquid also containing colloidal hydrated silica. The coating material may be applied to the electrode by spraying, painting, dipping or by other suitable means. The liquid in which the colloidal silica and finely divided electron inhibiting material is suspended is a volatile liquid, such as water, alcohol or the like. After being coated the electrode or other part may, if desired, be air dried or heated to evaporate the liquid.

A liquid binder comprising a colloidal silica solution, in which the finely divided particles of the electron emission inhibiting material are advantageously suspended to form the material of which the surface is formed, may be prepared in various ways. Thus the colloidal silica solution may be prepared by dispersing silica gel in a suitable suspending liquid, such as water or ethyl alcohol, by ball milling or by some other suitable method. However, it appears that such colloidal silica solution may be very advantageously prepared by hydrolysis of an organic silicate, such as ethyl silicate. The hydrolysis may be performed by merely agitating the organic silicate with a suitable amount of water. It is advantageous to include in the water a small amount of an acid, such as hydrochloric acid, since this facilitates the hydrolysis. The hydrolysis is conveniently carried out in the presence of a solvent, such as ethyl alcohol, in which the water necessary for the reaction and the ethyl silicate are mutually soluble. The finely divided electron emission inhibiting material may then be mixed with the colloidal silica solution and the desired surface formed. If desired, water or a suitable organic solvent may be added before, during or after the addition of the finely divided electron emission inhibiting material further to reduce the concentration of the colloidal silica or, if desired, to reduce the consistency of the suspension of finely divided particles in the liquid to a point permitting ready application as by spraying.

The following are examples of advantageous methods of forming on electrodes coatings of a finely divided electron emission inhibition material and a silica binder.

Example 1

Ethyl silicate, a commercially obtainable material, was mixed with 0.06N dilute hydrochloric

acid in the proportion of 5 milliliters of ethyl silicate to 2 milliliters of the dilute acid, the mixture being agitated until the reaction was complete. The resulting colloidal solution of silica was then diluted to 50 milliliters with ethyl alcohol, although any one of many other volatile solvents, such as amyl acetate, could have been employed. Finely divided tantalum oxide powder in the amount of 10 grams was moistened with water or alcohol and added to 20 milliliters of the binding liquid containing colloidal silica described above. This suspension was agitated until it was thoroughly mixed. A coating of the material was applied to the electrode to be coated by a standard spraying procedure. Since the coated electrode was not immediately incorporated into the tube assembly, it was air dried, although it could have been heated, to evaporate the water in alcohol to cause the colloidal silica to deposit and form a binding material firmly holding the tantalum oxide in place. The coated electrode was then incorporated into tube assembly in the envelope of the tube and the tube heated and outgassed. Any of the other electron emission inhibiting oxides indicated above could be substituted for the tantalum oxide in this example.

Example 2

A colloidal silica solution was prepared by mixing five milliliters of ethyl silicate and 2 milliliters of 0.06 normal hydrochloric acid solution and the mixture agitated until hydrolysis was complete. A 2½ per cent solution of colloidal silica was then made by diluting to 50 milliliters with water. The final coating material was prepared by mixing ten grams of "Aquadag," a commercial product consisting of a paste of finely divided graphitic carbon with 10 milliliters of the above colloidal silica solution and 50 milliliters of water. The grid of a tube was then sprayed with the resulting material, air dried and incorporated in a vacuum tube assembly where it was subjected to the usual heating and outgassing operation.

The amount of silica which is employed as a binder depends upon the severity of the treatment to which the electrodes are subjected in handling and construction of the tube and under the outgassing and operating conditions of the tube. It is advantageous, in general, to employ as small an amount of silica as possible, since in this manner any possibilities of inhibition of the action of the electron emission inhibiting material are reduced. The proportion of the silica in the coating material should be less than the proportion of the finely divided electron emission inhibiting material, and, in general, it is advantageous to employ silica in an amount which is from about 2 per cent to about 10 per cent by weight of the finely divided electron emission inhibiting material. The amount of the volatile suspending liquid or liquids employed may vary widely, but it is desirable that it be in such proportion as to permit ready application to the surface.

The finely divided electron emission inhibiting material may be of any one of various particle sizes, although in general the more finely divided the material is, the better is its activity. The particle size, however, should not be so large that the material does not remain suspended in the binding liquid for a sufficient period to permit application of the material to the parts which it is desired to coat in the coating processes employed.

The drawing illustrates one form of electron discharge device in connection with which the

present invention may be advantageously employed. Said device is a three-electrode electron discharge tube comprising a cathode 1, control grid 2, and an anode 3, which are contained in a sealed glass envelope 4 which is shown as broken away to reveal the electrodes in the tube. The electrodes are supported in said envelope by any suitable means, such as that shown comprising insulators 5 of which only the upper one is shown and brackets 6 which are supported from the base 7. Leads 8 passing through said base provide electrical connection to the electrodes of the tube in the known manner.

In the illustrated embodiment the cathode is shown as a directly heated filament formed of thermionic emitting material such as thoriated tungsten.

In the illustrated embodiment of the invention, the anode and grid may be formed of a suitable metal, such as nickel, tungsten, molybdenum, iron or the like, and are preferably formed of a refractory metal such as tungsten or molybdenum. In this embodiment, moreover, both the anode 3 and the grid 2 have a surface coating which comprises a finely divided electron emission inhibition material, such as carbon, tantalum oxide, tungsten oxide, molybdenum oxide, or the like, held in place on the electrode by means of a binder which is substantially pure silica. Either one of said electrodes alone could be so coated. The illustrated anode 3 is coated on both its interior surface which faces the cathode, and its exterior surface. It could be coated on only one of said surfaces. Thus, if the coating inhibits electron emission primarily by increasing the heat radiation of the anode, it may be advantageous to apply the coating only to the exterior surface of the anode; if the coating inhibits electron emission by reacting with or otherwise neutralizing electron emissive material deposited on the anode from the cathode, it may be advantageous to apply the coating only to the interior surface of the anode.

In the manufacture of this tube the electrode to be provided with such a coating material is, after being constructed or formed, coated with a suspension of the finely divided electron emission inhibiting material and colloidal silica which is applied by spraying, painting, dipping or other suitable means.

Various modifications may be made in the methods and electron discharge devices indicated above. Thus electron discharge devices of both the gas-filled or high vacuum types may be provided according to the invention with anodes, grids or other parts in their envelopes having surfaces of finely divided electron emission inhibiting materials and a silica binder. The invention is applicable to amplifying tubes and rectifying tubes including those of the mercury vapor type, since surfaces of the kind contemplated by the present invention, particularly when employed on anodes or on grids, provide marked advantages in such tubes. As indicated above, the present invention contemplates electron discharge devices in which the grid alone, or the anode alone, or both such electrodes are provided with surfaces embodying the invention. Moreover, only a portion of the surface area of a grid or anode may be provided with a surface according to the invention.

The colloidal silica solution employed as a binder in the formation of the surface of the invention, and which, after removal of the liquid provides the resulting silica binder, may be pro-

pared in other ways than those indicated. Mixtures of finely divided electron emission inhibiting materials, as well as other finely divided electron emission inhibiting materials than those indicated above, may be employed with a silica binder, in surfaces of anodes, grids or other parts in the envelopes of electron discharge devices embodying the invention.

The mixtures of colloidal silica, finely divided electron emission inhibiting materials, and liquid employed to form the surfaces of the invention may be prepared in other ways than those indicated. Thus, instead of preparing the finely divided material and adding it to a prepared colloidal solution of silica, both silica and the electron inhibiting material may be simultaneously suspended in the liquid. It is also possible to grind to the desired particle size the electron emission inhibiting material while it is in a colloidal silica solution. As another alternative method, an organic silicate may be hydrolyzed in the presence of the finely divided material; thus, ethyl silicate may be hydrolyzed in the presence of "Aquadag."

Moreover, the present invention includes a process in which a surface is formed of a silica binder firmly holding in place finely divided particles of a material which after a subsequent treatment is transformed into an electron emission inhibiting material. For example, an anode or a grid may be provided with a surface coating of tantalum or zirconium hydride held in place by a binder of finely divided silica, and the hydride decomposed to the metal by subsequent heating in an inert atmosphere, as during the outgassing of the tube. Other modifications will be apparent to those skilled in the art.

It is intended that the patent shall cover by suitable expression in the appended claims whatever features of patentable novelty reside in the invention.

What is claimed is:

1. A non-emissive electrode adapted to be disposed within the sealed envelope of an electron discharge device comprising a metal body portion having a surface coated with an electron emission inhibiting layer which is electrically conductive through the layer and which comprises finely divided electron emission inhibiting material and a binder firmly holding the particles of said finely divided electron emission inhibiting material which is substantially only chemically combined silicon and oxygen in the form of silica derived from drying of a solution of colloidal silica.

2. An electron discharge device comprising a sealed envelope, electron emissive means in said envelope, and a metal element in and separated from said envelope and adapted to be heated having a surface coated with a layer which is electrically conductive through the layer and which comprises finely divided electron emission inhibiting material and a binder firmly holding the particles of said electron emission inhibiting material which is substantially only chemically combined silicon and oxygen in the form of

silica derived from drying of a solution of colloidal silica.

3. An electron discharge device comprising a sealed envelope, electron emissive means in said envelope, and a non-emissive electrode in and separated from said envelope comprising a metal body portion having a surface coated with a layer which is electrically conductive through the layer and which comprises a mixture of finely divided carbon and a finely divided metal oxide having electron emission inhibiting properties and a binder firmly holding the particles of said carbon and said metal oxide which is substantially only chemically combined silicon and oxygen in the form of silica derived from drying of a solution of colloidal silica.

4. An electron discharge device comprising a sealed envelope, electron emissive means in said envelope, and a non-emissive electrode in and separated from said envelope comprising a metal body portion having a surface coated with a layer which is electrically conductive through the layer and which comprises finely divided electron emission inhibiting material and a binder firmly holding the particles of said electron emission inhibiting material which is substantially only chemically combined silicon and oxygen in the form of silica derived from drying of a solution of colloidal silica.

5. An electron discharge device as in claim 4 in which said electron emission inhibiting material is finely divided carbon.

6. An electron discharge device as in claim 4 in which said electron emission inhibiting material is a finely divided oxide of tantalum.

7. An electron discharge device as in claim 4 in which said electron emission inhibiting material is a finely divided oxide of tungsten.

8. The method of forming a coating on a surface of an element of an electron discharge device comprising applying to said surface a suspension in a volatile liquid of a finely divided electron emission inhibiting material and colloidal hydrated silica in an amount between about 2 per cent to about 10 per cent by weight of the electron emission inhibiting material, and evaporating said liquid to form a coating in which the particles of said finely divided electron emission inhibiting material are firmly bound by silica.

9. The method of forming a coating on a surface of an element of an electron discharge device comprising hydrolyzing an organic silicate to form a solution of colloidal silica, adding a finely divided electron emission inhibiting material to said solution to form a suspension in a volatile liquid of said material and colloidal silica in an amount between about 2 per cent to about 10 per cent by weight of said electron emission inhibiting material, applying said suspension to said surface, and evaporating said liquid to form a coating in which the particles of said finely divided electron emission inhibiting material are firmly bound by silica.

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