

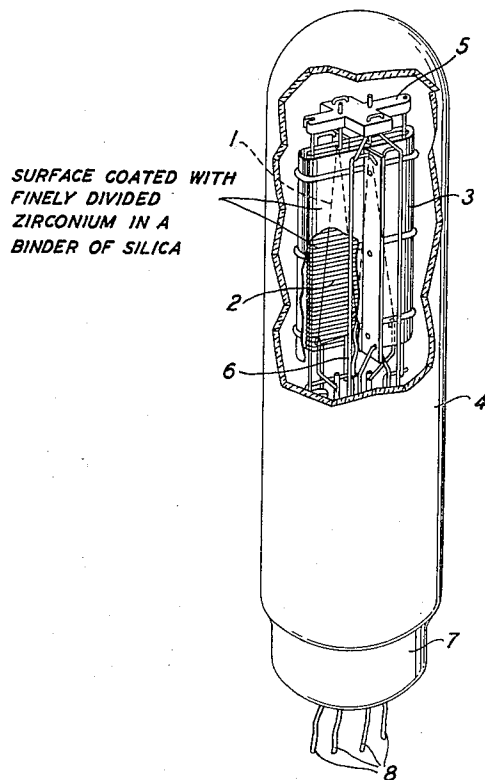
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COATING OF ELECTRON DISCHARGE DEVICE PARTS

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COATING OF ELECTRON DISCHARGE
DEVICE PARTS

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This invention relates to electron discharge devices or similar devices comprising evacuated or gas-filled envelopes containing elements of the devices and having in their element-enclosing envelopes surface layers which are of highly advantageous properties, and to methods of forming such layers. More particularly, the invention relates to such devices containing in their envelopes elements having surface layers which are free of prior disadvantages comprising a finely divided gettering material and a permanent, non-decomposable, non-emissive binding material, and to methods of forming elements having such surface layers.

For the purpose of illustration the invention will be discussed hereinafter in connection with electron discharge tubes.

To remove to as great an extent as possible from the interior of the enclosing envelope of such a tube, deleterious gases it has been proposed to employ in the envelope of such a tube a member having a surface layer comprising a finely divided metal, such as zirconium, titanium, tantalum, vanadium, niobium or molybdenum, which has the property of absorbing deleterious gases at elevated temperatures and which member is heated during operation of the tube to a temperature sufficient to cause such metal to absorb gases which are released during operation of the tube.

It has heretofore been the usual practice to apply a finely divided or powdered metal of this type to a member in the tube envelope, such as an anode, by sintering it to a metallic base. This is a difficult and expensive operation, however. Moreover, when such metal is so sintered it appears that its gas absorbent efficiency greatly decreases, evidently because it alloys with the base metal.

It has been proposed to overcome this difficulty by applying the finely divided metal with a carbonaceous binder, such as pyroxylin or the like. However, such binder is invariably decomposed by the high temperatures occurring during the out-gassing operation and during operation of the tube. As a result the finely divided metal particles lose their adherence to the supporting metal and drop off or are knocked off by an electronic or ionic bombardment, particularly in gas-filled tubes. Moreover, the residue of the carbonaceous binder is carbon, which tends to combine with occluded or diffused oxygen discharged into the tube during operation of the tube to form carbon monoxide and carbon dioxide. These gases cause considerable difficulties because they are greater in quantity than the original quantity of oxygen and hence cause a greater pressure in the tube, and because they are not absorbed as readily, if at all, by the gettering material as is oxygen.

The present invention overcomes these and

other difficulties. According to the invention a finely divided material, such as zirconium which has gas absorbing and electronic emission inhibition properties, is held on a supporting surface, advantageously that of a grid or anode of an electron discharge tube, by means of a binder which is substantially entirely pure silica (silicon dioxide). This binding material tenaciously holds the powdered metal in place without requiring alloying of the powdered metal to a base metal and is permanent since it is not affected by the high temperatures achieved during out-gassing and operation of the tube. Moreover, this binding material does not combine with any gas to form deleterious gases and hence is superior to the carbonaceous binding materials, and does not tend to emit electrons.

The drawing illustrates one form of electron discharge tube in connection with which the present invention may be advantageously employed and in connection with which the invention will be discussed more in detail hereinafter. Said device is a three-electrode electron discharge tube comprising a cathode 1, control grid 2, and 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 in the tube in the known manner.

In the illustrated embodiment the cathode is a directly heated filament formed of thermionic emitting material such as thoriated tungsten or is coated with thermionic emitting material, such as compounds of barium or the like, but could be of the indirectly heated type.

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 finely divided zirconium metal held in place on the electrode by means of a binder which is substantially pure silica, although either one of said elements alone could be so coated. The anode 3 is coated on both its interior surface, which faces the cathode, and its exterior surface, although it may be coated on either one of said surfaces.

In the manufacture of the tube, the illustrated electrode to be provided with the coated surface, is, after being constructed or formed, coated with a suspension of finely divided zirconium metal powder in a liquid containing colloidal silica, which may be applied to the electrode by spray-

ing, painting, dipping or by other suitable means. The liquid in which the colloidal silica and finely divided zirconium powder is suspended is a volatile liquid such as water, alcohol or the like. After being coated the electrode may, if desired, be heated to evaporate such liquid.

A liquid binder containing colloidal silica, in which the metal powder is suspended to form the coating material, may be advantageously prepared by hydrolysis of an organic silicate, such as ethyl silicate. The following is an example of the preparation of such a coating material and its use in a tube of the kind described above.

Ethyl silicate, a commercially obtainable material, was mixed with 0.6N 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 zirconium metal 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. The suspension was agitated until it was thoroughly mixed. A coating of the material was applied to the electrode to be coated by a standard spray 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 and alcohol to cause the colloidal silica to be deposited and form a binding material firmly holding the zirconium powder in place.

The coated electrode was then incorporated in the tube assembly in the envelope of the tube. During pumping and outgassing of the tube, the tube assembly was heated to a high temperature in the usual manner, the temperature being determined by the heat resistance of the electrode metals. During this outgassing treatment the zirconium acted as a gettering material to remove by absorption gas from the interior of the tube, thus reducing the amount of pumping necessary. The tube was then sealed in the usual manner after the desired degree of evacuation had been achieved.

During operation of the tube, the electrode coated with the zirconium powder held in place by the binder of substantially pure silica produced as above was heated to a relatively high temperature, as occurs in normal operation of such tubes. Observation of the operating characteristics of the tube over a long period indicated that at such temperatures the zirconium-containing coating on said electrode removed from the interior of the envelope, as they were released by the operating conditions of the tube, substantially all deleterious gases, such as oxygen and nitrogen, which had been occluded or diffused in the materials of the glass envelope, electrodes, and other parts in said envelope and which gases otherwise by their release would have caused a harmful change in the operating characteristics over such period of time. Moreover, the operating characteristics of the tube indicated that such coating on the electrode greatly inhibited the undesired electronic emission which would have occurred in the absence of such coating. Examination of the tube after a long period of operation indicated that the binder of substantially pure silica firmly and permanently bound the finely divided zirconium on the electrode, since none

of the metal was dislodged. Surprisingly, no evidence could be found that the silica binder, in the quantity employed, appreciably interfered with the action of the finely divided zirconium, or caused an appreciable decrease in the conductivity at the surface of the electrode.

The presence of a small amount of an acid, such as the hydrochloric acid employed during the hydrolysis in the above example, facilitates the hydrolysis of the organic silicate, although if desired the hydrolysis could be carried out with water alone. The organic solvent, such as the alcohol employed in the example, aids in suspending the colloidal silica and the finely divided zirconium metal and dilutes the concentration of such substances sufficiently to permit their ready application, as by spraying. When such an organic solvent, which is a solvent for both water and the organic silicate, is employed during the hydrolysis reaction, it also promotes the hydrolysis reaction.

The amount of silica which is employed as a binder depends upon the severity of the conditions to which the electrodes are subjected during handling and construction of the tube and during operation of the tube. It is advantageous, in general, to employ as small an amount of silica as possible to reduce the possibility of inhibiting the action of the zirconium metal. The proportion of silica in the coating material should be less than the proportion of zirconium powder, and in general it is advantageous to employ silica in an amount which is from 2 per cent to 10 per cent by weight of the finely divided zirconium. The amount of suspending liquid employed may vary widely but should be in such proportion as to permit ready application to the surface.

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

While it appears that the colloidal silica binding liquid may be most advantageously and conveniently prepared by hydrolysis of an organic silicate, it may also be prepared in other manners, as by dispersing silica gel in a suitable suspending liquid, such as ethyl alcohol, by ball milling or by some other suitable method.

Other metals having desired properties may be coated in the finely divided form according to the present invention besides the zirconium metal discussed above. Thus metals such as titanium, tantalum, vanadium, niobium, and molybdenum have gas absorption properties which render them desirable for gettering materials, and some of them have desirable electron emission inhibiting properties also. Zirconium and such other metals may be formed into coatings according to the invention in the form of finely divided metals as described above, but may also be formed into coatings according to the invention when in the form of compounds which are readily decomposable to the metals, as by heat. Thus, for example, tantalum is more easily obtainable in the form of tantalum hydride than as a metal powder. According to the present invention a finely divided hydride of the metal or other easily decomposable compound of the metal may be applied to a surface of an element of an electron discharge tube by means of a binder containing colloidal silica as indicated above. After the

silica has solidified, the hydride or other compound may be heated in a suitable atmosphere to decompose it to the metal. Thus, a part coated with a finely divided hydride of a metal held in place by a binder of substantially pure silica may be built into the electron discharge tube, and the hydride reduced to the metal by heating during the outgassing operation, during which the hydrogen is removed, or even by heating during operation of the tube. The resulting coating consists of a finely divided metal firmly held in place by a binder of substantially pure silica. Zirconium, tantalum, and other metals capable of forming hydrides may be thus formed into coatings.

As has been indicated above, various modifications may be made in the method and apparatus indicated above. Thus, parts coated with finely divided metal according to the invention may be incorporated in high vacuum tubes or in gas or vapor-filled tubes, and provides advantageous results in each case. A coating containing a finely divided gettering metal embodying the present invention will provide beneficial results when employed in a gas or vapor-filled tube in removing deleterious gases from such gas or vapor without removing such gas or vapor since such gas or vapor invariably is of the type which is not absorbed by such metal. The invention may be applied to electron discharge tubes other than the kind indicated above, and to devices having sealed envelopes from which it is desired to remove deleterious gases other than electron discharge devices.

In the above embodiment of the invention the coatings of the invention were applied to electrodes of the electron discharge tube. This is advantageous since the finely divided zirconium metal not only can act as a gettering agent but also can inhibit undesired electronic emission from such electrodes and can reduce the operating temperature of such electrodes because of its good heat radiating qualities. However, according to the present invention it is possible to apply coatings containing such finely divided metals which have gettering properties to parts other than electrodes in the envelopes of the electron discharge or other devices. It is necessary, however, that such a part coated with a gettering metal according to the invention be directly heated, or be disposed in such relation that it becomes heated during operation of the device. For example, it is possible to coat according to the invention, an auxiliary or other member which is mounted in an electron discharge tube in close proximity to the cathode so that it can become heated and perform its gettering function. Other modifications of the invention will be apparent to those skilled in the art.

The present invention thus provides coatings containing one or more finely divided materials which may have gettering and, if desired, other desirable properties, the particles of which are firmly and permanently held by a binding material of substantially pure silica which is inert, which contains no active substances which might emit electrons and which provides no carbonaceous or other residue capable of evolving deleterious gases which can harm the operation of the electron discharge device or other device containing such coatings in their envelopes. Other advantages of the invention will be apparent.

It is intended that the patent shall cover by suitable expression in the appended claims what-

ever features of patentable novelty reside in the invention.

What is claimed is:

1. 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 comprises a finely divided gettering metal and a binder firmly holding the particles of said finely divided gettering metal which is substantially only chemically combined silicon and oxygen in the form of silica derived from drying of a solution of colloidal silica, said layer being electrically conductive therethrough and said particles of said finely divided gettering metal in said layer having gettering properties.

2. An electron discharge device as described in claim 1 in which said gettering metal is finely divided zirconium metal.

3. An electron discharge device as described in claim 1 in which said gettering metal is finely divided titanium metal.

4. An electron discharge device as described in claim 1 in which said gettering metal is finely divided tantalum metal.

5. An electron discharge device as described in claim 1 in which said silica binder is present in an amount which is between about 2 and about 10 per cent by weight of the gettering metal.

6. An electrical tube device comprising a sealed envelope in which deleterious gases must be kept at a minimum; a filament in said envelope; means for electrically heating said filament; and a metal element in and separated from said envelope which has a surface coated with a layer comprising a finely divided gettering metal and a binder firmly holding the particles of said finely divided gettering metal which is substantially only chemically combined silicon and oxygen in the form of silica derived from drying of a solution of colloidal silica, said layer being electrically conductive therethrough and said particles of said finely divided gettering metal in said layer having gettering properties whereby deleterious gases are removed from said envelope.

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

8. 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 a layer which comprises a finely divided gettering metal and a binder firmly holding the particles of said finely divided gettering metal which is substantially only chemically combined silicon and oxygen in the form of silica derived from drying of a solution of colloidal silica, said layer being electrically conductive therethrough and said particles of said finely divided gettering metal in said layer having gettering properties.

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