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## PROCESS OF CARBONIZING

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This invention relates to the formation of hard, adherent layers of carbon on surfaces, particularly those of materials difficult to carbonize. The invention may be particularly advantageously applied to the formation of such layers of carbon on electrodes for electron discharge devices.

Electron discharge devices, of which amplifying and rectifying tubes are examples, 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, a grid or control electrode is also disposed in the envelope of the device.

The anode, and the grid if one is employed, tend to become heated from the heat generated by the cathode, and from bombardment by electrons emitted by the cathode or by ions in a gas-filled electron discharge device actuated by the cathode. This is particularly true in high-power tubes where high voltages are employed. It is desirable that such heating of the anode or grid be inhibited to as great an extent as possible, since otherwise the temperature of these elements may become high enough to damage them and to cause undesired electronic emission from one or both of them. High temperature of such elements, indeed, is one of the main factors which limits the outputs of electron discharge devices.

In most electron discharge devices electron emission from the anode or grid 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 a phenomenon known as "blocking effect" occurs, which impedes or paralyzes the operation of the electron discharge device.

Undesired electronic emission falls into two distinct classes and may be defined as primary emission and secondary emission. Primary emission is caused by thermionic material which is thrown off or evaporated from the cathode and deposited on the grid or anode where it becomes a source of electrons, particularly when the electrode on which it is deposited is at a high temperature. This usually occurs in electron discharge devices in which are employed cathodes coated with thermionic material, such as alkaline earth metals or oxides thereof. Secondary emission is caused by high velocity electrons emitted from the cathode impinging upon the grid or anode and liberating electrons therefrom, the lib-

eration of such secondary electrons being facilitated by a high temperature of the anode or grid.

Such undesired emission of electrons from the anode or the grid must be wholly or substantially prevented if the electron discharge device is to operate normally. It is particularly important that a grid from which electronic emission is undesired should not emit such electrons in substantial amounts if it is to perform its normal and intended function of controlling the flow of electrons from the cathode to the anode.

It has been proposed to lower the operating temperature of the grid or anode and to reduce such undesired electronic emission from such elements by coating the grid or the anode or both with a black substance which increases the heat radiation from such an electrode and thus maintains it at a lower operating temperature and which in some cases combines with the thermionic material deposited upon the grid or the anode to form inactive compounds. It has been proposed to coat the grid and the anode with a carbon layer for these purposes.

To this end, it has heretofore been proposed to heat a nickel electrode, which has had its surface oxidized, in an atmosphere of a hydrocarbon gas, the heating being performed at such a temperature that the hydrocarbon decomposes or cracks and deposits a layer of carbon on the electrode. It has been found, however, that nickel electrodes coated with carbon in this manner have a disadvantage in that the carbon layer often peels or loses adherence, particularly when such electrodes are employed in mercury vapor tubes. It is believed that the peeling of the carbon layer in such tubes probably results from amalgamation of mercury with nickel at the carbon-nickel interface, thus destroying the adherence of the carbon.

It is often desirable, however, to employ for the electrode material metals other than nickel, either because they are more refractory or because they are less expensive or more readily available. Materials having relatively high melting points, such as molybdenum, tungsten or the like, are usually employed for the anodes and grids of such electron discharge devices, although metals such as copper and stainless steel are also widely used. Such metals, however, even if oxidized, in general resist direct carbonization by cracking methods such as that described above, wherefore it has heretofore been found very difficult to form satisfactory layers of carbon on the surfaces of electrodes formed of such metals. In particular, molybdenum is very resistant to carbonization. If it is attempted to overcome this difficulty by

applying the carbon by means of an organic binder or the like, the resulting coating has the disadvantage that it is poorly adherent and in time peels or flakes, due to volatilization or decomposition of the binder, thus permitting the troubles indicated above. Moreover such organic binders release deleterious gases into the envelope of the electron discharge device, both because such binders release occluded gases and because they form deleterious gases due to decomposition of the binder under the high temperatures occurring during outgassing and operation of the electron discharge device.

These difficulties are overcome by the present invention, which provides a simple, efficient process for applying to the surfaces of elements, such as anodes or grids, of electron discharge devices, even though such surfaces are formed of materials resisting carbonization, carbon layers of any desired thickness which are firmly adherent and may be hard and crystalline, which do not readily flake or peel during use or during shelf or inactive life, and which do not produce the harmful gases caused by binder decomposition in other cases.

The carbon layers applied on such electrodes according to the present invention provide surfaces having a high black-body constant which serves efficiently to dissipate the heat generated in such electrodes, thereby rendering them cooler. The lower operating temperatures thus obtained overcome the difficulties described above as caused by high temperatures of such electrodes and make possible higher outputs from electron discharge devices. The lower operating temperatures of such coated electrodes alone tend to reduce or inhibit electronic emission from them. Moreover, it appears that such carbon coatings tend to inhibit or prevent primary emission effects by forming with thermionic material from the cathode deposited on such carbon coatings compounds which are not thermionically active or sufficiently stable at the lower temperatures of such carbon coated electrodes to be non-emissive. Such carbon coatings also tend to inhibit or prevent secondary emission because of the high work function of such coatings at the lower temperatures thereof.

Moreover, such carbon layer according to the invention can be readily applied to a desired portion only of the surface of an electrode, thus making it possible to produce an electrode having surfaces which are partially carbonized and partially bare. Such electrodes are desirable in certain types of electron discharge devices. Other advantages of the invention will be apparent from the following discussion.

Such advantages are provided by the process of the invention according to which an electrode, even though formed of or having a surface of a material resistant to carbonization such as molybdenum or tungsten, is before its incorporation into the electron discharge device coated on the portion of its surface on which the carbon layer is desired with a layer of an oxide of a metal, which oxide has a catalytic effect in promoting carbonization such as an oxide of a metal of the iron family, advantageously by coating with a suspension of a finely divided oxide of such a metal, after which the electrode is heated in the presence of a hydrocarbon gas to a temperature sufficient to cause the gas to crack or decompose and deposit upon the oxide-coated portion of the electrode in the form of an adherent layer of carbon.

It is desirable that the surface of the electrode

on which it is desired to deposit the carbon be first thoroughly cleaned. It is also desirable that such surface be roughened, since this increases the adherence of the layer of carbon to the electrode. Such roughening may be advantageously accomplished by etching by an electrolytic process, the electrode being made the anode in a suitable electrolytic bath through which a suitable current is passed.

The layer of the oxide of the metal of the iron family is advantageously deposited on the surface of the electrode or on the portion of the surface on which it is desired to deposit carbon by applying a suspension of such finely divided oxide in a suitable volatile liquid medium such as alcohol, or other organic liquid, or water or the like. The suspension is advantageously applied by spraying. The suspension need not be colloidal in character, but may have coarser particles; it should, however, be sufficiently stable for at least a short period to permit the oxide particles to be applied to the electrode surface in suspension, as by spraying.

For increasing the adherence of the catalytic metal and coating to the electrode before carbonization it is advantageous to incorporate in the suspension containing the metal oxide a binding material. Thus, an organic binding material such as pyroxylin or the like, dissolved in a suitable volatile organic solvent may be employed. As another example an inorganic, permanent binder, such as silica, may be advantageously employed. In this case the suspension may contain in addition to the finely divided metal oxide a small portion of colloidal silica, advantageously from about 2 to about 10 per cent of the weight of the oxide, in a volatile suspending liquid such as water, alcohol, or the like which, upon evaporation, leaves behind a coating of finely divided metal oxide firmly held by a silica binder. The colloidal silica may be obtained in various manners, as by hydrolysis of an organic silicate such as ethyl silicate or by dispersing silica gel in a suitable volatile suspending liquid, as by ball milling. It appears that the employment of a silica binder for the oxide enhances the catalytic properties of the oxide, and causes the formation of a carbon layer which is blacker, softer and more amorphous than when it is not employed, such carbon coating being more advantageous in certain cases. The silica binder is also advantageous in that it is heat resistant and non-emissive.

The freshly coated electrode may or may not be baked to drive off the volatile suspending liquid before carbonization.

It is preferable to employ nickel oxide as the coating since this oxide appears to have the highest catalytic activity of any of the oxides of the iron family in cracking hydrocarbons. The black oxide prepared by heating basic nickel carbonate at about 500° C. appears to be the better catalyst, but it appears to be desirable to employ a mixture of this oxide and the green nickel oxide prepared from basic nickel carbonate by heating at about 1000° C., because the black oxide shrinks considerably during the carbonization step. Alternatively, good results may also be obtained with the oxide produced by heating the carbonate at about 800° C.

The deposition of carbon may be caused to take place under various conditions and by means of various types of apparatus. Thus it has been found advantageous to employ a furnace comprising a tubular member, in which is disposed

the electrode to be carbonized, surrounded by insulating material and by suitable electrical heating windings connected to a suitable source of current, the tubular member being provided with means for maintaining therein an atmosphere of the desired hydrocarbon gas. One type of furnace which may be employed to advantage is that described in Patent 2,314,816, issued March 23, 1943, to J. R. C. Brown, Jr., and L. A. Wooten.

Various kinds of hydrocarbon gases or mixtures thereof may be employed, such as methane, propane, butane, acetylene, suitable natural gases, or the like, or vapors of volatile liquid hydrocarbons, such as vapors of volatile petroleum products. Temperatures sufficient to crack or decompose such gases should be employed; in general, temperatures of from about 700° C. to 1000° C. are satisfactory. The time during which the electrode is thus heated and subjected to the hydrocarbon gas may vary from a few minutes to a half hour or more, depending upon the thickness of the carbon layer which is desired and the kind of hydrocarbon gas employed. Usually it is advantageous to dilute the hydrocarbon gas with a non-carbonaceous gas which has no oxidizing action, such as hydrogen or nitrogen. In such case the rate of deposition of carbon is retarded, better control over carbonizing conditions is possible, and a harder, more adherent carbon layer is more easily attained. During the carbonization treatment, carbon resulting from the cracking or decomposition of the hydrocarbon gas is deposited on that portion of the electrode coated with the nickel oxide, and the nickel oxide or other oxide of the iron family which is employed as a catalyst is reduced.

The sheet from which the electrode is formed may be thus carbonized either before or after being formed into the final electrode shape. If the sheet is carbonized before fabrication, it is desirable after the electrode has been fabricated into its final form that it be given a second treatment for a few minutes more to recarbonize any spots from which the carbon has been removed by abrasion during the fabrication and to remove grease which may accumulate in handling.

According to the invention, the nickel or other metal of the iron family the oxide of which has been employed may be substantially if not entirely removed after the carbon layer is formed. This is made possible by the porous, graphitic nature of the carbon layer. Such removal, may be effected by treating the electrode for a few minutes in a suitable acid which will remove such metal of the iron family without harmfully attacking the electrode base metal. The removal of such metal is advantageous since it permits the electrode coated with such carbon layer according to the invention, when disposed in the electron discharge device, to be outgassed at higher temperatures, without loss of carbon, than would otherwise be possible. Moreover, the removal of such metal obviates difficulties which might arise during operation of the electron discharge device from evaporation or magnetic effect of such metal due to heating of the electrode.

The following is an example according to the present invention of a process for forming a carbon layer on molybdenum anodes. A molybdenum anode blank, intended to constitute the plate of a three-electrode electron tube, stamped to the correct size but flat, was cleaned and etched by making it the anode in a 5 per cent

sodium hydroxide solution for a time of approximately 1 minute, a voltage of around 30 volts being employed. The anode blank was then washed free of the caustic solution and dried. A layer of finely divided nickel oxide was deposited on the surface of the anode blank on which a carbon layer was desired, by spraying the anode blank with a suspension of finely divided nickel oxide in ethyl alcohol. If it was desired to have a carbon layer on only a portion of the surface of the anode blank, this could have been accomplished by spraying only the desired portion of the blank with the suspension, using a mask, if desired. The coating weight was not less than 2 milligrams of nickel oxide per square centimeter since this weight was found to be advantageous. The nickel oxide employed consisted of a mixture of about 80 per cent of the green oxide prepared from basic nickel carbonate at 1000° C. and about 20 per cent of the black nickel oxide prepared from the basic nickel carbonate at about 500° C. This proportion of these oxides was employed to reduce the shrinkage which would tend to occur if only the black nickel oxide or nickel oxide prepared at about 800° C. were employed. These latter oxides could have been employed also, if desired. The anode blank was then placed in a nickel boat and inserted into a tubular furnace which was surrounded with an electrical heating element and suitably insulated. The blank was heated at a temperature lying between about 750° C. to about 950° C. for a period of between fifteen to twenty-five minutes in a stream of gas consisting of methane and hydrogen in a ratio of 1:2 by volume. During this operation the nickel oxide was reduced and carbon was deposited on the nickel as a result of the cracking of the methane. The carbon-coated molybdenum anode blank was then fabricated to the desired shape, after which it was given a second carbonizing treatment in the same gas mixture and at the same temperature for about five minutes. This repaired any portions of the carbon layer which might have been damaged by abrasion in fabricating and removed the grease which might have accumulated in the handling during fabrication.

In order to substantially remove the nickel from the carbon layer, the anode was then treated for about ten minutes in a hot 50 per cent hydrochloric acid solution. Substantially if not all of the nickel which was produced by reduction of the nickel oxide during carbonization was thus removed, while the molybdenum base metal was not attacked.

It was found that when this anode was built into an electron discharge device, the device could be outgassed at temperatures as high as 1200° C. for a period up to ten minutes without serious loss of carbon from the anode. It was found that it was advantageous to outgas such an electron discharge device containing such an anode by stages, by heating for about ten minutes at about 800° C.-900° C., then for about five minutes at about 1100° C.-1200° C., and finally by a final heating at about 1300° C. for a period of about one minute.

Electron diffraction studies of the carbon layer on this anode indicated that the crystal structure, size of unit cell and mean dimensions of the crystallites approached very closely those of graphitic carbon. The layer of carbon was a deep black in color. It was hard, thin, very adherent to the base metal, and had high abrasion resistance. The layer of carbon did not impair the

conductivity of the surface of the anode sufficiently to affect deleteriously the operation of the electron discharge device into which the anode was built.

It was found that a power tube having this anode and a coated cathode, and operated at high temperatures and voltages, satisfactorily operated for long periods of time with no "blocking effect" due to electronic emission from said anode. It was found that such a tube could be operated at higher powers and for longer periods of time than a similar tube having a similar uncoated molybdenum anode, due to the cooler condition of the anode and the freedom of electronic emission therefrom.

While molybdenum has been mentioned above as an example of a metal which may be carbonized according to the present invention, other metals, particularly those resistant to carbonization, may be so carbonized. For example, electrodes for electron discharge tubes having surfaces of copper, stainless steel and tungsten, all of which are difficult to carbonize and which, with molybdenum, are usually employed for electrodes, may be so carbonized.

Moreover, while the above example related to the formation of a carbon layer on an anode, it is apparent that the process of the present invention is applicable to the formation of carbon layers on other electrodes, such as grids and on other parts in the envelopes of electron discharge devices on the surfaces of which parts such carbon layers may be desirable. In certain aspects at least, the present invention is applicable to the formation of carbon layers on articles other than electrodes, and on materials, particularly those difficult to carbonize, other than those of the type indicated above. It is apparent that the invention is also applicable to readily carbonizable materials. Thus it is in some cases advantageous to carbonize, according to the invention, electrodes or other parts of electron discharge devices formed of metals which do not resist carbonization by ordinary methods, particularly when it is desired to carbonize only a portion of the surface of such a part. Thus, it is advantageous to form a carbon coating on only a portion of a surface of a nickel part such as an anode, by applying as by spraying to said portion of the surface a suspension of an oxide of a metal of the iron family, with or without a suitable binder such as colloidal silica, and carbonizing by heating the surface to the cracking temperature of a surrounding hydrocarbon gas. Because of the catalytic activity of the oxide, it is possible to carbonize only the oxide coated portion of the part without carbonizing the other portions of the part.

Various modifications other than those indicated above may be made in the described process without departing from the spirit of the invention. Electrodes coated with carbon according to the present invention may be employed to advantage in numerous types of electron discharge devices, such as vacuum tubes, gas-filled tubes, mercury-vapor tubes and the like. Electrodes coated according to the invention can be made to provide exceptional advantages in mercury-vapor tubes. Such electrodes can be made free of nickel or any other metal which will tend to amalgamate with the mercury and thus cause peeling of the carbon layer. Electrodes thus can be easily made according to the invention which will retain their advantageous carbon layer even

under the exceptionally severe conditions which occur in mercury-vapor tubes.

The present invention also makes it possible readily to form carbon coatings on non-magnetic metals, such as molybdenum, tungsten, or the like. Electrodes having carbon coatings which have a high black body radiation constant, but which electrodes are non-magnetic, are advantageous in certain types of electron discharge tubes. In this connection the removal according to the invention of the metal of the iron family the oxide of which is employed as the carbonization catalyst is advantageous.

It is thus apparent that the present invention makes possible the ready production of electron discharge device electrodes, such as grids and anodes, even though they are formed of or have surfaces of materials which resist carbonization, which electrodes have surfaces entirely or partially covered with a hard, closely adherent layer of graphitic carbon. Such carbon layer does not peel or flake readily, if at all, during use of the tube or during its idle periods, and is very resistant to abrasion. The high black-body constant provided by such layer makes possible considerable cooling and hence a lower operating temperature of the electrode coated with it. Undesired electronic emission is reduced for this and other reasons indicated above.

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. The process of forming an adherent layer of carbon on a metal surface comprising applying to said surface a mixture of finely divided particles of an oxide of a metal of the iron family in a colloidal silica suspension; drying said colloidal silica suspension to produce on said surface a coating of said finely divided oxide particles held in place by a binder of silica resulting from drying of said colloidal silica suspension; and heating said coated surface in the presence of a hydrocarbon gas to a temperature which will crack said gas and cause an adherent layer of carbon to deposit on said coated surface.

2. The process of forming an adherent layer of carbon on a metal surface comprising forming on said surface a coating of an oxide of a metal of the iron family containing in the coating a colloidal silica suspension; drying said colloidal silica suspension in said coating; and heating said metal surface covered with said metal oxide coating containing silica derived from drying of said colloidal silica suspension in the presence of a hydrocarbon gas to a temperature which will crack said gas and cause an adherent layer of carbon to deposit on said surface covered with said coating.

3. The process of forming an adherent layer of carbon on a surface of a part for an electron discharge device formed of a metal which resists carbonization, comprising applying to said surface a suspension in a volatile liquid of finely divided particles of an oxide of a metal of the iron family; evaporating said liquid to form on said surface a coating of said finely divided oxide particles; heating said coated surface in the presence of a hydrocarbon gas to a temperature which will crack said gas and cause a layer of carbon to deposit on said coated surface together with metal of the iron family resulting from the reduction of said oxide; and removing substantially all of said reduced metal without substan-

tially disturbing the deposited carbon layer by dissolving out said reduced metal by means of an acid liquid applied to said carbon coated surface.

4. The process of claim 3 in which said surface on which said carbon layer is deposited is formed of molybdenum.

5. The process of claim 3 in which said surface on which said carbon layer is deposited is formed of copper.

6. The process of claim 3 in which said surface on which said carbon layer is deposited is formed of stainless steel.

7. The process of claim 3 in which said oxide of a metal of the iron family is nickel oxide.

8. The process of forming an adherent layer of carbon on a surface of a molybdenum part for an electron discharge device comprising apply-

ing to said surface a suspension in a volatile liquid of finely divided particles of nickel oxide; evaporating said liquid to form on said surface a coating of finely divided particles of nickel oxide; heating said coated surface in the presence of a hydrocarbon gas at a temperature that will crack said gas and cause a layer of carbon to deposit on said coated surface together with nickel resulting from the reduction of said nickel oxide; and removing substantially all of said nickel without substantially disturbing the deposited carbon layer by dissolving out said nickel by means of an acid liquid applied to said carbon coated surface.

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