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PROCESS OF CARBONIZING METALS

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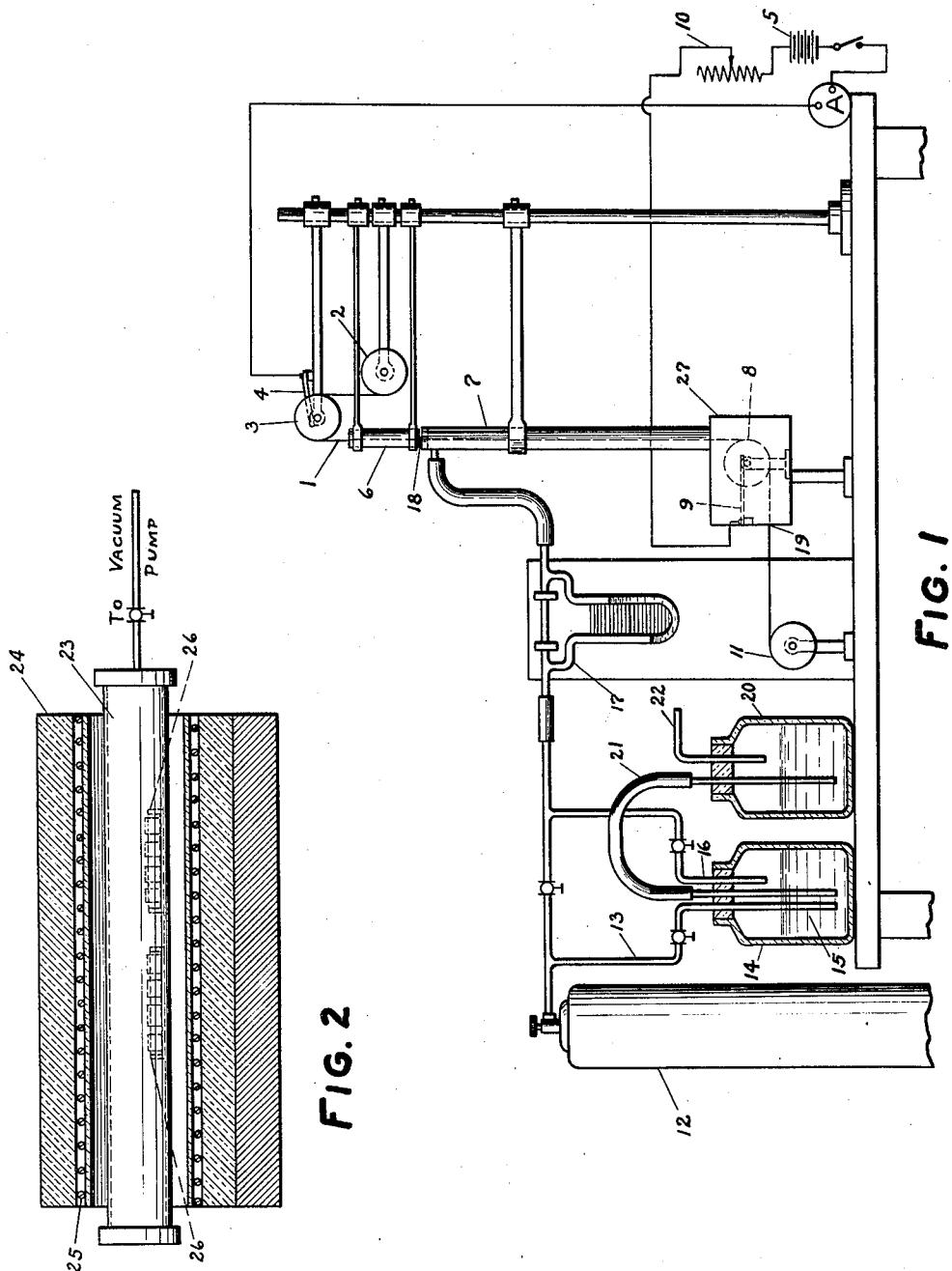


FIG. 2

FIG. 1

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## PROCESS OF CARBONIZING METALS

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This invention relates to the art of carbonizing metal surfaces and more particularly relates to a method of carbonizing nickel or other metals which are used as the grid 5 and plate materials in electron discharge devices.

In electron discharge devices such as radio tubes, power tubes, etc., it is customary to apply to the anode surface an adherent coating 10 of carbon to augment the heat emissivity or the heat dissipating property of the material of the anode. In electron discharge devices utilizing one of the so-called "oxide coated" type cathodes there is a tendency for 15 the alkaline earth metal oxides comprising the cathode coating to sputter and be deposited upon the grid and the anode and when considerable power output is employed it is often found that the anode and grid 20 electrodes become incandescent sufficiently for the sputtered or deposited alkaline earth metal oxides to become emitters of electrons. It has also been determined that in electron 25 discharge devices utilizing other type hot cathodes and employing extremely high anode or plate voltages the grid electrode becomes sufficiently incandescent by electron bombardment to substantially emit electrons.

It is customary to eliminate the tendency 30 of the anode and grid electrodes to emit electrons under the above described conditions by coating these parts with a closely adherent carbon coating as the carbon coating not only prevents the emission of electrons due 35 to the relatively high temperature to which it must be heated before such emission may be obtained from the carbon surface but the black surface obtained thereby increases the heat radiating ability of these metal parts 40 and decreases the operating temperatures at any given output current.

It is essential that the carbon surface of such cooperating electrodes in electron discharge devices must be substantially pure 45 and must also be substantially free from deleterious adsorbed or absorbed gases or intermetallic compounds reducible or dissociable by electronic bombardment to yield products which are deleterious to the electron emitting hot cathode member of the de-

vice. The carbon coating must also be strongly adherent to the metal surface and preferably entirely covering the same.

The physical characteristics of deposited carbon varies with the method of depositing 55 it. In general, that deposit which is best suited for radiation of heat is most satisfactory for the purpose of this invention.

It has been proposed heretofore to effect 60 the deposition of the carbon by heating the metal body to elevated temperatures in hydrocarbon gases. It has also been proposed to facilitate the deposition of carbon under 65 these conditions by first oxidizing the surface of the metal body and then heating to elevated temperatures in hydrocarbon gases whereby the catalytic action of the metal oxide and the metal particles produced therefrom by the reducing action of the heated hydrocarbon gas facilitates the 70 decomposition of the hydrocarbon gas and deposition of the carbon upon the metal surface.

It is customary in the art to carbonize 75 the metal sheet comprising the anode or plate material prior to forming or shaping the anode. It is also customary to carbonize the grid wires prior to forming the grid, as in this way the two steps of oxidizing followed by carbonizing may be conducted 80 consecutively and in a continuous manner. It is essential for the pure carbon coating thus obtained to be strongly adherent to the metal base and substantially not disturbed or removed by the subsequent forming operations 85 as it is obvious that it would be inexpedient to repeat a carbonizing operation to replace or to impart a carbon coating following the forming operation.

It is also essential for the successful use 90 and application of the formed or shaped carbonized sheet or wire, (that is plate (anode) or grid (control) electrodes), that the metal body and the carbon coating be substantially freed of deleterious gaseous and intermetallic 95 compounds subsequent to the forming or shaping operation and prior to the utilization of the same in the electron discharge devices.

It is one of the objects of this invention 100

to provide an improved method of carbonizing metal surfaces whereby a closely adherent substantially pure carbon surface is obtained.

5 It is another object of this invention to provide a substantially pure adherent gas free carbon coating upon cooperating electrodes in an electron discharge device.

10 It is another object of this invention to improve the method of depositing carbon upon metal surfaces.

Other objects and advantages will become apparent as the invention is more fully disclosed.

15 In accordance with the objects of my invention I have determined that I may improve the carbonizing step of the hereinbefore mentioned prior art process of carbonizing metal surfaces, through the addition 20 to the carbonizing hydrocarbon gas heretofore employed of a proportion of the vapor of a liquid hydrocarbon such as petroleum ether, petroleum naptha, benzine and the like.

25 I have also determined that after coating the metal surface and forming the same to desired shapes, such as plate or grids by the method hereinbefore mentioned I may further improve the formed article by subjecting 30 the same to a heat treatment step at elevated temperatures in a continuously maintained high vacuo, whereby all or substantially all the deleterious impurities introduced by the said forming operation, such as oxides, greases, etc., and the adsorbed or 35 absorbed gas content of the metal body and carbon coating are substantially removed or rendered substantially non-decomposable under subsequent heat or electronic dissociation effects.

40 By this general improved process I am enabled to produce anode or grid articles for use in electron discharge devices with a minimum of shrinkage loss and a maximum in material and operating efficiency.

45 As a specific embodiment of the application of this invention, the invention will be described with respect to the forming of carbonized grid electrodes and reference 50 should be made to the accompanying drawing wherein:

55 Figure 1 shows a side elevational view partly in cross section of the apparatus employed in the continuous oxidizing and carbonizing steps of the process of carbonizing nickel wire which is subsequently to be formed into grids for use in electron discharge devices; and

60 Figure 2 shows partly in cross-section the vacuum apparatus I may employ in the third or degasifying step of my process.

65 As may be noted in Figure 1, the wire 1 which is to be carbonized is wound on the unwinding head 2, from which it passes over a movable wheel contact 3, electrically con-

nected by spring contact 4 to any convenient electrical energy supply source such as the battery 5 herein indicated. The wire 1 is then passed vertically downward through oxidizing furnace 6 which may be an ordinary glass or iron tube movably mounted in position as shown and from thence into carbonizing chamber 7 maintained in close relation thereto and which may be made from an ordinary iron tube rigidly mounted in position as shown and thence over a second wheel contact 8 entirely enclosed in box mounting 27 and electrically connected by spring contact 9 back to the other side of battery 5 over variable resistance 10 connected in series therewith. The current and therefore the temperature of the wire, may be controlled by the variable resistance 10. From the second contact the wire is conducted to winding head 11, actuated by mechanism not shown.

The carbonizing gas utilized in the carbonizing chamber 7 which comprises the main feature of my invention, is substantially obtained by passing any hydrocarbon gas, such as acetylene, which may be obtained from a compressed source, such as indicated by cylinder 12, through a liquid hydrocarbon, such as petroleum ether. The hydrocarbon gas is conducted by conduit 13 from the cylinder 12 to the bottom of chamber 14, which is filled to an appreciable height with a liquid hydrocarbon 15 such as petroleum ether, petroleum naptha and the like. The gas bubbles released by conduit 13 in chamber 14 passes out of the chamber through conduit 16, the volume or pressure thereof being controlled by flow meter 17, and is then passed into the carbonizing chamber 7. Gas exits from the carbonizing chamber 7 are provided at the entrance orifice 18 and exit orifice 19 of wire 1 being carbonized.

A siphoning means for replenishing the liquid hydrocarbon in chamber 14 is shown in Figure 1, wherein chamber 20, siphonically connected by connection 21, is filled from an external source with liquid hydrocarbon as desired through opening 22.

In Figure 2 the apparatus I may employ in performing the third or degasifying step of my process is shown, with the vacuum chamber 23 in position in a furnace, which may be heated in any convenient manner such as by wire wound resistance electrical heating units as indicated at 25. Within the vacuum chamber are shown (26) in position two batches of formed articles such as grids. The exhaust means such as mercury diffusion, oil, or standard molecular vacuum devices are indicated but not shown as they form no integral part of the invention.

In the specific embodiment of the practice of my invention I will describe the process I employ in the carbonizing of 8 mil (.008

inches) nickel wire for use in forming grid electrodes.

The spool of nickel wire is placed upon the unwinding head 2 in Figure 1, and 5 passed over the contact wheel 3, thence vertically downward through the oxidizing furnace 6 and carbonizing furnace 7 over second contact wheel 8 and thence to winding head 11.

10 Suitable adjustment is made in variable resistance 10 of the electrical circuit from current supply source indicated as battery 5, to incandesce the nickel wire stretched between the two contact wheels 3 and 8 to 15 give a wire temperature which will suitably affect the decomposition of the hydrocarbon atmosphere and deposition of the carbon upon the surface thereof in the desired condition.

20 For this size wire I prefer to limit the length of wire exposed to the oxidizing conditions in furnace 6 to approximately 11 to 12 inches, and the length of wire within the carbonizing furnace 7 to approximately 35 25 to 36 inches, or approximately 3 times the length that is exposed to the oxidizing conditions. I find this a good general rule to follow as I may consequently regulate or 30 vary the speed of the wire through these furnaces and the rate of hydrocarbon gas flow into the carbonizing chamber with greater ease and uniformity in result if some such standard relation between the oxidizing and carbonizing operations is established. With .008 inch nickel wire I have 35 found that the required current to give the requisite temperature in approximately 48 inches incandesced length will vary from 2.85 to 3.0 amperes at 40 to 50 volts.

40 Inasmuch as there is no accurate means available to measure the actual wire temperature within the carbonizing chamber an approximate estimate thereof only may be made. It is believed that the temperature 45 is approximately 800° C. to 1000° C. but reference hereafter will only be made to "elevated" temperatures rather than definite temperatures.

With this size wire the inside diameter of 50 either the oxidizing chamber 6 or the carbonizing chamber 7 does not need to be over 11/4 inches and the carbonizing gas flow therethrough does not need to exceed 0.10 cu. ft. per hour although it may be varied 55 from .05 cu. ft. to 0.3 cu. ft. per hour without deleterious results. With this gas flow range bubbling through petroleum ether having a specific gravity approximating .620 or petroleum naptha specific gravity 60 approximating .680 (at 20° to 30° C.) the amount of liquid hydrocarbon vapor carried along is sufficient to effect the desired amount of carbonization on the heated wire surface. The wire speed through the furnaces may be varied from 2 to 5 ft. per

minute but I prefer to maintain a constant speed closely approximating 4 ft. per minute. Under these conditions a carbonized wire of approved appearance is obtained having a heavy adherent velvety black carbon coating which is extremely resistant to being removed during the forming operation. 70

The carrier hydrocarbon I prefer to employ is acetylene which may readily be obtained upon the market in a high state of purity compressed into cylinders. Whereas I specifically prefer acetylene gas, other hydrocarbons of the acetylene series which are gases at room temperatures may be utilized if desired, provided they may be obtained in a sufficiently pure condition and substantially free from deleterious volatile impurities such as sulfur, arsenic and phosphorous compounds which subsequently deleteriously react with and effectively destroy the electron emissivity of associated hot cathodes in an assembled device. 75 80 85

Other liquid hydrocarbons than those specified may be utilized including those of the paraffine series having relatively high boiling points 90 to 150° C. or higher, such as kerosene, and I may even augment or increase the vapor pressure of said liquid hydrocarbons by the application of heat either 90 to the liquid hydrocarbon or to the carrier hydrocarbon gas. 95

Many variations and departures of this specific embodiment or description may be made without essentially departing from the 100 nature of my invention.

After the incandesced wire has traversed the length of the two furnaces, oxidizing and carbonizing respectively, it is wound upon winding head 11, Figure 1. 105

The carbonized wire is then wound upon grid supports and attached thereto in the usual manner following which the formed grid is subjected to the third or degasifying step of my process. 110

As above mentioned, I have found that such carbonized metal bodies tenaciously retain gases which are subsequently difficult to remove when the formed metal parts are put through the usual degasification step in the manufacture of electron discharge devices. I therefore take the formed grids and place them in nickel or molybdenum boats and insert them in a vacuum chamber such as indicated in Figure 2. The particular apparatus I employ in this step is substantially comprised of a calorized iron tube 23 approximately 5 1/2 inches inside diameter, hermetically sealed at one end and connected at the other end in any suitable manner to a vacuum pumping system. There are many ways of accomplishing this general result and the apparatus disclosed in Figure 2 is just illustrative of one method, which gives ready means of inserting and removing the 115 120 125 130

treated degasified grids. The vacuum chamber and the enclosed grids are then heated to 850°-950° C. in any suitable manner such as by gas or oil burners or as indicated in Figure 2, by electrical heating elements 25.

At this temperature practically all of the adsorbed and absorbed and all deleterious impurities such as oil, grease, oxide compounds are substantially decomposed and converted to gases or inert carbide compounds, and the applied carbon surface substantially cemented to the base metal through cementation to the intervening metallic carbide core.

After thorough degasification the vacuum chamber and enclosed metal parts are cooled to room temperature before exposure to the atmospheric gases. I have noted that the type of carbon coating I obtain through decomposition of the liquid hydrocarbon vapor in association with the hydrocarbon gases is more graphitoidal in nature where it contacts with the metal surface and appears to be overlaid with a velvety black amorphous carbon coating which is substantially less susceptible to gas absorption than the carbon coating heretofore obtained by decomposition of gaseous hydrocarbons alone such as casing head gasoline. The degasified carbonized metal grids may be re-exposed to atmospheric gases without the reabsorption of deleterious amounts of difficultly removable gases, and may be incorporated in electron discharge devices in the usual manner and will readily give up this adsorbed gas content upon heating by induction in vacuo.

By the practice of the special carbonizing gas mixture of my invention I am substantially able to produce a superior coating to that heretofore obtained wherein the metal surface is coated with substantially pure carbon firmly and adherently cemented to the metal surface by an interposed metallic carbide layer, and from this material I am enabled to produce without deleterious loss or destruction of the carbon coating, formed and shaped articles such as grid electrodes which when subjected to the degasification step of my invention provides a finished carbon coated article which evidences superior qualities from a manufacturing, assembling and operating standpoint from what has heretofore been prepared.

Although I have specifically described my invention with respect to the carbonizing of nickel wire for forming the grid electrodes, it is obvious that it could require but little modification to adapt the process to continuously carbonizing sheet metals or carbonizing other wires, such as tungsten, molybdenum, nickel alloys and similar refractory metals useful in an analogous manner or for the carbonization of formed metal bodies, and such variations and modifica-

tions are anticipated as may fall within the scope of the following claims:

What is claimed is:

1. The process of carbonizing the surface of nickel which comprises first producing an oxidized surface thereon and then exposing the oxidized metal at elevated temperatures to the action of a hydrocarbon gas of the acetylene series containing a proportion of the vapor of a petroleum ether. 70

2. The method of coating nickel wire with an adherent carbon coating which comprises initially oxidizing the surface of said nickel wire and then subjecting the wire at elevated temperatures to the action of acetylene gas containing a proportion of the vapor of the petroleum ether. 75

3. The method of forming an adherent carbon coating on nickel surfaces which comprises initially oxidizing the surface and then subjecting the oxidized surface at elevated temperatures to the action of acetylene containing a proportion of the vapor of a liquid hydrocarbon of the paraffine series. 80

4. The method of forming an adherent carbon coating on nickel surfaces which comprises initially oxidizing said surface and then heating said oxidized metal body to approximately 800° C. to 1000° C. in an atmosphere of acetylene containing a proportion of the vapor of a liquid hydrocarbon of the paraffine series. 85

5. The method of forming an adherent carbon coating on nickel surfaces which comprises initially oxidizing said surface and then heating said oxidized metal to approximately 800° to 1000° C. in an atmosphere of acetylene containing a proportion of the vapor of petroleum ether. 90

In testimony whereof, I have hereunto subscribed my name this 23rd day of January 1929.

CHARLES V. IREDELL.

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