June 7, 1932. H. M. ELSEY 1,862,138

CARBONIZED ELECTRODE AND METHOD OF PRODUCING SAME

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Fig. 1.

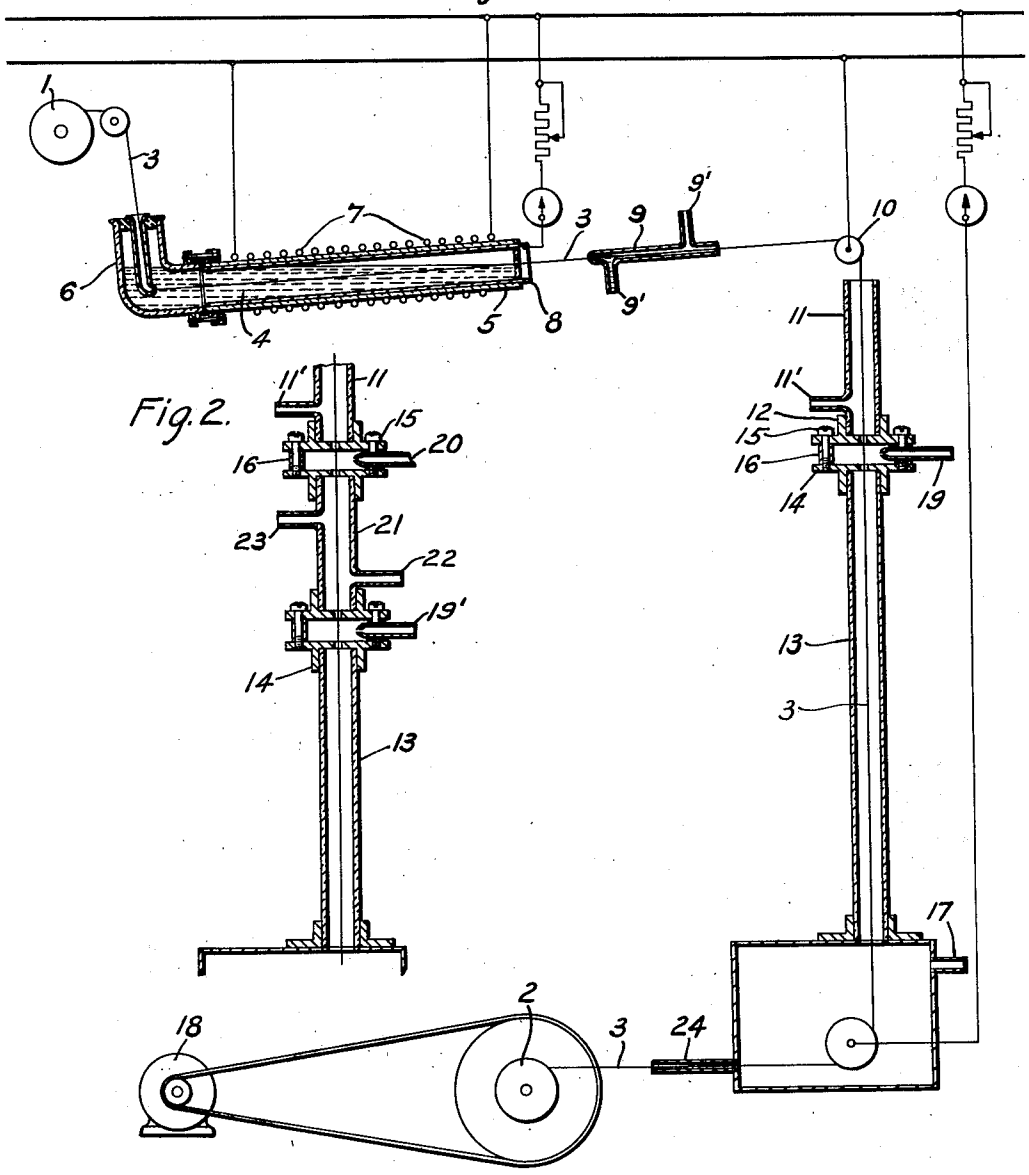


Fig. 2.

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UNITED STATES PATENT OFFICE

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CARBONIZED ELECTRODE AND METHOD OF PRODUCING SAME

Application filed May 3, 1928. Serial No. 274,784.

My invention relates to carbonized electrodes and more particularly to grids or plates utilized in electron tubes and to a process of producing the same.

An object of my invention is to provide carbonized grids or plates for electron tubes that will not soften or lose their strength at the operating temperature of the tubes.

Another object of my invention is to provide a process of preparing wires or strips from which grids or plates for electron tubes may be produced which consists essentially in coating the surface of a wire or metal strip having a relatively high melting point with a metal which does not become as brittle when carbonized and then oxidizing and carbonizing the coated surface.

A further object of my invention is to provide a continuous process of preparing wires or strips for use in manufacturing electrodes which consists in plating wire or strip having a relatively high melting point with a metal that does not become as brittle when carbonized, cleaning the wire or strip after it has passed through the plating bath, and then subsequently oxidizing and carbonizing the plated metal.

A still further object of my invention is to provide a continuous process of preparing wires or strips for use in manufacturing electrodes which consists in plating a wire or strip having a relatively high melting point with a metal that does not become as brittle when carbonized, oxidizing the plating on the wire, reducing the oxidized plating and then carbonizing the reduced metal surface.

In my copending application, Serial No. 252,047, filed February 14, 1928, I have described a method of producing a uniformly carbonized nickel wire or ribbon for the purpose of providing a material from which grids or plates utilized in electron tubes may be produced. As stated in my copending application, carbonized nickel is considerably superior to untreated nickel when employed as a plate or grid in electron tubes because, when untreated nickel grids or plates are utilized in tubes in conjunction with thermionically emissive cathodes, particularly cathodes comprising oxides of the alkaline earth metals, there is a tendency for the cathode-coating material to volatilize or disintegrate and deposit upon the plates or grids which, upon becoming heated, fail to perform their expected function and become emitters of electrons. When the plates or grids are carbonized, however, the carbonized surface not only prevents the emission of electrons but also increases the ability of the grids or plates to radiate heat and, consequently, decreases their operating temperatures.

Nickel wires or strips, carbonized in the manner specified, have been found satisfactory when utilized as grids or plates in small tubes, but when attempts have been made to employ them in power tubes, the nickel softens on heating and has the tendency to lose its shape, while, in high-power tubes, it completely loses its strength at the operating temperatures of the tubes. In order to overcome this difficulty, it has been proposed to utilize metals having a high melting point, say, above 1000° C., and a correspondingly high strength at the operating temperature of the tube, such as molybdenum, zirconium, tungsten or tantalum. When attempts have been made to carbonize such metals, however, they become highly brittle and are unsuitable for use.

I have made the discovery that, when a metal, having a sufficiently high melting point so that its strength will be preserved at the operating temperature of the tube, such as molybdenum or tungsten, is coated by any suitable method, such as by electrodeposition or spraying with a metal that may be easily carbonized, such as nickel, cobalt, iron, or an alloy, such as nichrome, a wire or strip may be produced which may not only be carbonized but which is suitable as a material from which the grids or plates of high-power electron tubes may be produced.

My invention will be better understood when taken in conjunction with the accompanying drawing, in which:

Figure 1 is a cross-sectional view of an apparatus for continuously plating, oxidizing and carbonizing a metallic wire or strip.

Fig. 2 is a modified form of a portion of the apparatus shown in Fig. 1, showing a re-

ducing chamber between the oxidizing and carbonizing chambers.

Referring to Fig. 1 of the drawing, the numeral 1 represents a supply reel upon which the untreated wire or ribbon is wound and 2 a receiving reel that is operated by any suitable means, such as a motor 18, which serves to draw the wire or ribbon through the plating and carbonizing apparatus. The wire or ribbon 3, which may be composed of molybdenum or tungsten, is slowly drawn through a suitable plating bath 4 which is enclosed in a tube made of glass or other suitable insulating material. The glass tube comprises a longitudinal portion 5 and an elbow portion 6. A series of coils 7, connected to a source of electrical energy, are disposed around the outer surface of the glass tube and serve to heat the bath which may consist of any suitable electrolyte, such as the chloride or sulphate of the metal to be plated. The interior of the longitudinal portion of the tube is lined with the desired plating metal 8 which serves as the anode, and the wire passing through the solution serves as the cathode. As the wire or ribbon is slowly drawn through the plating bath, which is maintained at the desired temperature by the exterior coils, a current is passed through the bath, and the wire or ribbon is plated with the desired metal.

The metal wire or ribbon is then washed to remove any excess plating solution by drawing it through a tube 9 provided with nipples 9′ through which water or other cleansing fluid is circulated. The wire is then passed over the guide roller 10 and through an oxidizing tube 11. During the passage of the wire through the oxidizing tube, it is maintained at a high temperature by means of electrical energy. The lower end of the tube 11 is provided with a nipple 11′ by means of which air may be drawn through the tube and with a closure 12, which is maintained in contact therewith by frictional engagement. The closure 12 has an opening at its central portion to permit the passage of the wire or ribbon 3 from the oxidizing tube. The ribbon or wire 3 is then conducted through a longitudinal tube 13 which is provided with a closure 14 at its upper portion similar to closure 12. Closures 12 and 14, in conjunction with bolts 15 and spacers 16, serve to hold the tubes 11 and 13 in spaced coaxial alignment.

Air or other suitable gas may be blown through a jet 19 against the wire while it is pasing from the oxidizing to the carbonizing chamber so as to prevent the entrance of carbonizing gases into the oxidizing chamber. While the wire is passing through the tube 13, it is maintained at a temperature of from 700° to 1000°C. by means of electrical energy or, if desired, the tube 13 may be heated by external means, as disclosed in application Serial No. 251,868 of Upp et al., filed February 4, 1928, which is assigned to the Westinghouse Electric & Manufacturing Company.

During the travel of the wire or ribbon through the tube 13 at the temperature specified, it is exposed to the action of a hydrocarbon gas, such as acetylene or a mixture of acetylene and casing-head gasoline, which is forced into the carbonizing chamber 13 through the nipple 17 and escapes through the aperture in the closure 14 or through the capillary tube 24. The plated wire or ribbon, after passing through the carbonizing chamber, is wound around the receiving reel 2. The wire or ribbon is then heated in vacuum to remove any occluded gas, after which it may be formed or shaped into grids or plates.

Referring to Fig. 2 of the drawing, the oxidizing and carbonizing chambers are similar to those shown in Fig. 1, with the exception that a reducing chamber 21 is interposed between the oxidizing and carbonizing chambers. The corresponding parts have, accordingly, been referred to by the same numerals. It has sometimes been found desirable to effect the reduction of the oxidized metal before it passes into the carbonizing chamber, as freshly reduced metal is more sensitive to the action of the carbonizing gases than plated metal which has not been oxidized and then reduced. For this purpose, a reducing chamber 21 is introduced between the oxidizing and the carbonizing chambers so that, after the electrodeposited metal has been oxidized, it may be first reduced to the metallic state before it is carbonized. Nipples 22 and 23 may be provided for the purpose of passing a reducing gas, such as hydrogen or natural gas, through the reducing chamber 21. I do not desire, however, to be limited to this particular method for effecting the reduction of the oxidized metal, as any desirable method and means may be utilized, such as by making the metal the cathode in an electrolytic bath. Jets 19′ and 20, similar to jet 19 shown in Fig. 1, are provided between the respective chambers. The air or other gas blown through jet 20 prevents reducing gases from entering the oxidizing chamber, and jet 19′ prevents hydrocarbons from entering the reducing chamber. As most hydrocarbons, however, act as reducing agents, it is obvious that jet 19′ may sometimes be omitted.

Although I have described the plating and carbonizing action as being a continuous operation, it will be understood that it may sometimes be desirable to perform the plating operation independently of the oxidizing and carbonizing processes. It is essential for the successful operation of my process that care be exercised in producing a plated metal of the desired thickness. If the layer of plated metal is too thin, the foundation metal

will become carbonized and brittle and if the coating produced is too thick, it will break and peel, leaving the foundation metal exposed to the action of the carbonizing gases. For this reason, it is sometimes desirable to plate the foundation metal while holding it stationary in the bath. It will also be understood that, if desired, the oxidizing step may be omitted, in which case, the plated nickel may be directly carbonized after being plated. I prefer, however, to oxidize the plated surface and pass the oxidized plated metal directly into the carbonizing chamber, as shown in Fig. 1 of the drawing, as this method eliminates the reducing step and is effective in producing a uniformly carbonized surface. The metal may also be carbonized while maintaining it in a stationary position in the carbonizing chamber, but, for economic reasons, it is desirable that the process be made continuous.

While I have described a specific form of my invention, various modifications may be made therein without departing from the spirit of my invention. For example, instead of plating nickel on the surface of the tungsten or molybdenum, it may be sprayed or coated upon the surface in any well-known manner. Other metals that may be readily carbonized, such as iron, cobalt or alloys, such as nichrome, may be substituted for the nickel. Members of the iron family, however, are preferred. Other hydrocarbon gases may also be substituted for acetylene and particularly those that are rich in carbon, such as natural gas, ethylene or butane. When carbonizing wire, however, it is desirable to utilize a hydrocarbon that is particularly rich in carbon, such as acetylene. The thickness of the carbonized layer may also be controlled by mixing the hydrocarbon gases with inert gases, such as nitrogen, argon or helium, or by varying the time of exposure.

Other modifications of my invention will suggest themselves to those skilled in the art, and I desire, therefore, that only such limitations shall be imposed upon my invention as are required by the prior art and the appended claims.

I claim as my invention:

1. In the process of producing electrodes for vacuum tubes, the steps which comprise plating a foundation metal having a relatively high melting point with a metal that may be carbonized without becoming highly brittle and carbonizing the last named metal.

2. In the process of producing electrodes for vacuum tubes the steps which comprise plating a foundation metal having a relatively high melting point with a metal that may be carbonized without becoming highly brittle, oxidizing and carbonizing the last named metal.

3. In the process of producing electrodes for vacuum tubes the steps which comprise continuously plating wire with an electrodeposited layer of another metal and then continuously oxidizing and carbonizing the electrodeposited layer.

4. In the process of producing electrodes for vacuum tubes, the steps which comprise continuously drawing a wire composed of a metal having a relatively high melting point through an electrolyzing bath, of a metal which does not become highly brittle when carbonized, passing the electroplated wire through an oxidizing chamber and then passing it through a carbonizing chamber while maintaining the wire at a temperature of 700 to 1000° C.

5. The process of producing electrodes for vacuum tubes, the steps which comprise plating a foundation metal having a relatively high melting point, oxidizing the plated metal, reducing the oxidized plated metal and carbonizing the freshly reduced plated metal.

6. In the process of producing electrodes for vacuum tubes, the steps which comprise continuously plating ribbon with an electrodeposited layer of another metal, oxidizing the plated metal and subjecting the oxidized metal to the action of a hydrocarbon gas at a sufficient temperature to reduce the oxidized metal and carbonize the surface.

In testimony whereof, I have hereunto subscribed my name this 27th day of April, 1928.

HOWARD M. ELSEY.