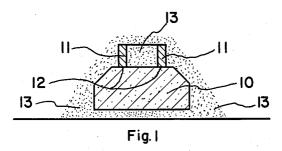
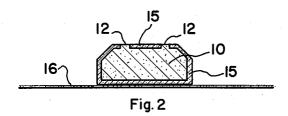
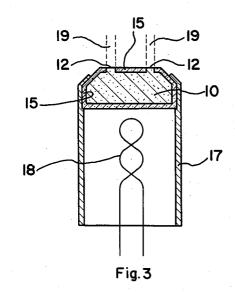
CARBURIZATION OF DISPENSER CATHODES

Filed Jan. 23, 1959







INVENTOR.

BY ROBERTO LEVI

Junk R. Lifai

1

2,972,078

CARBURIZATION OF DISPENSER CATHODES

Roberto Levi, New York, N.Y., assignor to North American Philips Company, Inc., New York, N.Y., a corporation of Delaware

Filed Jan. 23, 1959, Ser. No. 788,603 20 Claims. (Cl. 313—346)

This invention relates to barium-containing dispenser 15 cathodes. In particular, it relates to methods for both enhancing or improving the emission capabilities of certain types of dispenser cathodes and inhibiting emission from parts of dispenser cathodes or other electrode elements, to novel dispenser cathodes as made by the foregoing methods, and to tubes and devices containing the cathode or electrode element.

There are three main types of barium-containing dispenser cathodes available in the art. The earliest developed type is known as the L-type cathode, and is 25 described in United States Patent No. 2,543,728. In this cathode, a barium-containing emissive or activating material is located in a cavity behind a porous refractory metal wall portion. Heating such a structure by a suitably-arranged filament causes a chemical reaction to 30 occur between the emissive material and the refractory metal of the wall resulting in the generation of free barium metal, which then diffuses through the pores of the wall to form a monatomic layer on an external surface of that wall. The resultant heated barium on refractory metal surface constitutes an excellent primary source of electrons, which is found especially useful in microwave tubes because of its high emission densities, its extreme resistance to ion or electron bombardment, and its inherent accuracy of shape and dimensions as well as flatness of the emissive surface. A later modification of this cathode has been termed the "impregnated" cathode, and the main structural difference between it and the L-type cathode is the placing of the emissive material inside the pores of the porous refractory metal wall portion, which is described in United States Patent No. 2,700,000. This is done by melting the emissive material in a protective atmosphere directly into the porous wall portion. In this broad category of impregnated eathodes two main types exist. The first, which is termed the "type A" impregnated cathode, uses a fused mixture of barium oxide and aluminum oxide, which forms a barium aluminate mixture, as the emissive material impregnant. A later-developed impregnated cathode has been termed the "type B" cathode, and uses a fused mixture of barium oxide, aluminum oxide and calcium oxide as the emissive material impregnant. The type B cathode is described in my copending application Serial No. 487,042, filed February 9, 1955. The main advantage of the type B impregnated cathode over the type A impregnated cathode is an increase of emission at the same temperature by a factor of four, accompanied by a reduction in activation time. The third type of dis-penser cathode is known as the "pressed" cathode, and comprises compacting and sintering together a mixture of tungsten and barium aluminate particles to form the refractory metal-emissive material combination required to function as a dispenser type cathode. This is described in United States Patent No. 2,769,708.

These three types of dispenser cathodes all have in 70 common for certain applications the drawback that both free barium and barium oxide are constantly being evapo-

2

rated from the emissive surface, and this vapor deposits on cathode surfaces that should not emit and adjacent electrode elements in the tube, such as a control-grid member or accelerating anode or cathode support member. As these other surfaces or electrode or support members are generally at an elevated temperature by virtue of their close proximity to the heated cathode, and because of deposition thereon of barium and barium oxide, they in turn generate primary electrons. This is quite disadvantageous for various reasons. For example, in a magnetron tube, emission from electrode or support elements outside of the emitting cathode area introduces a host of non-synchronized electrons into the desired stream which interferes with the proper oscillating mode of the magnetron. In a gridded type of electron tube, excessive grid emission causes severe loading of the grid circuit, which detrimentally affects its proper performance of its control function. Hence, a need has arisen in the art of preventing the non-emitting cathode portions as well as other electrode elements close to the dispenser cathode from producing excess quantities of electrons due to deposition thereon of barium metal and barium oxide evaporated from the dispenser cathode emissive surface.

As was mentioned earlier, the main advantage of the type B impregnated cathode over the type A impregnated cathode is the increase in emission by a factor of four. However, the type B cathode does have some limitations relative to the type A, which include lower resistance to poisoning, and an operating temperature range whose upper limit is somewhat below that of the type A cathode, and there are applications for such cathodes where the dispenser cathode requires a higher poisoning resistance, or attains a high elevated temperature by reason of back bombardment of the cathode by returning electrons or ions which has required the employment of a type A cathode because of its somewhat higher permissible operating temperature. Thus, there is also a need in the art for a dispenser cathode having some of the advantages of the type A impregnated cathode as well as the higher emission densities associated with a type B cathode.

Strangely enough, I have found that both of these needs can be fulfilled by employing carburization with a dispenser cathode. In particular, I have found that a tungsten or molybdenum carbide surface while maintained at an elevated temperature and although contaminated with barium metal and barium oxide exhibits an astonishingly low emission density. Thus, primary emission from contaminated elements in the electron tube can be inhibited by providing the element concerned with a tungsten or molybdenum carbide surface, and ensuring that that surface is maintained during tube operation at an elevated temperature above about 950° C. This can be assured by the mounting arrangement of the element and its proximity to the heated cathode, or its location in the path of bombarding electrons and ions, or, if necessary, by providing separate heating means such as a heating filament or the like for raising the temperature of the element to the value desired. I have also found that I can obtain the high emission densities of the type B impregnated cathode using the type A impregnant by melting the latter into the porous refractory metal member through a carbon-containing matrix or carburized skin on said metal member. Thus, the resultant impregnated dispenser cathode has the higher emission densities associated with these dispenser cathodes and at the same time possesses higher poisoning resistance, and may be operated at higher temperatures.

The invention will now be described in greater detail with reference to the accompanying drawing, in which:

Fig. 1 is a cross-sectional view of an assembly of ele-

ments illustrating the first step in one way of making an impregnated-type dispenser cathode producing a hollow beam of electrons;

Fig. 2 is a cross-sectional view illustrating the second step in the manufacture of a hollow beam source;

Fig. 3 is a cross-sectional view of the completed cathode made in the manner illustrated in Figs. 1 and 2.

The invention will first be described in detail in connection with the making of a hollow cathode source using both the enhancing and inhibiting techniques above-de- 10 scribed. There are microwave tube applications, such as the traveling-wave tube, in which a beam of electrons of generally cylindrical form traverses an extended beam path within a delay line, along which is passed an electromagnetic wave. Operation results from interaction of 15 the electrons and the electromagnetic wave. As it is primarily the electrons on the periphery of the beam that participate in this phenomenon, it is desirable to remove the center core of electrons. This can be done by providing a hollow beam source. To manufacture such a 20 source in accordance with this invention, one starts first by providing a porous tungsten pellet or disc 10 as shown in Fig. 1. Although tungsten is preferred, other refractory metals or combinations, such as molybdenum-tungsten, or tantalum-molybdenum may also be employed. 25 The method for making a porous tungsten disc with about 83% density is described in detail in my United States Patent No. 2,721,372. A short hollow cylinder ably has a flat end surface, acts as a mask for a contacted annular surface portion 12 of the disc. Next, the assembly of disc and hollow cylinder is surrounded and contacted on all its exposed surfaces with fine carbon or graphite powder 13. Thereafter, the assembly is heated in hydrogen to an elevated temperature of about 1500° C. brightness and maintained at that temperature for about 5 minutes.

During this process, the carbon-contacted tungsten surfaces react to form a tungsten carbide skin on the disc 40 10 with a depth of about 10-40 microns. The annular surface 12 masked off by the hollow cylinder 11 remains substantially unaffected by this process, although it does become slightly smaller due to carbon diffusion from the sides. For this reason, the cylinder 12 should be slightly oversize so that the final dimensions of the annular surface portion 12 will have the required value. The resultant structure of the disc includes, except for this annular surface 12 on its top, a tungsten carbide skin 15 around all the remaining surfaces of the disc. This is 50 shown in Fig. 2. Next, a type A impregnant comprising a fused mixture of barium oxide and aluminum oxide in a 5:2 mole ratio—see United States Patent No. 2,700,000 for a description of other suitable barium compositionsis provided as a thin layer 16 on a surface and the disc 55 placed on top of the layer 16 as shown in Fig. 2. Alternatively, the aluminate powder can be suspended in an amyl acetate carrier and painted as a thin layer on the support. The combination is now reheated to an elevated temperature of about 1750° C. in a non-oxidizing atmosphere, such as hydrogen, whereby the prefused barium aluminate material melts and is drawn into the pores of the tungsten disc by capillary action, in the process of which the molten aluminate traverses the tungsten carbide skin 15 on the disc 10. As shown in Fig. 3, the resultant impregnated disc 10 is then mounted in a suitable support 17 containing a heating filament 18, and is then ready for assembly into an electron tube in the usual manner in which such dispenser cathodes are handled.

It has been found that a cathode made as described 70 above exhibits the following properties. Under the usual operating conditions, which means that the cathode is maintained at a temperature in excess of 950° C., it is found that only the uncarburized annular surface 12 on

by reference numeral 19, whereas the other carburized disc surface portions 15 are essentially non-emitting and thus, as illustrated in Fig. 3, emission from such a structure is in the form of a hollow cylinder, as required. Moreover, it is found that the emission density from the emitting portions of such a cathode is of the same order as that from a type B impregnated cathode, although the type A impregnant has been employed and although the emission densities of such impregnants in the usual impregnated cathode have been below that of the type B impregnated cathode by a factor of four. Moreover because the type A impregnant is employed, the cathode will possess a higher resistance to ion bombardment and poisoning, and operate at higher temperatures where this required.

With regard to the emission-inhibiting mechanism, it is again emphasized that it is operable only when the carburized surface is maintained at an elevated temperature. This temperature will generally be in excess of 950° C., and will depend upon the arrival rate of the barium metal and barium oxide contaminants to the carburized surface. With high arrival rates, the temperature of 950° C. or higher is required. At lower arrival rates, lower temperatures, e.g., 900° or 800° C., are permissable. It is believed that the explanation for this phenomenon is connected with the sticking ability of the barium metal and barium oxide on the carburized surface. The depth of the carburized surface is not too critical. Inhibition has been obtained with carburization depths produced with 11 of refractory metal is placed on the top or emitting been obtained with carburization depths produced with surface of the pellet 10. This cylinder 11, which prefer30 heating temperatures of 1400-1700° C. for times of 5-15 The only limitation would appear with very thin carbide skins, which may become decarburized after several hundred hours of lifetime, causing the emission to increase. If this occurs, it can be readily overcome by simply lengthening the carburizing process. the manner in which the carburization is initially obtained does not appear to be critical. It can be obtained by heating the element concerned while in contact with carbon or graphite powder. It may also be obtained by painting the desired surface portions with a suspension of carbon in a binder, followed by heating. Similarly, carbon in a binder may be sprayed onto the element. As described above, masking can be used to prevent the desired emitting surface areas on a cathode from becoming carburized. However, another technique with cathodes is to carburize the entire surface, and then later to remove the carbide skin from the desired emitting areas to expose the uncarburized tungsten. This may be done by a machining process using a diamond tool, or by sandblasting off the carbide skin where desired. As another possibility, carburized and uncarburized porous tungsten portions can be mechanically assembled together to form the emitting and non-emitting areas or can even be joined together by welding to form the desired structure. Also, the non-emitting area can be painted with a suspension of tungsten or molybdenum carbide, which is later heated to sinter the carbide coating in position.

Carburization can also be obtained in other ways. For example, the tungsten pellet or electrode element to be carburized can be heated in a hydrocarbon gas atmosphere of such a nature that the hydrocarbon disassociates on contact with the heated pellet and the resultant carbon then can react with the tungsten to form the carbide desired. For example, the element to be carburized can be heated in a naphthalene atmosphere. Insofar as the impregnated-type cathode is concerned, it will be apparent that carburization of a surface portion to prevent emission can also be done after it has been impregnated with its activating material.

It will be clear from the foregoing detailed description that I have found that carburized and uncarburized surfaces of the tungsten or molybdenum metal matrix of a dispenser cathode, when maintained at an elevated temperature, produce substantially no and many electop of the disc 10 generates copious electrons, indicated 75 trons, respectively. This same principle is also employed

for inhibiting emission from other tube elements in the electron tube which are subject to contamination by the evaporation products of barium metal and barium oxide from the dispenser cathode. For example, the molybdenum hats at opposite ends of a dispenser cathode structure in a magnetron are frequent sources of undesired This undesired emission is suppressed by carburizing the molybdenum hats in the manner previously described. Similarly, if excessive emission from the support for the cathode, which is also usually molyb- 10 denum, is present, this too can be carburized to suppress emission. Also, where grids or accelerating anodes constructed of tungsten or molybdenum are disposed close to the dispenser cathode and are likely to be contaminated by barium and barium oxide, resulting in exces- 15 sive primary emission from these electrodes, this too can be suppressed by carburizing the surfaces on which the evaporants may fall.

The mechanism whereby impregnated-type dispenser a carburized surface result in a cathode with an emission level several times greater is not completely understood but is believed based on the following principles. It has been thought that the reduced emission of the type A impregnated cathode was due to the presence of a 25 poisoning agent that is generated during operation, preventing the level of emission from reaching that of the type B impregnated cathode. It was also thought that this poisoning agent is in some way tied up by the emission-increasing additive calcium oxide in the type B cathode. It has therefore been deduced that a similar phenomenon occurs when the type A impregnant is passed in a molten condition through the carbide surface. It is possible that the poisoning agent is either permanently inhibited during this process, or a reaction occurs with 35 the carbide during which the poisoning agent is removed from the molten impregnant.

In the manufacture of an ordinary planar impregnated cathode, it is not necessary first to carburize the surface as described earlier. Such a cathode can be sim- 40 ply made by providing an organic compound that when decomposed by heat will furnish a porous carbon matrix on the tungsten disc or pellet, and then melting the barium aluminate through this carbon mask formed prior to or while attaining the melting temperature into the 45 tungsten interior. Ordinary household sugar has worked well in this technique. Thereafter, the carbon mask may be brushed off or otherwise mechanically removed from the cathode surface together with the excess aluminate high emission can be obtained. Also, to avoid any possibility of carburization of the surface occurring, which would inhibit emission, a thin layer of tungsten powder may be painted on the pellet before applying thereto the carbon-forming compound, which thus prevents contact 55of the carbon with the surface of the disc. As indicated earlier, machining can be employed for removing any slight carbide layer that results or other mechanical material-removing treatments. Another technique that may be used involves oxidizing the surface of the cathode by heating it in air after which it is heated in a reducing atmosphere. Such successive oxidation-reduction treatments cause material removal by sublimation and can be employed for removing any thin carbide layers present.

When using these cathode in electron tubes in which excessive back bombardment of the cathode surface by returning electrons or ions results in excessive secondary emission, this can be alleviated by removing the impregnant from the surface pores of the cathode. This may be done by leaching out the impregnant in the surface pores of the cathode. As the barium aluminates are water-soluble, placing the cathode element in boiling water for about 5 minutes will dissolve and remove the

of about 100 microns. This technique may also be employed for reducing the evaporation of the barium and barium oxide from the cathode during operation.

While I have described my invention in connection with specific embodiments and applications, other modifications thereof will be readily apparent to those skilled in this art without departing from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A method of making an improved dispenser-type cathode, comprising providing a porous refractory-metal body, providing surface portions of the body with a layer of a substance selected from the group consisting of tungsten carbide and molybdenum carbide, and impregnating the pores of said body with activating material by passing molten barium-containing activating material through the said carbide surface layer into the pores, the carbide surface portions of said body when heated at an elevated temperature possessing substantially no cathodes made with a type A impregnant passed through 20 emissive capabilities, surface portions of said body free of the carbide layer and when heated at an elevated temperature possessing improved emission capabilities.

2. An electron device comprising a dispenser-type cathode generating a barium-containing contaminant, a surface receiving said contaminant and tending to emit electrons, and a substance selected from the group consisting of tungsten carbide and molybdenum carbide on said surface and inhibiting its emission, said surface being

maintained at an elevated temperature.

3. A device as set forth in claim 2 wherein the surface is on an electrode in said device and adjacent said cathode.

4. A device as set forth in claim 2 wherein the surface is a portion of the cathode that should not emit.

- 5. An electron tube comprising a dispenser-type cathode containing a barium-type activating material, means for heating the cathode at an elevated temperature at which the cathode generates barium and barium oxide, an element having a surface receiving said barium and barium oxide and tending to emit electrons, and a surface layer of a substance selected from the group consisting of tungsten carbide and molybdenum carbide on said surface and inhibiting its emission, said surface being maintained at an elevated temperature above about 950° C.
- 6. A tube as set forth in claim 5 wherein the surface is maintained at an elevated temperature by radiation from the heated cathode.
- 7. A tube as set forth in claim 5 wherein the surface to leave a surface of impregnated tungsten from which 50 is maintained at an elevated temperature by particle bombardment.
 - 8. A tube as set forth in claim 5 wherein heating means are provided for maintaining the said surface at an elevated temperature.
 - 9. A dispenser-type cathode comprising a refractorymetal-containing body associated with a barium-containing activating material and generating a barium-containing contaminant, an emissive surface on said body and also a non-emissive surface receiving said contaminant 60 and tending to emit electrons, a surface layer of a substance selected from the group consisting of tungsten carbide and molybdenum carbide on said non-emissive surface and inhibiting its emission, and means for heating the cathode at a temperature in excess of 950° C.

10. A dispenser-type cathode comprising a tungsten matrix impregnated with barium aluminate and generating a barium-containing contaminant, emissive and nonemissive surface portions on said matrix, a tungsten carbide surface at said non-emissive surface portion and inhibiting its emission, and means for heating the cathode at an elevated temperature in excess of 950° C.

11. A method of inhibiting the emission from a surface exposed to barium and barium oxide evaporated from a dispenser-type cathode, comprising providing the said barium aluminates from the surface pores to a depth 75 surface with a surface layer of a substance selected from

the group consisting of tungsten carbide and molybdenum carbide, and maintaining the said surface at an elevated temperature above about 950° C.

12. A method of making an improved impregnated-type dispenser cathode, comprising the steps of providing a porous refractory-metal body, and impregnating the pores of said body with molten barium-containing activating material through a carbon-containing element.

13. A method as set forth in claim 12 wherein the carbon-containing element is a perous carbon matrix. 10

14. A method as set forth in claim 12 wherein the carbon-containing element is a porous carbide matrix.

15. A method of making an improved impregnatedtype dispenser cathode, comprising the steps of providing a porous tungsten body, and impregnating the pores of 15 said body with molten barium aluminate through a carbon-containing porous member.

16. A method as set forth in claim 15 wherein the tungsten body is provided with a tungsten carbide surface layer, and the body impregnated through the carbide 20

surface layer.

17. A method as set forth in claim 16 wherein portions of the carbide surface layer are removed after the impregnation step.

18. A method of reducing the secondary emission from 25

a dispenser cathode of the type comprising a porous refractory-metal body whose pores are filled with a bariumcontaining activating material, comprising removing the activating material from the surface pores of the emissive surface of the body.

19. A method of reducing the secondary emission from a dispenser cathode of the type comprising a porous refractory-metal body whose pores are filled with a barium-containing activating material, comprising leaching-out the activating material from the surface pores of the

emissive surface of the body.

20. A method of reducing the evaporation from a dispenser cathode of the type comprising a porous refractorymetal body whose pores are filled with a barium-containing activating material, comprising removing the activating material from the surface pores of the emissive surface of the body.

References Cited in the file of this patent UNITED STATES PATENTS

1,922,244	Hunter Aug. 15, 1933
	FOREIGN PATENTS
701,871	Great Britain Jan. 6, 1954
705.126	Great Britain Mar. 10, 1954