May 8, 1956 R. W. NEWMAN 2,744,838

ELECTRON DISCHARGE DEVICE CATHODE
AND METHOD OF MAKING SAME
Filed Nov. 3, 1951

Fig. 1.

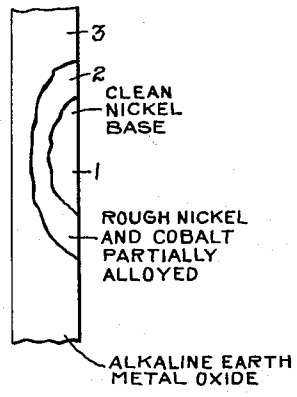
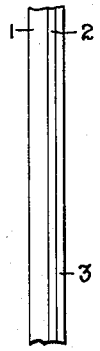


Fig. 2.



Inventor:
Robert W. Newman,
by Morton D. Morse
His Attorney.

United States Patent Office

2,744,838

Patented May 8, 1956

2,744,838

ELECTRON DISCHARGE DEVICE CATHODE AND METHOD OF MAKING SAME

Robert W. Newman, South Schenectady, N. Y., assignor to General Electric Company, a corporation of New York

Application November 3, 1951, Serial No. 254,704

15 Claims. (Cl. 117—217)

My invention relates in general to electron discharge device cathodes and processes of making same. My invention relates in particular to nickel cathodes which are inhibited against flaking or peeling of the electron emissive substance applied to the surfaces thereof.

In the use of electron discharge devices, one of the commonest limitations to the useful life thereof is a reduction of the electron emissive capabilities of the cathodes therein which is occasioned by the flaking or peeling of the surface coating of emissive oxide material from the surface of the cathodes. This problem is especially accented in discharge devices employing nickel cathodes in a mercury vapor atmosphere, presumably because of an amalgamating or wetting tendency of mercury with nickel whereby mercury destroys the bond at the interfaces between the nickel cathodes and the emissive oxide layers thereon. It, therefore, follows that reduction of this flaking or peeling results in an improved cathode imparting longer useful life to electron discharge devices.

It is a primary object of my invention to provide a new and improved cathode for use in electron discharge devices.

It is a further object of my invention to provide a nickel cathode capable of holding an electron emissive oxide surface coating thereon with less flaking or peeling of the surface coating than occurs from prior art type cathodes.

It is a further object of my invention to provide a process of cathode treatment to produce the new and improved cathode of my invention.

And it is a still further object of my invention to provide such an improved cathode from which flaking of an emissive oxide coating in a mercury vapor atmosphere is particularly greatly reduced.

Briefly stated, the cathode of my invention comprises a cathode base member which may have any physical shape and which includes a surface portion thereof containing at least 3 percent cobalt and the remaining percentage, by weight, substantially pure, i. e., commercially pure, nickel. A suitable electron emissive oxide layer, for example, an oxide of one or more alkali earth metal elements, is coated on the surface portion to emit electrons when raised to an elevated temperature. I have found that such a surface portion having at least 3 percent cobalt in nickel provides a mossy, dendritic base upon which the emissive oxide coating is held, small tooth-like dendrites projecting from the surface portion to anchor the oxide coating against flaking thereof otherwise caused by mechanical and thermal shocks. The cobalt in the surface portion of the cathode further provides a rougher more porous metallic base upon which the emissive oxide is coated, therefore providing a base which has little tendency to wet or amalgamate with mercury in the presence of mercury vapor, as does nickel, so that the bond between the oxide coating and the surface portion of the cathode is not weakened by the action of mercury.

The cathode of my invention may be of either the directly or indirectly heated type and may comprise a base

member which is composed of a commercial grade of nickel, as is commonly employed for cathodes. In accordance with my invention, the surface of the nickel base for the cathode is processed to inhibit flaking or peeling of a later applied emissive oxide coating therefrom. This inhibiting treatment comprises a powdered mixture of cobalt and nickel compounds suspended in a binder vaporizable by heat, and a solvent for the binder. The cobalt and nickel compounds are selected from those which are reducible by heat to metallic cobalt and nickel respectively, for example, oxide, carbonate, or hydroxide compounds of cobalt and nickel. The second step is to heat the cathode and applied powder to a sufficient temperature in a manner to vaporize the binder, reduce the cobalt and nickel compounds to metallic cobalt and nickel respectively, and to at least partially alloy the cobalt and nickel thus formed. The resulting surface portion of the cathode, which contains an appreciable amount of cobalt at least partially alloyed with nickel, is darker than a nickel surface and has a mossy, dendritic structure. Electron emissive oxide compounds are then coated on this surface portion in a conventional manner, being held mechanically by the dendrites of the surface portion. The bond between the oxide coating and the surface is immune to damage by the effects of mercury because the cobalt oxide has little or no affinity for wetting or amalgamating with mercury. As a result, the emissive oxide coating is maintained on the cathode with much more stability, even in mercury atmospheres. While I have found it possible to make the entire cathode member, including a surface portion thereof, of a cobalt-nickel alloy to successfully inhibit oxide coating flaking, the extremely high cost and difficulty in procuring adequate amounts of cobalt for this practice renders it more practical to employ the inhibiting process described whereby only a small amount of cobalt is required in the surface portion of the cathode base member. In practice, as little as 3 percent, by weight, of cobalt in the surface portion of the cathode base member definitely inhibits oxide coating flaking. Accordingly, in the process described, the mixture of the cobalt and nickel compounds may be so proportioned that, when reduced, the resultant deposit is at least 3 percent cobal and the rest substantially nickel.

The novel features of my invention are pointed out with particularity in the appended claims. However, for a better understanding of the invention, together with further objects and advantages thereof, reference should be had to the following description taken in conjunction with the accompanying drawing, wherein:

Fig. 1 is an enlarged elevational view of a cathode embodying the features of my invention, the cathode being only partially shown and partially broken away for clarity; and Fig. 2 is a side elevational view taken of Fig. 1.

Referring now to the drawing, I have illustrated for simplicity and convenience only a strip portion of a cathode which embodies the features of my invention and which serves as a source of electrons in an electron discharge device. The cathode of my invention comprises a base member 1 of commercially pure, or purer, nickel which has a surface portion 2 thereon containing cobalt, at least 3 per cent by weight, and nickel to the remaining percentage of the surface portion 2. Upon surface portion 2, there is a surface coating 3 of a thermionically electron emissive substance, preferably an oxide of one, or a mixture of oxides of more than one, alkaline earth metal, e. g., calcium, strontium, or barium. As is well known in the art, alkaline earth metal oxides serve as an emitter of electrons when elevated to a sufficiently high temperature by electric current flowing through the cathode itself (direct heating) or by heat radiated from a separate heater element (indirect heating). A cathode

embodying my invention may have any desired physical shape and may be either of the directly or indirectly heated type. It will be understood that the strip portion of a cathode I have illustrated in the drawing may be a part of a ribbon or wire cathode which is directly heated by the passage of current therethrough, such as shown and described in U. S. Patent 1,895,858, issued January 31, 1933, in the name of W. G. Morgan. Further, the illustrated strip portion may be a part of a hollow tubular cathode within which a heating filament is positioned to radiate heat to the cathode itself. Such an indirectly heated tubular cathode is shown, for example, in the patent of M. Bariess et al., #1,855,901, issued April 26, 1932.

There has long been a problem in the art of electron discharge devices occasioned by the flaking or peeling of this emissive surface coating when applied directly to the nickel base because the nickel base at the interface between the nickel and the emissive coating is smooth and the bond is not appreciably strong. Mechanical or thermal shock may cause all or part of the emissive coating to be flaked or peeled off the nickel base, thereby considerably reducing the emissive capabilities of the cathode and impairing useful operation of the discharge device of which it is a part. This problem is particularly significant with regard to cathodes employed in devices having mercury vapor therein, because during storage or non-operating times of the device when the cathode is cool, mercury condenses on the cathode and penetrates small openings in the emissive coating to amalgamate with or form a mercury monolayer on the nickel base. Mercury at the interface between the nickel and the emissive coating spreads and destroys the bond between the nickel and the coating and it has been observed that in periods of less than one month substantially all of the coating is flaked off and useful emission from the cathode precluded.

A cathode embodying my invention, as described, is free from this flaking or peeling action of the emissive coating. This results from several important effects produced at the interface between the emissive coating 3 and the surface portion 2 containing cobalt and nickel. First, the surface portion 2 is at least partially a nickel-cobalt alloy which is fused and alloyed into the nickel base member 1 because of characteristic similarities of cobalt and nickel, so that the surface portion 2 is strongly bonded to the base member 1. Second, the surface portion 2 consists of a dark, mossy, dendritic composition with dendrites projecting therefrom so that when the emissive coating 3 is applied, the dendrites stick into, and some entirely through, the coating 3, thereby firmly anchoring the coating against mechanical and thermal shocks. Third, the rough, dark surface provided by the cobalt and nickel in the surface portion 2 is one which has much less affinity for mercury than a plain nickel surface. Liquid mercury has little tendency to amalgamate with this surface portion through the small openings in coating 3 and thus does not destroy the bond between the surface portion 2 and coating 3. It has been found that a roughened, plain nickel surface does not prevent flaking of the emissive coating in the presence of mercury and that the action of the mercury in wetting the nickel surface causes an extremely great amount of oxide coating flaking. On the other hand, it has been found that a cathode having a surface portion 2 in accordance with my invention does not flake because the surface portion 2 does not wet with mercury. According to an important aspect of my invention, I provide a convenient, economical and successful process for providing the flaking inhibited surface portion 2 on a nickel base member and the following is an example of the process steps that may be employed.

A powdered mixture of cobalt and nickel compounds, which are readily reducible to metallic cobalt and nickel, is suspended in a volatile solution of a binder which completely decomposes into volatile products upon heating. For example, such compounds may be oxides, hydroxides, or carbonates of cobalt and nickel; a suitable binder is cellulose nitrate or a polyvinyl resin; and a suitable volatile solvent is acetate or amyl acetate. This solution is applied to the surface of base member 1 in any suitable manner, both painting with a brush and spraying being satisfactory. The cathode is next heated in a reducing atmosphere to vaporize the binder, reduce the compounds to metallic cobalt and nickel, and to at least partially alloy the resultant metallic cobalt and nickel. The surface portion 2 is then complete. The proportion of the cobalt and nickel compounds in the mixture is so chosen that at least 3 percent cobalt, by weight, is provided in the surface portion 2 and, if desired, up to 100 percent of the cobalt compound in the mixture may be employed, but percentages in the order of ten (10) percent are high enough in most cases. The emissive coating 3 may next be applied to surface portion 2 in a conventional manner. A powdered carbonate compound of an alkaline earth metal, or a powdered mixture of carbonate compounds of more than one alkaline earth metal, suspended in a volatile solvent containing a binder completely vaporizable by heat, is sprayed or brushed on to the surface portion 2. Then the coating is heated in a vacuum to vaporize the binder and change the carbonate compounds to oxides of alkaline earth metals, the resultant gaseous products being drawn off by a suitable means. The flaking inhibited cathode is then ready for use.

In a preferred specific process for treating the nickel base member to provide the flaking inhibited surface portion 2 prior to the application of emissive coating 3 thereon, I employ a powdered mixture of cobaltic and nickelic oxides suspended in a solution of suitable binder such as nitrocellulose or a polyvinyl resin binder and a volatile carrier such as acetone or amyl acetate and brush the solution on to the base member. The cathode is then fired at 1000° C. for 30 minutes in a reducing atmosphere, such as hydrogen or cracked ammonia gas whereupon the binder volatilizes, the oxides are reduced to cobalt and nickel, and the cobalt and nickel are in turn at least partially alloyed. The emissive coating is applied as described above.

As will be understood by those skilled in the art, the heating times and temperatures may be varied considerably with the lower temperatures being accompanied by longer heating times, for example, with temperatures as high as 1075° C. to 1100° C. heating times in the range of 3 minutes to 1 minute may be employed while temperatures below 975° require an hour or more.

While the present invention has been described by reference to specific illustrations and examples thereof, it will be understood that numerous modifications may be made by those skilled in the art without actually departing from the invention. I, therefore, aim in the appended claims to cover all such equivalent variations as come within the scope of the foregoing disclosure.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. For use in electron discharge devices, the combination consisting of a nickel base member having a surface portion thereon containing at least three percent cobalt for minimizing flaking of an emissive coating to be applied thereto and a remainder of substantially pure nickel.

2. For use in electron discharge devices, a cathode consisting of a nickel base member, a surface portion on said base member composed of at least three percent cobalt for minimizing flaking of an emissive coating applied thereto and the remainder of said surface portion of substantially pure nickel, and a coating of an electron emissive substance on said surface portion.

3. An indirectly heated cathode for use in a mercury vapor discharge device consisting of a nickel base member having only the surface portion thereof alloyed with cobalt, the cobalt comprising in excess of three percent by weight of the surface portion, for minimizing flaking off of an emissive coating applied thereto, and a coating

of an electron emissive material on the surface portion thereof.

4. The process of inhibiting flaking of an electron emissive oxide coating from a nickel cathode base member which comprises the steps of applying to the surface of said base member a powdered mixture of a cobalt compound and a nickel compound, said compounds being reducible to metallic cobalt and nickel respectively, and heating said cathode base member and applied powders in a reducing atmosphere to a temperature in the order of 1000° C. to reduce said compounds to metallic cobalt and nickel, and to at least partially alloy the metallic cobalt and nickel thus formed with each other and the surface of said base member.

5. The process of a flaking inhibiting treatment of a nickel cathode prior to the application thereon of an electron emissive material which comprises the steps of applying to the surface of said nickel cathode a mixture of cobalt oxide and nickel oxide in a binder which completely decomposes into volatile products upon heating and a volatile solvent for said binder; and heating said cathode in a reducing atmosphere to decompose and volatilize said binder, and to reduce said cobalt oxide and said nickel oxide to metals and at least partially alloy and fuse said metals with each other and said surface of said cathode.

6. The process of treating a nickel cathode prior to the application thereon of an emissive oxide material which comprises the steps of applying to the surface of said cathode a powdered mixture of at least three percent cobalt oxide and the remaining percentage of a powdered nickel oxide by weight suspended in a binder which completely decomposes into volatile products upon heating and a volatile solvent for said binder; and heating said cathode in a reducing atmosphere to decompose and volatilize said binder, to reduce said cobalt oxide and said nickel oxide to cobalt and nickel metals and at least partially alloy and fuse said metals with each other and the surface of said cathode.

7. The process of treating a nickel cathode prior to the application thereon of an electron emissive oxide material which comprises the steps of applying a coating to the surface of said cathode of a powdered mixture including at least three percent by weight of cobalt oxide and the remaining percentage by weight of nickel oxide suspended in a binder which completely decomposes into volatile products upon heating to a temperature less than 1000° C. and a volatile solvent for said binder; and heating said cathode to at least 1000° C. in a reducing atmosphere to decompose and volatilize said binder, to reduce said cobalt oxide and said nickel oxide to metallic cobalt and nickel respectively and to at least partially alloy and fuse said metallic cobalt and said nickel with each other and the surface portion of said cathode.

8. The process of making a cathode for use in electron discharge devices having mercury vapor therein which comprises the steps of initially applying to the surface of a piece of nickel a powdered mixture consisting of at least three percent by weight of powdered cobalt oxide and the remaining percentage of nickel oxide, said mixture being suspended in a first binder which completely decomposes into volatile products upon heating and a volatile solvent for said first binder; secondly, heating said nickel piece in a reducing atmosphere to decompose and volatilize said first binder, to reduce said cobalt oxide and said nickel oxide to metallic cobalt and nickel, respectively, and to at least partially alloy and fuse said metallic cobalt and nickel with each other and the surface portion of said piece of nickel; thirdly, applying a powdered carbonate of at least one alkaline earth metal element suspended in a second binder which completely decomposes into volatile products upon heating and a volatile solvent for said second binder; and fourthly, heating said cathode to decompose and volatilize said second binder and to reduce said alkaline earth metal carbonate to an alkaline earth oxide, whereby the resultant alkaline earth metal oxide is adhered to the nickel cobalt alloy on the surface of said piece of nickel.

9. For use in an electric discharge device, a member consisting of a base portion of at least commercially pure nickel and an alloy surface portion containing approximately ten percent cobalt and a remainder of substantially pure nickel only, said surface portion being adapted for minimizing flaking of an emissive coating to be applied to said member.

10. For use in an electric discharge device, a cathode comprising a base member consisting of a base portion of at least commercially pure nickel and an alloy surface portion containing approximately ten percent cobalt and a remainder of substantially pure nickel only, and a coating of an emissive substance held firmly on said base member by said surface portion.

11. For use in electric discharge devices, a metallic cathode base member having a dendritic surface portion comprising an admixture of cobalt and substantially pure nickel only, said dendritic surface portion being adapted for minimizing flaking of an electron emissive substance to be applied thereto.

12. For use in electric discharge devices, the combination of a base member having a dendritic surface portion comprising an admixture of cobalt and substantially pure nickel only, and a coating of an electron emissive substance firmly held on said base member by said dendritic surface.

13. For use in electric discharge devices, the combination of a substantially pure nickel base member, said base member having a dendritic surface portion fused and alloyed thereto, said dendritic surface portion comprising an admixture of at least three percent cobalt and a remainder of substantially pure nickel only and being adapted for minimizing flaking of an emissive coating to be applied thereto.

14. For use in electric discharge devices, the combination of a substantially pure nickel base member, said base member having a dendritic surface portion fused and alloyed thereto, said surface portion comprising an admixture of at least three percent cobalt and a remainder of substantially pure nickel only, and a coating of electron emissive substance firmly held on said base member by said dendritic surface.

15. The process of producing a nickel cathode base member adapted for inhibiting flaking of an electron emissive material coating applied thereto which comprises the steps of applying to the surface of said member an admixture of compounds which are reducible to metallic cobalt and nickel, reducing said compounds to metallic cobalt and nickel, and at least partially alloying and fusing the resultant metallic cobalt and nickel with each other and the surface portion of said base member.

References Cited in the file of this patent

UNITED STATES PATENTS

1,553,394	Pilling	Sept. 15, 1925
1,823,984	Nicolson	Sept. 22, 1931
2,049,372	Hamada et al.	July 28, 1936
2,072,575	Acker et al.	Mar. 2, 1937
2,072,576	Acker et al.	Mar. 2, 1937
2,122,860	Gorlich	July 5, 1938
2,140,367	Lowry	Dec. 13, 1938
2,154,633	Mitchell	Apr. 18, 1939
2,176,597	Sweeney et al.	Oct. 17, 1939
2,192,491	Widell	Mar. 5, 1940