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[54] **COATED COIL EMISSIVE ELECTRODE**

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[52] **U.S. Cl.** ..... **117/224,** 117/230, 117/231, 313/345, 313/346 R

[51] **Int. Cl.** **H01j 1/4,** B44d 1/02

[58] **Field of Search** ..... 117/224, 230, 231, 223; 313/345, 346 R, 346 DC

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[57] **ABSTRACT**

A coated coil emissive electrode of the type utilized in fluorescent lamps and a method for making such an electrode. The electrode includes a tungsten coil, a bonding layer of an emissive form of barium tungstate coating said tungsten coil, and a layer of porous barium oxide coating said barium tungstate, said barium tungstate bonding said barium oxide to said tungsten coil. The electrode is made by coating said tungsten coil wuth a mixture of barium peroxide, cellulose nitrate and butyl cellosolve and heating said coated coil to the exothermal decomposition temperature of said cellulose nitrate. The exothermal decompositon of said cellulose nitrate raises the temperature of the barium peroxide to its exothermal decomposition temperature thereby forming said bonding layer of the emissive form of barium tungstate and releasing bubbles of oxygen causing the pores in said barium oxide.

6 Claims, 4 Drawing Figures

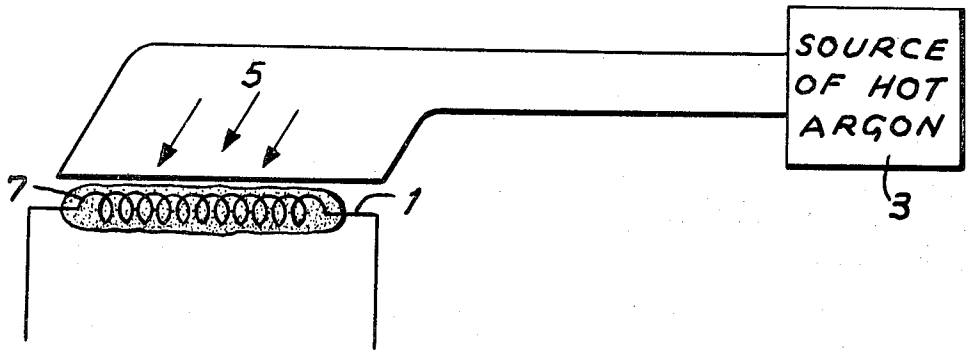


Fig. 1

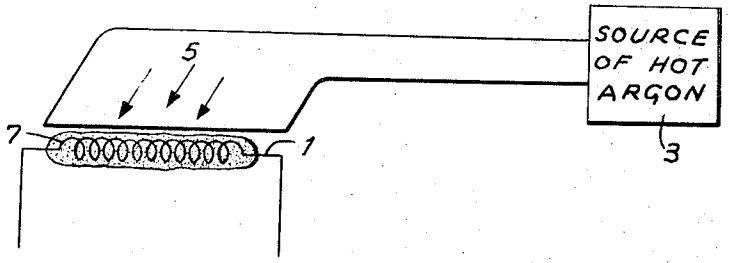


Fig. 2

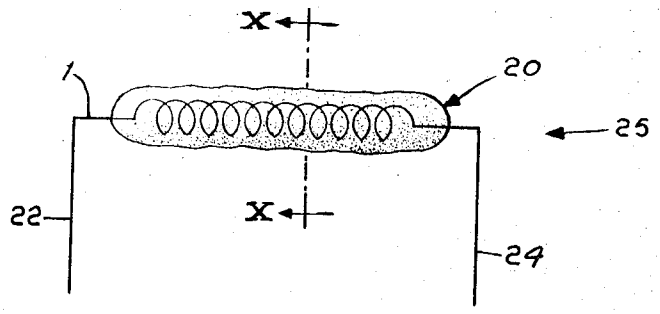


Fig. 3

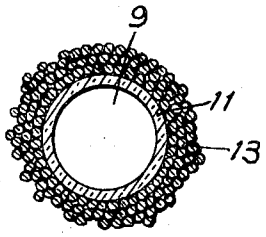
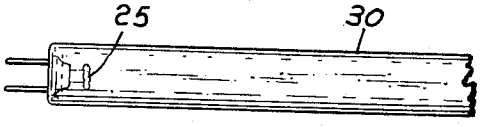


Fig. 4



COATED COIL EMISSIVE ELECTRODE

BACKGROUND OF THE INVENTION

This invention relates to coated coil emissive electrodes and to a method of making such electrodes, and more particularly to such electrodes having a bonding layer between the emissive material coating and the coil substrate of the electrode.

Emissive electrodes are utilized in fluorescent lamps to supply free electrons, thereby enabling current flow in the fluorescent tube and may, therefore, be called cathodes.

The cathodes normally comprise one or more of the alkaline earth metals and compounds thereof, as these materials have relatively low work functions and are therefore able to supply free electrons without requiring the expenditure of great amounts of energy. The provisions of said free electrons by the emissive alkaline earth material will of course consume the electrode material and when the material is depleted to the point where it can no longer supply sufficient electrons for lamp operation upon the application of standard fluorescent lamp voltages, the lamp will fail and will have to be discarded. It is therefore clear that it is advantageous to provide emissive electrodes incorporating the greatest amount of emissive material possible. The cathodes presently utilized in the art are normally one of two types, both of which are, for operation, heated to what is termed the "thermionic emission temperature," at which temperature they emit electrons. The first of these cathodes is heated to its emission temperature by a heated filament and is therefore termed, for the purposes of this specification, a "hot" cathode, while the other of said cathode types is heated to its emission temperature by ionic bombardment and is therefore termed, for the purposes of this specification, a "cold" cathode. One specie of cold cathode is here referred to as a "hybrid cathode" and is so termed because it has a structure similar to that of the hot cathode but is rendered electron emissive by ionic bombardment. The instant invention relates to cathodes of both the hot and hybrid type and a brief general discussion of both hot and hybrid cathodes is here provided as an aid to understanding the invention.

Hot cathodes of the type well known in the art, which are the type commonly utilized, for example, in 40-watt fluorescent lamps of the "rapid start" type, as well as lamps of the HO and VHO type, which are available in various wattage ratings, are normally made by painting, dipping or otherwise adhering a co-precipitated triple carbonate, usually comprising strontium carbonate, calcium carbonate, and barium carbonate to a coil of tungsten wire. This cathode is subsequently activated to improve its electron emissive properties by methods well known to those skilled in the art and is subsequently utilized as an emissive electrode in fluorescent lamps. This type of cathode is termed a hot cathode since it operates, in its thermionic emission mode, by the direct application of heat to the cathode body. Electrical energy, in the order of 3.6 volts, is provided by external circuitry associated with the lamp, more specifically the lamp ballast, to the low resistance coil of tungstem wire, said coil having a resistance of approximately 9 ohms. The voltage applied heats the tungsten coil and the heated coil directly heats the cathode material to a temperature sufficient to initiate

electron emission. The hot cathode, although widely utilized, has been found limited in that it has a life span in the range of 10,000–20,000 hours, this range depending primarily on lamp wattage rating. This limited life span is due to the fact that only a limited quantity of electron emissive alkaline earth material can be coated onto the aforementioned low resistance tungsten filament, and for the reasons discussed above, cathode life is directly related to the quantity of electron emissive material which is available for use. Within the limits of present technology, only 6 or 7 milligrams of the electron emissive material can be coated onto such a tungsten filament utilized in, for example, the above-mentioned "rapid start" family of fluorescent lamps. Although numerous attempts have been made to provide a greater quantity of emissive material on the electrode filament so as to extend lamp life, these attempts have always failed, since when additional emissive material has been painted, sprayed or otherwise adhered to the coiled filament it has flaked off, primarily for the following reasons. The emissive material which comprises, as stated above, alkaline earth carbonates, is adhered to the coil substrate by temporary adhesive binder such as cellulose nitrate. This binder is removed by thermal decomposition and the cathode is subsequently heated to a sufficiently high temperature to decompose the carbonates to their respective oxides, this being the aforementioned activation process. The only binding force remaining after the removal of the cellulose nitrate and the subsequent activation of the cathode is the result of a weak sintering of the oxide particles, which now comprise the cathode, during said activation process. As the mass of the emissive material coated onto said coil substrate is increased, the binding force becomes insufficient to hold the particles together and to the coil substrate when the lamp in which the cathode is utilized is subjected to normal shock and vibration during manufacture and use.

The hybrid cathode has, as stated above, a structure similar to that of the aforementioned hot cathode; that is, a quantity of emissive material, approximately 6 to 7 milligrams, is coated onto a coiled tungsten filament substrate, as discussed above, but the filament leads are not connected across a source of electrical energy as was the case with regard to the hot cathode and, therefore, the emissive material of the hybrid cathode is not raised to a temperature sufficient for thermionic emission in the same manner as that previously discussed with regard to a hot cathode. Rather, this hybrid cathode, which presently enjoys wide use in 8-foot instant-start fluorescent lamps, commonly referred to as a Slimline fluorescent lamp, is rendered electron emissive by ionic bombardment. These hybrid cathodes are ignited or driven into their thermionic emission mode by the provision of a relatively high ignition voltage, approximately 400 to 450 volts across the lamp electrodes. The ignition voltage ionizes the atmosphere in the fluorescent lamp, said atmosphere usually being a combination of an inert gas such as argon, at a pressure of approximately 2.5 to 3 millimeters and mercury vapor at a pressure of approximately 9 microns. The ions thus provided impinge upon the cathode material with sufficient force to heat the cathode, thereby causing it to become electron emissive. Since hybrid cathodes are constructed in much the same manner as the aforementioned hot cathodes, it is seen that the quan-

tity of emissive material which can be coated onto the hybrid cathodes is limited by the same factors as discussed above with respect to the hot cathodes.

The above-mentioned hot and hybrid cathodes presently known in the art are deficient for the previously stated reason; that is, they have limited life spans due to the limited quantities of emissive material which can be coated onto the refractory metal coil substrate. In addition, they are not wholly satisfactory due to the fact that they are constructed utilizing the aforementioned carbonate coatings, which, during the activation process, which is well known to those skilled in the art, release carbon dioxide gas which seriously impairs the visible light emitting efficiency of the calcium halophosphate phosphor customarily used in commercial fluorescent lamps.

SUMMARY OF THE INVENTION

The main object of this invention is to provide an improved coated coil emissive electrode having a substantially longer lifetime than presently known coated coil electrodes.

It is a further object of this invention to provide such an electrode embodying substantially more emissive material than coated coil electrodes presently known in the art.

It is yet another object of this invention to provide such an electrode which will not impair the light-emitting efficiency of the phosphor coating of a fluorescent lamp in which the electrode is utilized.

It is a still further object of this invention to provide a method of making such an electrode.

According to the present invention there is provided a coated coil emissive electrode comprising a metal substrate, a bonding layer of an emissive compound of an alkaline earth metal and said substrate metal, said bonding layer coating said substrate, and a layer of porous electron emissive material coating said bonding layer, said bonding layer bonding said emissive material to said substrate.

According to another aspect of this invention there is provided a method of making a coated coil emissive electrode comprising the steps of coating a metal substrate with an emissive material which evolves gas upon decomposition and heating said coated substrate to the decomposition temperature of said emissive material.

It is a feature of this invention that electrodes constructed according to the instant method are relatively air stable; that is, they may be exposed to reasonably dry air, by which is meant air containing less than 75 grains of water per pound of dry air, for at least 24 hours after activation and they are thus suitable for batch activation processes.

Further objects and features of this invention will become more apparent by reference to the following description taken in conjunction with the accompanying drawings, in which:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates a step in the construction of a coated coil emissive electrode according to the invention;

FIG. 2 illustrates a completed electrode constructed according to the invention;

FIG. 3 illustrates a cross-sectional view of the subject electrode taken along line *x—x* of FIG. 2; and

FIG. 4 illustrates the electrode of FIG. 2 positioned in a fluorescent lamp.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The subject electrode and the method of constructing said electrode will now be described.

Turning first to the method of preparation of the electrode, a coil of refractory metal, for example tungsten or tantalum, or of a transition element metal, for example, niobium, is formed for use as the cathode substrate, in the commonly known double or multiple wound configuration. The coil is then coated with an emissive compound of the type which releases gas upon decomposition such as, for example, the peroxides or nitrates of barium, calcium or strontium, or mixtures thereof. In the embodiment here discussed, approximately 50 grams of barium peroxide, having an average particle size of 2 to 3 microns, is suspended in a 100 cc mixture of an organic binder, here cellulose nitrate and a solvent for said binder, which may be one of the cellosolves, e.g., ethyl cellosolve or methyl cellosolve, and which in this example is butyl cellosolve. The resultant mixture of the barium peroxide cellulose nitrate and butyl cellosolve is thoroughly agitated, in for example, a high speed blender, to insure homogeneity, until it has a consistency somewhat similar to cream. The mixture is now coated onto all portions of the wound coil excepting the legs thereof by the usual dip-coating process in a manner well known in the art.

The butyl cellosolve solvent is now removed from the coating mixture by, for example, evaporation in air, or, by the application of heat if it is desired to speed the removal of the butyl cellosolve solvent. This results in an opaque plastic-like coating of barium peroxide and cellulose nitrate on the refractory metal coil, tungsten here having been utilized, which, as above stated, is completely covered except for the legs thereof.

It is here noted that although it is not necessary for the construction of the instant electrode, it has been found advantageous to add approximately 10% by weight of zirconium dioxide to the barium peroxide prior to the suspension of the mixture in the cellulose nitrate and butyl cellosolve to extend cathode life. Zirconium compounds are frequently added, in the fluorescent lamp industry, to barium compounds in order to retard the loss of barium from the finished cathode, thereby, it is believed, extending cathode life. However, it should also be noted that the addition of zirconium dioxide to the barium peroxide will tend to increase the work function of the finally formed fused electrode which is to be more fully described below.

Referring now to FIG. 1, there is illustrated the method utilized to accomplish the desired fusion of the emissive material coating to the refractory metal coil substrate 1. A source 3 of a hot inert gas, for example, argon, said argon gas being at a temperature of approximately 500° C, directs a flow of said gas in the direction of arrows 5 toward coil 1, which is coated with the aforementioned plastic-like coating 7 of barium peroxide and cellulose nitrate. When the temperature of the coil and plastic-like coating reaches a temperature of approximately 400° to 500° C, the barium peroxide begins to melt and flow over the tungsten coil substrate 1. As the temperature of the coil and coating increases to approximately 500°, the cellulose nitrate binder reacts exothermally, decomposing into gases, the major-

ity gas being nitric oxide, which are expunged from the mixture. The exothermal reaction of the cellulose nitrate raises the temperature of the coil and coating 7 to approximately 700° C which in turn causes the barium peroxide to react exothermally, causing the barium peroxide to decompose into barium oxide and to simultaneously release its excess oxygen causing a multiplicity of oxygen bubbles within the liquid. The coating mass begins to solidify during this process due to the fact that the barium oxide resulting from the above-mentioned decomposition has a higher melting point than the temperature sustained in the exothermic reaction. The result of the above process is a porous coating of barium oxide, the pores caused by the release of the oxygen bubbles, firmly bonded, by a bonding layer to be discussed below, to the tungsten substrate. It is here noted that the tungsten coil substrate is only superficially oxidized due to the short duration of exposure to the released oxygen and to the flushing away of said oxygen by the argon stream.

The intermediate bonding layer, mentioned above, has been found to comprise an emissive form of barium tungstate, Ba_3WO_6 which must be distinguished from the non-emissive form of barium tungstate, $BaWO_4$, which is commonly formed in coated coil cathodes known in the art through the reduction of barium oxide by the common tungsten coil. The emissive form of barium tungstate which forms said bonding layer between the porous barium oxide and the tungsten is of a ceramic like nature which is caused by the reaction between the tungsten substrate and the briefly produced liquid phase of the barium peroxide.

Referring now to FIG. **2**, there is shown a completed coated coil emissive electrode **25** constructed according to the invention wherein the coating of emissive material **20** adheres to the refractory metal substrate **1**. FIG. **2** illustrates the fact, as above stated, that the entire tungsten coil **1**, excepting legs **22** and **24** thereof, is coated with the fused emissive material. After the above-discussed reaction forming the electrode is ended and the completed electrode is cooled, it is available for standard processing, i.e., activation, and subsequent use in a fluorescent lamp of the type which normally utilizes either "hot" or "hybrid" cathodes.

Referring now to FIG. **3**, there is illustrated a cross-sectional view of the subject electrode taken along line *x—x* of FIG. **2** which illustrates a substrate **9** which is, of course, the aforementioned refractory metal tungsten, covered with a layer of a compound which is the result of the chemical reaction between the electrode substrate material and the coating material, here tungsten and barium peroxide, and which is therefore, in this instance Ba_3WO_6, the aforementioned emissive form of barium tungstate. The barium tungstate layer is in turn surrounded by a porous layer of barium oxide **13**.

Since the electron emitting process necessary for lamp operation depends on the presence of a few micrograms of barium at the electrode emitting surface, and due to the fact that said free barium is created at the substrate-emissive coating interface, i.e., the layer of emissive barium tungstate, it is therefore seen that the free barium must diffuse through openings and voids in the emissive coating of barium oxide in order to reach the coating surface. For this reason particular care has always been exercised in the past to avoid fusion of said emissive coating, fusion being accomplished by heating the coating to its melting point and allowing the coating to flow. In this instance, of course, it is seen that layer of emissive material **13** is porous and thus the barium atoms may easily travel to the surface of the electrode.

Emissive electrodes constructed according to the instant method have been found to have an ignition voltage, when utilized as a hot cathode, of approximately 175–180 volts which is comparable to, although slightly below, the 190–195 volts required for ignition of hot cathodes presently known in the art. When utilized as a hybrid cathode the instant electrode has been found to have an ignition voltage of approximately 400–450 volts which is also comparable to the ignition voltage of presently known hybrid cathodes.

It has been found that by using the above-described method large quantities of barium oxide can be deposited upon a refractory metal coil substrate and that the quantity so deposited is dependent only upon the number of coats of barium peroxide which are applied before the heating of the coil. After the construction of a number of such coils it has been found that the average coating weight of emissive material, i.e., barium oxide, is approximately 50 milligrams, or approximately *eight* times the coating quantity normally obtained with this type of electrode.

Referring now to FIG. **4**, there is shown a partial cross-section of a coated coil emissive electrode, according to the invention, mounted in a fluorescent lamp **30**. FIG. **4** illustrates the fact that the instant electrode is mounted in a standard phosphor coated fluorescent lamp envelope in precisely the same manner as emissive electrodes of the "hot" type previously known in the art, and it is clear that the subject electrode may be mounted in the same manner as presently known "hybrid" electrodes if legs **22** and **24**, illustrated in FIG. **2**, are conductively connected one to the other.

The subject electrodes are, as previously stated, processed in a manner similar to that utilized with regard to standard hot and hybrid cathodes; that is, by the application of heat. However, the activation of conventional electrodes involves dissociation of the carbonates utilized in coating the standard refractory metal coil, while the heat applied during processing in the case of the subject cathode is utilized to remove slight traces of residual water and carbon dioxide. The barium carbonate dissociation in conventional electrodes results in the evolution of large quantities of carbon dioxide gas and phosphors which are deposited upon the inner surface of the lamp wall present a large surface for the adsorption of this carbon dioxide gas. After a few hundred hours of lamp operation the carbon dioxide gas is photochemically dissociated into carbon and carbon monoxide due to the action of the ultraviolet radiation which is generated during lamp operation. The adsorption by the lamp phosphor of the carbon and carbon monoxide gas seriously reduces the ability of the phosphor to generate visible light and, therefore, the lumen output from the fluorescent lamp is substantially reduced. Since the subject emissive electrode does not undergo a carbonate dissociation process, very little carbon dioxide gas is evolved from the electrode and the luminosity of the lamp remains substantially constant relative to conventional lamps.

It is thus seen that there has been provided a coated coil emissive electrode, and a method for making such an electrode, which embodies substantially more emis-

sive material than coated coil electrodes presently known in the art and which, therefore, has a substantially longer life than presently known coated coil electrodes. Further, there has been provided an electrode which, due to the fact that its activation does not require carbonate dissociation, will not impair the light emitting efficiency of the phosphor coating of the fluorescent lamp in which the electrode is utilized.

It is here appropriate to note that cathodes constructed according to the instant method have been discovered to be relatively air stable subsequent to their activation; that is, they will remain activated for a period of at least 24 hours when maintained, after said activation, in reasonably dry air, by which is meant air containing less than 75 grains of water per pound of dry air. Thus, the cathode here described, while being greatly improved over the cathodes known in the prior art for the reasons previously discussed, additionally is suitable for batch processing, thus providing an additional valuable advantage.

While the principles of the invention have been described in connection with specific structure it is to be clearly understood that this description is made only by way of example and not as a limitation to the scope of my invention as set forth in the objects thereof and in the accompanying claims.

I claim:

1. A method of coating refractory metal cathodes for gas discharge lamps comprising:

a. preparing a suspension of at least one alkaline earth peroxide in a solution of cellulose nitrate binder and cellosolve solvent;

b. coating the suspension onto the surface of said refractory metal cathodes;

c. evaporating the cellosolve from the suspension coated on said cathodes to form a dried suspension thereof; and

d. heating said cathodes coated with the dried suspension of alkaline earth peroxide and cellulose nitrate to form an exothermal reaction between the alkaline earth peroxide and the cellulose nitrate in said dried suspension resulting in a fused and porous coating of air stable alkaline earth oxide on the surface of said cathodes.

2. The method according to claim **1** wherein the alkaline earth peroxide is selected from the group consisting of barium peroxide, calcium peroxide and strontium peroxide.

3. The method according to claim **1** wherein the alkaline earth peroxide is barium peroxide.

4. The method according to claim **3** including the step of adding zirconium dioxide to the barium peroxide prior to preparing the suspension.

5. The method according to claim **1** wherein said heating includes the step of flowing a heated inert gas over the dried suspension to cause said exothermal reaction and remove the gaseous byproducts therefrom.

6. A method of providing improved emissive coatings for long life gas discharge lamps comprising:

a. preparing a suspension of 50 g of barium peroxide powder in a 100 cc solution of cellulose nitrate binder and cellosolve solvent;

b. coating the suspension onto the surface of tungsten metal cathodes;

c. evaporating the cellosolve from the suspension coated on said cathodes to form a dried suspension thereof; and

d. heating said cathodes coated with the dried suspension of barium peroxide and cellulose nitrate by means of a heated stream of argon gas to a temperature range of 400°–500° C to form an exothermal reaction between the barium peroxide and the cellulose nitrate in said dried suspension resulting in a fused and porous coating of air stable barium oxide on the surface of said tungsten cathode.

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