Patented June 22, 1937 2,084,911

UNITED STATES PATENT OFFICE

2,084,911

GLOW LAMP ELECTRODE AND METHOD OF MANUFACTURE

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No Drawing. Application June 22, 1935
Serial No. 27,873

7 Claims. (Cl. 176—126)

The present invention relates to electric discharge devices and more particularly to electrodes for use therein. This invention pertains particularly to a process for the production, activation and operation of electrodes in luminous discharge tubes and includes the electrodes produced by such process.

One object of this invention is to produce electrodes which, when used in a glow lamp of the electric discharge type, will allow such lamp to be operated from the usual electric lighting circuits carrying potentials of the order of 90 to 220 volts, alternating or direct current.

Another object of the invention is to produce such electrodes without the employment of extensive chemical and/or mechanical cleaning processes to produce surfaces thereupon of a high degree of cleanliness or freedom from oxidation.

A further object is to produce electrodes of the character described which can be used to construct a glow lamp which latter will not require the employment of either high frequency heating furnaces or high intensity electrical discharges during its manufacture.

Another object is to produce a glow lamp which shall have a life of many thousand hours.

Yet another object of this invention is to produce electrodes which shall have a uniform glow or corona upon their surfaces when in operation. Another object is to practically completely prevent the disintegration of such electrodes during the life of the tube.

Another object is to produce electrodes whose surfaces shall be of a nature so that an emissive or activating coating such as hereinafter described, spread thereupon shall have no tendency to "creep" during the manufacture or operation of a glow lamp employing such electrodes.

Another object is to provide an electrode surface which can have applied thereto an activating agent without the need of any special binding material to cause such agent to adhere readily and uniformly to the surface.

Yet another object is to produce electrodes which will permit the exhaustion and activation of a glow lamp with less need for excessive precautions with regard to the complete removal of such gases as oxygen, nitrogen and so called occluded gases than hitherto found necessary.

A still further object is to produce an electrode whose surface will not require roughening in order to allow the ready adherence thereto of an activating or emissive coating.

This invention is applicable to electrodes of all shapes and sizes and electrodes produced according to this invention do not require any definite spacing from one another in a glow lamp, but will function over a wide range of interelectrode distances and also over a wide range of gas pressures.

By the term "glow lamp" as herein employed, I mean both the types where a cathode glow is produced and the types known as positive column glow or discharge tubes.

The prior art of constructing electrodes for gaseous glow lamps has universally employed a metal whose surfaces were carefully cleaned and which had all oxides or other compounds removed from such surfaces or else reduced to a metallic condition, before such electrodes were sealed into the glow lamp.

Such electrodes often necessitated the use of a high degree of heat after they had been sealed into a lamp, in order to properly clean their surfaces. Such intense heat was usually produced by the employment of a high frequency furnace within whose electromagnetic field the lamp was placed. As an alternative or ancillary method to the one just mentioned, the use of electrical discharges of high intensity, compared with those employed during normal operation of the lamp, produced between the electrodes themselves has also been common.

With my invention I have found that such heating procedures may be omitted and that such omission not only simplifies, cheapens and reduces the time required for the manufacture of such glow lamps, but also greatly increases the useful life of such lamps, due to the lessened rate of disintegration of the special surface of my electrode.

It also has been found that glow lamps manufactured by the usual methods show a tendency for the luminous area to spread over the entire electrode surface, even when it is desired that a portion of such surface remain non-luminous. This has been due to the creeping of the activating coating over parts not originally covered therewith.

In order to avoid this difficulty it has often been found necessary to employ special protective coatings which were spread over the portions of the electrode not covered by the emissive coating.

With this invention it has been found that the electrode itself has a surface which will retain the emissive coating substantially on the portions where it was applied and that there is no tendency for the coating to spread over other portions.

It has likewise been found that glow lamps of the ordinary type manufactured with electrodes

as previously known in the art have usually required very great precautions both during exhaust and before finally sealing off, in order that such "base" gases as nitrogen and oxygen be practically completely removed from the interior envelope surfaces of such tubes as well as from the electrodes and the gas content thereof.

With electrodes according to the present invention it has been found unnecessary to bring about such complete removal of these base gases. This I consider due to the stability of the electrode and the active coating when formed in accordance with my invention and also because with my electrodes the heat generated during the normal operation of the tube is not transmitted to the metallic plate in an amount sufficient to liberate detrimental gases. It is also possible, due to my treatment of the electrode and coating, to pass more current through the electrode and so to obtain greater brilliance without affecting the life detrimentally.

The electrodes of this invention may be employed in any form of glow lamp and may be supported therein in any desired manner and in any desired relationship to one another. Accordingly, since such glow lamps are well known in the art it has been thought unnecessary to describe the construction of any particular lamp, since this invention deals primarily with the production and activation of the electrodes per se, and not with any other features of glow lamp construction.

The following description of my electrodes and the process of their manufacture is illustrative and it is to be understood that the various steps thereof may be varied in detail without departing from the spirit of this invention.

As an electrode material I prefer to use a metal of the ferrous group, including iron, cobalt and nickel, although other metals which give stable oxides may be employed. I have found as an especially suitable material, iron of a high degree of purity such as Swedish iron or the material widely employed in electron discharge devices and known under the trade name of Svea metal.

The first step in my process is to remove substantially completely from the surface of the metal any grease or oils which may be present, as well as any foreign mechanical particles which may be adherent thereto. As a convenient cleansing agent for this step I have found clorosol or ether to be suitable, but other suitable cleansers may be used.

While I have found this an economically advantageous step, yet with my process this step may be omitted, since the next step of heating in the air will usually remove such impurities, provided that it is carried to a sufficient degree. The next step in my process is to mount the electrode upon some suitable support, so that it will not be necessary to touch the same with the fingers during subsequent handling. Such a support may conveniently but not necessarily be the one which is later to support the electrode in the glow tube. Furthermore it is possible to omit this mounting, provided that the electrode be thereafter kept away from excessive contact with the skin, which may deposit upon the surface of the electrode such materials as natural oils, sodium chloride or other foreign materials which may be undesirable.

The next step in my process is to heat the electrode in contact with air so as to form upon the surface thereof a coherent oxide film. It is to be understood that the temperature and length of time of such heating will necessarily vary with the metal employed. I have found that in the case of the comparatively pure forms of iron above mentioned, temperatures of the order of 500° C. or preferably higher will form such an oxide coating. The length of time necessary to form the coating will vary with the thickness of such coating required and also with the temperature.

Various methods of heating may be used such as either over a gas flame, in an oven or furnace heated by either gas or electricity or by bombarding or heating by induction in the presence of air. I have found that when using a flame or oven the best results are obtained when the electrode is first heated in such flame or oven, then quickly removed therefrom and allowed to cool with free exposure to air of room temperature.

I have found that with small electrodes having a surface of a few square centimeters and a thickness of a few millimeters or less, as commonly employed in small glow lamps, heating in air for from a few seconds to several minutes is usually sufficient, when an ordinary illuminating gas flame is employed, but my process is not confined to such time limits or to such a mode of heating.

It is also well known in the art that when alkali or alkaline earth metals were used as a surface layer on base metals or other metals such as iron, nickel, silver, etc., for low work function electrodes, considerable difficulties were experienced keeping the alkali and alkaline metals free from contamination by detrimental oxides and other materials, resulting in forming compounds or mixtures unfavorable for such electrodes.

Among such unfavorable and detrimental compounds or mixtures, I have found the red oxide of iron. Due to the ease with which these oxides are formed in the presence of air, oxygen and other certain gases and vapors, extreme care and precautions are necessary to produce devices containing electrodes of this type which will function properly.

I have found, however, that ferric oxides such as Fe_3O_4 or Fe_4O_5 are quite stable and form a surface which does not detrimentally affect the properties of alkali or alkaline earth metals, but results in a base for the alkaline metals, desirable for devices requiring alkaline coated electrodes.

I have also found that electrodes upon which there have been formed oxides of the Fe_3O_4 type coated with alkali metals require no special precautions to produce extremely satisfactory tubes or devices capable of operation at voltages as low as about 65 volts.

I have found also that in forming this higher oxide surface on electrodes, the permanent formation of the lower and detrimental oxide surface is prevented. Also in forming this higher oxide surface it follows that all surface films such as those of oil, grease and other detrimental materials are destroyed or decomposed, thus resulting in yielding a very desirable base for alkaline earth metal coated electrodes.

The oxide film which is formed on the surface has been found to consist principally of the magnetic oxide of iron Fe_3O_4, or Fe_4O_5, although there are usually present in small amounts other oxides of iron such as Fe_2O_3 so that the composition of this coating cannot be expressed in a specific formula but only by the general expression Fe_xO_x.

Electrodes made according to my invention may preferably be completely oxidized but only

a part of the surface thereof may be oxidized if so desired. The oxidization may be produced after the electrodes are formed of the desired shapes or patterns.

The electrode with its formed surface or coating, which will be referred to hereinafter as the base or first coating, is then allowed to cool, but before the next step of my process I prefer to have its temperature raised above the usual room temperature, if it has already completely cooled. The next step in my process is to apply a second or activating coating over the base or first coating.

Such a coating may readily be obtained by dipping the electrode in an aqueous solution containing dissolved salts of the azides of elements which possess electron emitting properties. Such elements include those of the alkali metal group and the alkali earth group.

While my process is not confined to any particular elements or mixtures of the same, I have found that a 20% solution of barium azide is suitable for this process. Furthermore I have found it advantageous also to have present in such solution a small amount, such as 1% or considerably less of sodium or potassium azide. I have also found that strontium azide may be substituted for part or all of the barium azide.

With my process there is no need to employ any binding material, since my oxide coating will retain upon its surface a sufficiently thick and uniform film of such aqueous solution as to preclude the necessity of any binding material.

In performing the step of applying the activating agent to the electrode I prefer to have both the electrode and the solution containing such agent at a temperature somewhat above room temperature, such as 40° C. or slightly higher.

The oxidized surface produced by my invention seems to be of a physical character which affords very ready adherence of such activating coatings and therefore no roughening of the surface, as previously practiced, is found necessary.

The solution may be applied to the electrodes either by being brushed or spread thereupon or else the electrodes themselves may be dipped into such solution. I have found that this somewhat elevated temperature seems greatly to facilitate the adherence of the activating material to the base coating, possibly by causing it to enter to a greater extent between the individual minute particles constituting such coating. This higher temperature also will speed up the drying of such activating coatings.

The next step in my process is to remove the water which has been used to transfer the activating material to the surface of my electrode. I have found that the best results are obtained when the electrode having upon its surface a film of the activating solution, is dried in air at a temperature not greatly in excess of 40° C. although it is possible to employ considerably higher temperatures, in order to hasten this drying step. It is important that the moisture be removed substantially completely in this step.

As the next step in my process I prefer to repeat the last two steps previously described, thus producing a thicker activating coating. While I have found one repetition of this step is usually sufficient to produce an electrode showing a good corona in a gas tube, yet it is possible to repeat these steps several times if so desired.

The next step of my invention is baking the thus coated electrode in an atmosphere of air at a temperature slightly below that at which the azides become volatile. The temperature preferred is about 150 degrees centigrade, although higher or slightly lower temperatures may be used. This process most probably oxidizes the surface of the azide particles. The thus oxidized surface of these particles serves to provide, when later decomposed in vacuum, a layer of active substance extremely stable and exceedingly efficient which does not sputter or spread during the entire life of the tube.

The electrode of my invention is now ready to be sealed into the lamp of which it forms a part and such lamp may have an envelope of course of any suitable form, shape and material as well known in the art. No especial precautions are required in mounting the electrode of my invention, other than to avoid touching it with the skin or contaminating it with foreign substances from other sources.

The device containing my electrodes may then be attached to a suitable exhaust pump and the pump operated while a heating oven is placed around the envelope of the tube. In the case of an ordinary glass envelope temperatures of 250 to 350° C. have been found satisfactory for such heating oven, but such temperatures may be varied if other materials are employed for the envelope.

The probable theory of these operations is here given but it is to be understood that such theory is merely explanatory and not limiting. The heat provided is of a temperature at which the oxide of the azide particles is not decomposed or destroyed but at which the remaining unchanged azide within the surface oxidized particles of azide liberates its nitrogen gas. The partly oxidized particles of azide are sufficiently stable, and are not affected by the otherwise detrimental occluded gases evolved from the surfaces of the walls of the envelope and other parts of the tube, and no special precautions are necessary so that the activation of the electrode surface and the evacuation of the device is completed within a few minutes after it is placed on the pump.

With the electrode of my invention I have found it unnecessary to effect a complete decomposition of the azide and I prefer either to allow some undecomposed nitride to remain or else to admit to the tube, while the electrode is still hot, a sufficient quantity of either nitrogen, oxygen, or air to secure upon the surface of the reduced metal a film either of the oxide or the nitride.

It will be noted at this point that by my employment of a base coating containing oxygen I have found it possible to use an active coating which is not composed entirely of a reduced metal but which may contain substantial amounts of compounds of such metal.

As previously mentioned I have found it unnecessary to carry the step of exhaustion to such a degree as previously has been necessary in the art, with the electrodes formerly used. On the contrary, I prefer to leave traces both of oxygen and nitrogen in the tube and have found such traces to be advantageous not only in establishing the desired corona effect but also in lengthening the useful life of the tube.

After my electrodes have been activated in accordance with the above description, the gas which is to produce the corona or glow effect is then introduced.

Preferred gas mixtures which can be used in

tubes employing my electrodes are neon, argon or helium, the gas in each case containing 1% of krypton or xenon, preferably the former. However any of these gases may be used singly or in suitable combination, although I have found the best proportion of krypton or xenon to be between 0.25% and 10% of the mixture.

These gas mixtures cooperate with my electrodes to produce a low work function device giving unique color effects of light and having long life and stable operating characteristics.

I have found it desirable but not essential that such gas be first admitted to a pressure of about 1 to 5 mm. of mercury and the regular operating voltage applied to the electrodes while the tube is still on the pump.

This causes the better activation of an electrode prepared according to my invention and seems to reduce the time necessary for seasoning after the tube is completed. Such application of voltage is only needed for a few moments and may be discontinued as soon as the uniform glow appears over the entire activated surface of the electrode. Additional gas may then be admitted to bring the pressure to any desired degree. I have found from 15 to 25 mm. a desirable pressure, although pressures ranging from 5 to 50 mm. or more may be employed.

If the pressure is toward the lower limit above stated the result is to produce a hazy or diffuse glow when the tube is in operation, whereas considerably higher pressures tend to confine the glow more closely to the electrode surface.

The tube may now be sealed off and seasoned under normal voltage and current until a uniform glow of the character described has been produced. While such seasoning period will vary greatly according to many different factors, I have found that usually from 2 to 24 hours is sufficient to season a tube using the electrode of my invention.

Electrodes produced in accordance with the oxidizing process above described may be employed without the use upon the surfaces thereof, of emissive coatings such as those of the alkaline type, provided that lamps constructed with such uncoated electrodes are supplied with voltages sufficiently high to secure the discharges desired, or provided that other means are provided to secure the emission necessary for their proper operation.

I claim:

1. A gas lamp electrode composed of iron having a coating of Fe_3O_4 thereupon and also having a second coating of an alkali metal in the reduced state, over said first coating.

2. A gas lamp electrode composed of iron having a coating of Fe_3O_4 thereupon and also having a second coating of barium over said first coating.

3. The method of manufacturing an electrode for gas glow lamps which includes forming said electrode from iron and oxidizing the surface thereof substantially to Fe_3O_4 and then forming a coating at least partly comprising a reduced element of the alkali or alkali earth group over said oxidized surface.

4. The process of treating an electrode to render it suitable for electrical discharge tubes which includes heating said electrode in contact with air so as to form thereupon a surface layer of oxide, coating said surface layer with an azide of an alkali earth metal and heating said azide so as partly to alter its composition.

5. The method of increasing the life of gaseous glow devices which consists of coating an electrode of said device with an oxide of the same material of which said electrode is constituted, applying a low work function coating over said oxide coating, incorporating said electrode in said glow device and activating said electrode, all while keeping said electrode at a temperature not materially in excess of 350° C., after said oxide coating has been applied thereunto.

6. In activating coatings for gas discharge tube electrodes, the method of preparing a coating which includes covering at least part of an electrode with a solution of an azide, drying said solution, heating the thus coated electrode to a temperature of about 150° C., whereby said azide coating is partly oxidized, incorporating said electrode in a tube and then heating said electrode to a degree sufficient to decompose the unoxidized azide upon said electrode.

7. The process for treating an electrode formed of a metal of the iron group to make it suitable for use in gaseous discharge tubes, which includes the steps of heating said electrode in a confined atmosphere to a temperature above its oxid forming point, exposing said electrode while still hot to an atmosphere of a temperature greatly below the oxid forming temperature, cooling said electrode to a temperature below the decomposition point of barium azide, coating said electrode with barium azide and at least partly decomposing said azide so as to yield metallic barium.

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