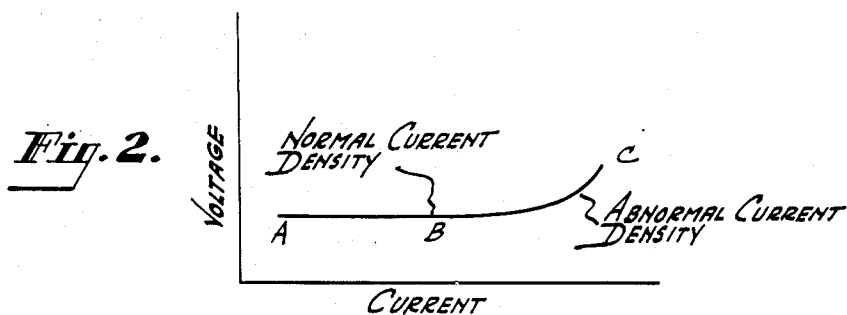
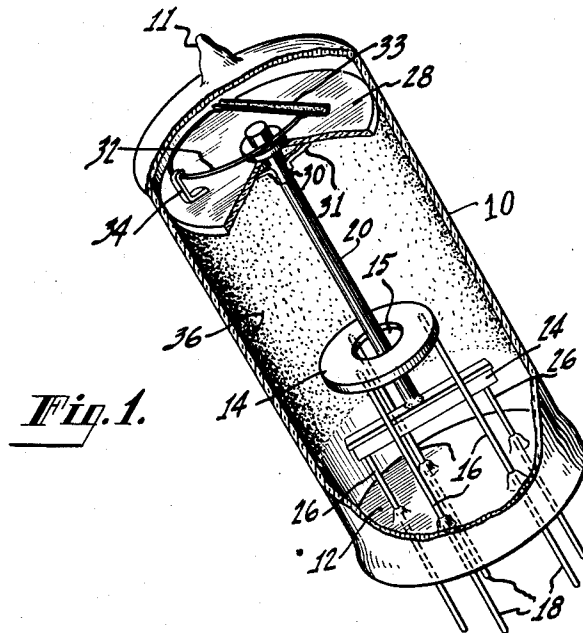


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VOLTAGE REFERENCE TUBE

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VOLTAGE REFERENCE TUBE

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1

My invention relates to a gaseous discharge device and more particularly to an improvement in a voltage reference tube.

Since the voltage drop across a cold cathode-glow discharge tube is substantially independent of the current through the tube over a wide range of current values, tubes of this type are used in voltage regulator circuits in applications where it is necessary to maintain a constant direct current output voltage across a load, independent of load currents and moderate line-voltage variations. Such a regulated power supply finds application with laboratory test equipment, as a substitute for batteries, or to provide a constant source of voltages for plate, screen or grid bias of vacuum tubes.

One of the most serious drawbacks to the use of known glow discharge tubes in direct current voltage regulator circuits for some applications, is the abrupt changes or jumps in the voltage of the tube in the order of tenths of volts. These jumps in voltage are observed to be a result of the "cathode glow" shifting from one section of the cathode area to another.

Another type of instability during the operation of certain kinds of tubes of the glow discharge type, takes the form of a slowly increasing voltage during the operational life of the tube. The voltage of such tubes has been known to increase an amount of 5 volts in 200 hours of tube operation. This voltage change requires constant adjustment whenever measurements are to be made. Such a voltage change has proved detrimental in some voltage regulator systems. This slow shift of tube voltage is due to a slowly changing cathode work function.

In one type of glow discharge tube as disclosed, the cathode electrode is coated with misch metal to provide a low work function for the electrode and relatively uniform tube operation. Such a tube is disclosed in my co-pending application Serial No. 748,270 filed May 15, 1947, which is now U. S. Patent No. 2,556,254 issued June 12, 1951. Tubes of this type sometimes have a certain disadvantage in that the misch metal is a non-uniform mixture of iron, cerium, and other rare earths. This non-uniformity of the misch metal surface provides a variation from tube to tube of operational characteristics. Thus, it is difficult to replace in service a tube of this type with another having identical operating characteristics. Also, during the life of a tube of this type, the misch metal coating on the cathode surface is gradually sputtered away due to the bombardment of the cathode surface by positive ions

2

during tube operation. Although it has been attempted to produce a synthetic misch metal for coating the cathode electrodes, such attempts have been unsuccessful due to complications involved, as well as the cost.

It is therefore an object of my invention to provide a glow discharge tube of improved operation.

It is also an object of my invention to provide an improved glow discharge tube in which the abrupt changes in tube voltage are eliminated.

It is also an object of my invention to provide a glow discharge tube having a constant voltage characteristic during the operational life of the tube.

It is a further object of my invention to provide a method for making a type of glow discharge tube resulting in tubes having close to identical characteristics.

The novel features which I believe to be characteristic of my invention are set forth with particularity in the appended claims, but the invention itself will be best understood by reference to the following description taken in connection with the accompanying drawing, in which:

Fig. 1 is an elevational sectional view of a gas discharge tube according to my invention.

Fig. 2 is a graph showing the relationship between changes in voltage and changes in current of my improved tube.

The tube of Figure 1 is a glow type discharge tube having an evacuated envelope 10. Within the envelope 10 there is enclosed a gaseous medium comprising principally a mixture of neon and argon. The envelope 10 has a tubular configuration in which the upper end is closed by sealing off at 11 after exhausting and filling with gas. The lower end of the tubular envelope is closed by having a glass button stem 12 sealed at its periphery to the tubular envelope 10. Sealed through the bottom of the glass stem base 12 are a plurality of metal base pins 13 which extend into the envelope and form electrical leads to the several electrodes enclosed therein. Supported from the stem base 12 of the tube is an annular cathode plate electrode 14 having a central opening 15. The cathode plate 14 is supported by metal rods 16 sealed through the glass stem 12 as extensions of respective base pins 13. Support rods 16 are fixed to the under side of the cathode plate. Also, supported from the button stem 12 is an anode rod electrode 20 extending coaxially within the tube envelope 10 and through the center of the cathode opening 15. The anode rod 20 is

3 spaced from the cathode plate 14. The lower end of the anode rod 20 is supported below the cathode plate 14 by a transverse metal support 24 which in turn is mounted on the button stem 12 by support rods 26. Rods 28 may also be extensions of respective base pins 18 sealed through the glass stem 12. The upper end of the anode rod 20 is maintained in alignment coaxially within the tube envelope 10 by a spacer mica 22. A rivet-sleeve 30 is welded to the top of the anode rod 20 and fastened by metal fasteners 31 to the mica spacer 22. The mica spacer 22 also supports a getter support wire 32 formed as a horse shoe loop. Between the ends of the wire loop 32 a channel member 33 is fixed. This channel member contains the getter material, which is flashed during manufacture as is well known in the art. Mounting the getter support loop 32 on the mica is a metal tab 34, mechanically locked through the mica.

The operation of the tube is such that, when an appropriate voltage drop is established across the cathode electrode 14 and the anode rod 20, a glow discharge will occur. By providing an appropriate metal for the emitting cathode surface of electrode 14 and an appropriate mixture of rare gases at a predetermined pressure within the tube envelope 10, it is possible to provide the desired tube characteristics. For example, it was desired to operate the tube of Figure 1 with an operating voltage of less than 100 volts across the tube and a current flow of around 1 milliamperere. To provide a cathode emitting surface having a sufficiently low work function as well as long life, pure molybdenum metal is used for the cathode electrode 14. A gas mixture of 99 percent neon and 1 percent argon is maintained at around a pressure of 37 millimeters of mercury within the tube. These conditions of gas mixture and pressure as well as the cathode material will provide approximately an 85 volt drop across the tube and a normal cathode current density of 1 milliamperere per square centimeter of cathode surface area.

The use of a pure molybdenum cathode electrode eliminates the difficulties which exist in using a misch metal coating described above. Previously, it has been extremely difficult to provide a satisfactory molybdenum cathode electrode in a glow discharge tube. The surface of the molybdenum metal is contaminated principally with certain oxides formed by exposure to air. It has been extremely difficult to remove these oxides from the molybdenum surface by any well known means. Even the heating of the molybdenum to temperatures close to the melting point of the metal fail to decompose all of the oxides on the molybdenum surface. A molybdenum cathode electrode cannot be successfully used in a glow discharge tube of the type described, relative to Figure 1, without the removal of all contamination from the electrode surface. The contaminating molybdenum oxides on the cathode provide a surface which is non-uniform in work function and result in an unstable tube. This is due to the fact that the molybdenum oxides on the electrode surface are decomposed and changed in composition during tube operation by positive ion bombardment. Thus, during the operation of such a tube, the continuous change of composition of the cathode surface results in a variable voltage drop across the tube and also provides a voltage shift during the life of the tube. Due to these inherent difficulties, the use of molybdenum has, up to

now, been avoided in gas discharge tubes of the type described.

My invention is directed to a method of ageing or processing a glow discharge tube, of the type described, having a molybdenum cathode electrode, in a manner which eliminates the inherent difficulties of a molybdenum cathode electrode. The tube, shown in Figure 1, is constructed along conventional lines as described above. After the envelope 10 is exhausted, the tube is filled with the mixture of neon and argon gas. The tube is sealed off at 11 and then the getter material 33 is flashed to absorb any deleterious gas within the tube. The tube is now submitted to an ageing process, which will remove all contamination from the molybdenum cathode surface 14. This ageing process provides a thorough cleaning of the cathode surface so that there results a surface of pure molybdenum metal. The ageing process is principally that in which a positive ion bombardment of the cathode surface 14 is established within the tube. The leads 18 of the cathode 14 and the anode rod 20 are connected to a source of rectified alternating current supply voltage of 220 volts root mean square. The current flow through the tube, which is a pulsating direct current, is limited by a series resistance consisting of a 10 watt 117 volt lamp. The rectified 220 volt root mean square alternating line voltage provides peak pulsating direct current line voltages of around 300 volts. The peak direct current voltages between the cathode 14 and anode 20 in the tube itself will be somewhat less than 300 volts, because of the potential drop across the limiting resistance. The application of this voltage to the tube initiates a gas discharge between the cathode 14 and the anode 20 such that the cathode electrode 14 is bombarded by positive gas ions. The pulsating direct current voltages across the tube produce a high energy ion bombardment of the cathode surface 14 without a high average current flow. In this manner, the cathode is not damaged by heat dissipation since the average current flow between the electrodes 14 and 20 only amounts to around 25 milliamperes. The tube is subjected to the ageing process for a period of 48 hours. During this ageing of the tube the cathode surface 14 is under continuous bombardment by the positive gas ions of the discharge. This ionic bombardment is sufficient to remove from the cathode surface 14, all of the contaminations which are on the surface. Also, quite a number of molecular layers of the surface are removed, such that there is left a clean, uniformly pure, molybdenum surface.

The ageing process described above need not be confined to the voltages used. However, those described have proved to be satisfactory. Furthermore, the ageing time is not critical since it has been found that any time between 48 to 60 hours will provide an optimum cathode surface. However, 48 hours has proved to be the best, shortest time for ageing of the tube under the conditions described. Increasing the ageing time to 60 hours provides a slightly better tube but not enough to warrant the additional time expended. It is well recognized that under different conditions of ageing, there will be also, corresponding times which provide the optimum results.

During the ageing of the tube as described above, the material sputtered off from the cathode surface 14 will be deposited upon the inner surface of the envelope 10 and form a layer thereon

as is shown in Figure 1 at 36. As the ageing process is continued, the resulting layer 36 will comprise essentially pure molybdenum on the exposed surface. In this manner, the contamination driven off of the cathode surface 14 will be first deposited upon the envelope wall 10 and then coated over with a molybdenum layer which effectively seals the contamination from being exposed to the discharge of the tube during tube operation. Also, the molybdenum layer 36 serves to effectively seal the surface of the glass envelope 10 to prevent the release of occluded gasses from the envelope wall during tube operation.

As described in my co-pending application, it has been found that the tube envelope 10 takes on a negative charge due to the affinity of the glass of the envelope for negative electrons produced during tube operation. This results in the inner surface of the envelope 10 becoming negatively charged and produces a positive gas ion bombardment of the envelope wall which will release occluded gasses from the envelope wall. Thus, the molybdenum film 36 effectively shields the glass wall from the ion bombardment, as well as forms a means for sealing the porous surface of the glass to prevent the escape of the occluded gasses during tube operation. Since the occluded gasses in the envelope wall 10 are prevented by the molybdenum film 36 from being released, there is no poisoning of the cathode surface 14 by these gasses. Previously, such poisoning of the cathode surface produced a discharge tube having an unstable characteristic evidenced by a slowly increasing voltage drop during the life of the tube. This increasing voltage drop necessitated a continual adjustment during the life of the tube. Glow discharge tubes of the type described and coated with a film 36 of molybdenum do not exhibit this gradual voltage shift. The sputtering of the molybdenum metal from the cathode surface is such that the film 36 will extend from the mica 28 to a point below the cathode disc 14. This portion of the inner surface of the envelope 10 is also that which is exposed to the discharge of the tube during operation and is thus the same portion of the envelope surface which would release any occluded gasses during tube operation.

Tubes, made in a manner similar to that described above, and similar to that of Figure 1, have a greater stability and very little variation in operating characteristics from tube to tube. Over a period of time, it has been found that tubes, made in this manner, operate at essentially the same voltage and at only a small variation over a short range. Furthermore, it has been found that tubes of this type and made according to the process described, show a very small voltage drift during the life of the tube. These improved operating characteristics of the tube are due to the pure molybdenum cathode surface which is less subject to shifts in the work function of the cathode surface due to contamination during tube operation. Furthermore, the highly cleaned molybdenum surface provides a uniformity of cathode surface which was impossible to produce in prior tubes.

The voltage drop across a gas discharge tube of the type described is a function of the kind of metal used. Molybdenum is a metal which gives a voltage drop below 100 volts. It is possible to provide tubes of the type described using other metals from the cathode electrode 14. However, the process described would be limited to metals which can be readily cleaned by ionic

bombardment and also to metals which have a work function providing the voltage drop desired. For example, zirconium metal may be substituted for the molybdenum in the glow discharge tube of Figure 1. Zirconium also will provide a low voltage drop in this tube. However, zirconium does not result in as stable a tube, since it is a more active metal and more susceptible to poisoning. Thus, for example, if there is deleterious hydrogen within the tube, it will poison the zirconium cathode and cause a drift in the voltage character of the tube during life. A molybdenum cathode is not as susceptible to hydrogen poisoning but is mainly affected by deleterious oxygen present in the tube. Cathodes may also be made of pure nickel, for example, which may be cleaned by positive ion bombardment. However, the use of a nickel cathode will provide a high voltage drop through the tube of approximately 150 volts.

Figure 2 discloses a well known relationship between the current and voltage of a glow discharge tube of the type described for Figure 1. If the current is maintained sufficiently low by means of an external resistance, the discharge covers only a portion of the cathode surface 14. An increase in the current through the tube causes the discharge to spread over a greater portion of the cathode surface so that the current discharge per unit area of the current density of the tube discharge as well as the voltage drop across the tube will remain constant during this period of current increase. This condition is shown in Figure 2 by the curved portion between the points A and B. This portion of the curve illustrates a condition of a constant normal current density. The curve between A and B is characteristic of glow discharge tubes and this range of operation is conventionally utilized in voltage regulator circuits, where it is necessary to maintain a constant direct current output voltage across a load. However, it is well known that one of the most serious difficulties in the use of glow discharge tubes operated within these limits is the rapid shifting or the abrupt small changes in voltage across the tube during tube operation. These jumps are not accumulative but merely are changes back and forth in the order of tenths of volts from the average tube voltage. Under some conditions, these abrupt changes of the tube voltage can be ignored. However, under other conditions, such rapid shifts in the voltage of the tube cannot be tolerated. It has been necessary then to design a glow discharge tube in which these rapid shifts in tube voltage are eliminated.

The principal cause for the rapid changes in tube voltages described above is the jumping of the glow discharge from one portion of the cathode surface to another unused portion of the surface, having a different work function. It is well known in tubes of this type that with the current density remaining constant, the total tube current may be increased until the glow discharge covers the entire surface of the cathode electrode. At this point the tube has reached the critical condition at which it is no longer possible to increase the current flow through the tube without a corresponding increase in the tube voltage and an increase in the current density of the cathode discharge. This critical point is represented by B in Figure 2 and the curve from B to C indicates the characteristic rise in tube voltage as the current flow through the tube is increased.

I have also designed the tube in Figure 1 to be operated on that portion of the curve between points B and C. The current density discharge from the cathode surface changes beyond the critical point B and in relation to a change in the tube voltage. This portion of the curve between B and C is known as that of abnormal current density. I have found, that when a glow discharge tube is operated at a point in the abnormal portion B—C of the curve, the rapid changes in tube voltage as described above are eliminated. When operating in this abnormal range the glow discharge or cathode emission takes place from the entire cathode surface 14 and there is no unused portion of the cathode surface to which the "cathode glow" or discharge may shift. To provide a cathode emission surface of constant area, I have coated the under surface of the cathode plate 14 with an aluminum coating. The higher work function aluminum coating prevents the discharge glow from spreading to the under surface and causing the above described small variations in the tube voltage.

In operating a tube similar to that of Figure 1, it may be connected in series with a resistance between the terminals of a source of regulated direct current voltage. The resistance may be adjusted to a value such that the current flow through the gas tube may be large enough to provide a cathode glow discharge over all of the upper surface area of the cathode electrode 14 and such that the cathode discharge has an abnormal current density. Under these conditions, the tube will be operating in the current density range represented by curve B—C of Figure 2.

As mentioned above, the work function of molybdenum is such that the voltage drop across the tube is around 85 volts. The normal current density of a molybdenum electrode at this voltage will be approximately 1 milliamperes per cm. Since it is desired that the total current flow through the tube of Figure 1 shall be approximately 1 milliamperes, the cathode surface 14 is designed to have an approximate area of 0.8 cm. This cathode surface area will result in the desired tube current of 1 milliamperes when the tube is operated within the abnormal current density range.

Tubes, which have been constructed according to the above described manner, have given excellent results. These tubes after being properly processed and aged have been operated for test periods greater than 100 hours. By operating these tubes entirely within the abnormal current density range during these test periods, I have observed no abrupt changes in voltage greater than 0.05 volt. In operation, tubes of this type have proved of great value in voltage regulator circuits and for voltage reference applications. In such applications, a constant current flow, which can vary only to the order of microamperes, is maintained through the tube by a control circuit. When the tube is being operated within the abnormal current density range, such changes in the current in the order of microamperes will produce shifts in tube voltage in the order of millivolts and under extreme conditions these shifts in tube voltage may reach only 0.02 volt.

The glow discharge tube described above which is designed according to my invention has eliminated two sources of trouble during tube operation, by solving the problem of rapid voltage shifts and also the problem of gradual tube voltage change. I have a gas discharge tube which has greater application than the conventional

glow discharge tube. This improved tube may be depended upon to maintain a more constant voltage in applications where shifts of tube voltage in the order of tenths of volts have proved detrimental. Also, this tube which maintains a more constant voltage drop has found much valuable use as a voltage reference source in equipment where voltage changes found in conventional tubes prove detrimental.

While certain specific embodiments have been illustrated and described, it will be understood that various changes and modifications may be made therein without departing from the spirit and scope of the invention.

What I claim as new is:

1. A glow discharge device comprising an envelope having a tubular portion, a gaseous medium within said envelope, a molybdenum plate forming a cathode electrode coaxially mounted within said tubular envelope portion, said cathode plate having an aperture at the center thereof, an anode electrode rod within said tubular envelope portion, said anode rod coaxially extending through the aperture of said cathode plate and spaced therefrom, said cathode electrode being of pure uncontaminated molybdenum to provide a constant work function of said cathode electrode, an aluminum coating on the other side of said cathode plate to inhibit a discharge between said other side of the cathode plate and said anode electrode, and a pure molybdenum coating on the inside surface of said tubular envelope portion in the region of said discharge.

2. The method of processing a glow discharge tube having an anode electrode and a metallic cathode electrode mounted within an envelope, said method comprising the steps of, filling said envelope with a neutral gas, connecting said anode and cathode electrodes in series with a limiting resistance and a source of pulsating direct current voltage having peak voltages of around 300 volts to establish positive ion bombardment of said cathode electrode, continuing said positive ion bombardment until metal is removed from said cathode and sputtered onto said tube walls.

3. The method of processing a glow discharge tube having an anode electrode and a pure metallic cathode electrode mounted within an envelope, said method comprising the steps of, filling said envelope with a neutral gas, connecting said anode and cathode electrodes in series with a limiting resistance and a source of pulsating direct current voltage to provide high-energy positive ion bombardment of the cathode surface, said voltage consisting of short voltage pulses of around 300 volts, continuing said positive ion bombardment until the contaminated surface layers of the cathode electrode are removed.

4. The method of processing a glow discharge device having an anode electrode and a pure molybdenum cathode electrode mounted within a gas filled envelope, said method comprising the steps of, connecting said anode and cathode electrodes in series with a limiting resistance and a source of pulsating direct current voltage electrodes to provide high energy positive ion bombardment of the cathode surface, said voltage consisting of short voltage pulses of around 300 volts, continuing said positive ion bombardment until the contaminated surface layers of the cathode electrode are removed.

5. The method of processing a glow discharge device having an anode electrode and a pure molybdenum electrode mounted within a gas

filled envelope, said method comprising the steps of, connecting said anode and cathode electrodes in series with a limiting resistance and a source of pulsating direct current voltage to provide high energy positive ion bombardment of the cathode surface, said voltage consisting of short voltage pulses of around 300 volts, continuing said positive ion bombardment until the contaminated surface layers of the cathode electrode are removed and a molybdenum film is sputtered from the cathode onto the adjacent envelope wall.

6. The method according to claim 5, wherein the average current flow between said electrodes during said positive ion bombardment is around 25 milliamperes.

7. The method according to claim 6, wherein said positive ion bombardment is continued for about 48 hours.

8. The method according to claim 5, wherein said limiting resistance is a 10 watt 117 volt lamp.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,128,817	Pickard -----	Feb. 16, 1915
1,680,367	Demarest -----	Aug. 14, 1928
2,017,278	Geffcken -----	Oct. 15, 1935
2,291,864	Bennett -----	Aug. 4, 1942
2,403,745	Norton -----	July 9, 1946
2,467,953	Bancroft et al. -----	Apr. 19, 1949

OTHER REFERENCES

"The Normal Cathode Fall of Molybdenum and Zirconium in the Rare Gases" by Jurriaance et al., Philips' Research Reports, volume 1, No. 3, April 1946, pages 225-238.