Aug. 19, 1952 G. H. ROCKWOOD, JR., ET AL 2,607,901

ELECTRONIC DISCHARGE DEVICE

Filed Dec. 31, 1946

FIG. 1

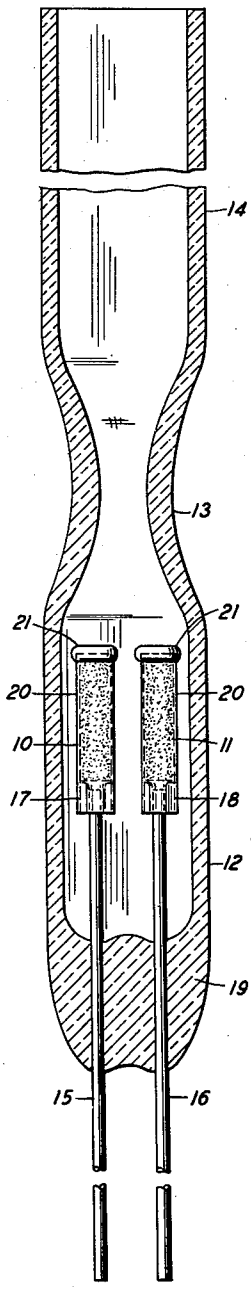


FIG. 3

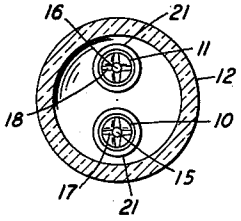


FIG. 4

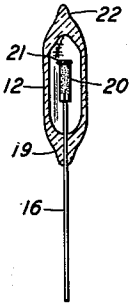


FIG. 5

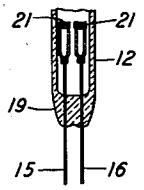


FIG. 2

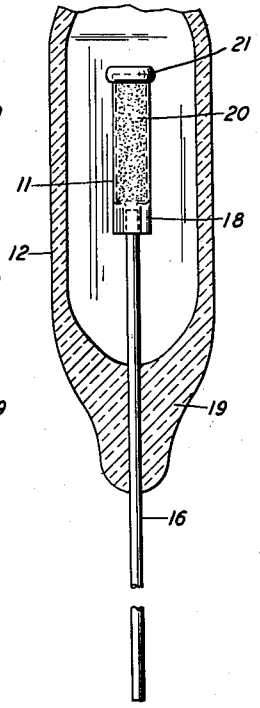
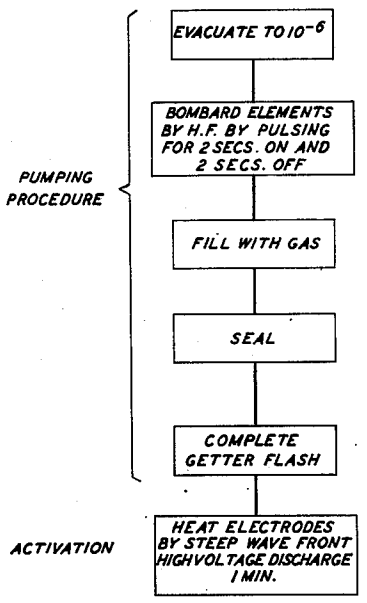


FIG. 6



INVENTORS: G. H. ROCKWOOD, JR.
R. L. VANCE

BY A. J. Guenther

ATTORNEY

Patented Aug. 19, 1952 2,607,901

UNITED STATES PATENT OFFICE

2,607,901

ELECTRONIC DISCHARGE DEVICE

George H. Rockwood, Jr., Summit, and Robert L. Vance, Westfield, N. J., assignors to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

Application December 31, 1946, Serial No. 719,562

5 Claims. (Cl. 313—185)

1

This invention relates to electronic discharge devices and more particularly to such devices of the cathode glow type for relay, regulator and control services in electronic switching systems.

The principal object of the invention is to maintain uniform tolerance between cooperative discharge electrodes in a sealed vessel of minimum proportions.

Another object of the invention is to facilitate the clean-up of deleterious gases in the device.

A further object of the invention is to avoid fracture of the seal of the vessel during the manufacturing processes of the device.

Still another object of the invention is to fabricate the electrode assembly in the device so that the breakdown gap therebetween will not vary over a long life and will withstand high impact shock of a few hundred times gravity.

A further object of the invention is to insure constant space relation between the electrodes by an assembly having a high resonant frequency to prevent deleterious vibration.

These objects are attained, in accordance with features of this invention, by providing a compact glow discharge device of extremely small size in which a pair of parallel tubular electrodes are sealed in a small tube of minimum dimension to insure constant and accurate parallelism between the electrodes and freedom from variation due to shock or vibration either in transit or use. This is accomplished by locating the seal of the electrode conductors as close as possible to the electrodes so that the electrodes resist shock impact transverse to the axis of the vessel. Therefore, the initial space relation between the electrodes which determines the breakdown voltage of the discharge path will be maintained constant throughout the operating life of the device.

A feature of the construction relates to the localization of the getter substance in the device for subsequent generation of a gas absorbing film in the final pumping processing during manufacture. The material is applied to the ends of the electrodes in annular form so that induction heating will flash the highly refractory mixture after the conditioning of the active emissive coating on the electrodes. The residual ring masses remaining on the electrodes after the flashing operation form glow discharge barriers and aid in preventing the spreading of the glow to the inner surfaces of the tubular electrodes.

A further feature of the invention relates to heat treatment of the electrodes in converting the externally applied coating to the active state without detrimentally affecting the hermetic joint of the electrode conductors sealed in the glass vessel. This is accomplished by evacuating the vessel and heating the electrodes intermittently for short periods so that heat conduction to the glass seal is minimized and the original carbonates

2

coating on the electrodes is broken down to the oxides. The vessel is filled with a gaseous medium, and the getter flashed to terminate the pumping procedure. The vessel is then sealed off after which the oxide coating is activated by a high voltage arc discharge to complete the manufacturing process.

The heating procedure during the breakdown step is controlled by uniform pulsing of the heating source for a predetermined duration so that the required conversion of the carbonates is accomplished without materially affecting the highly refractory getter substance on the ends of the electrodes and also without conveying heat energy by conduction to the conductors sealed in the glass. This method avoids premature flashing of the getter material and prevents cracking of the seal of the conductors due to the close proximity of the electrodes to the seal.

These and other features and advantages of the invention will be more clearly set forth in the following detailed description when considered with reference to the accompanying drawings in which:

Fig. 1 is an enlarged view in elevation of a device illustrative of this invention with the vessel shown in cross-section to illustrate the configuration of the electrodes and their close relation to the glass walls of the device.

Fig. 2 is a side view in elevation of the device of Fig. 1.

Fig. 3 is a plan view of the device of Fig. 2 on the same scale.

Fig. 4 illustrates the actual size of the device to clearly show the minimum tolerances of the dimensions of the vessel with respect to the electrodes and their location therein.

Fig. 5 is a partial view with the vessel broken away to show the electrodes and one electrode shown in section to indicate the end area covered by the getter substance; and

Fig. 6 is a block diagram of a pumping and activation procedure employed in the manufacture of a device illustrative of this invention.

Referring to the drawing and particularly to Figs. 1 to 3, inclusive, the device illustrated is a miniature glow discharge diode tube of minute dimensions to fit into confined space in switching equipment, although the tube is shown to an enlarged scale in these figures to more clearly present the features of the invention. In order to meet the dimensional tolerances of the tube and the operating characteristics with respect to breakdown discharge and sustaining voltages, and to insure a relatively long life in switching service, certain difficulties were encountered in the manufacturing technique of assembly and processing of the device which required solution. Also, certain optimum results had to be realized so that efficient functional operation would be assured within the

limits of size, ruggedness and high quality of the product, to achieve a suitable assembly capable of reliable operation over a long service life.

The strict dimensional requirements naturally restrict the size of the electrodes and since the electrodes must be hermetically sealed in the enclosing vessel to insure stable operation and these electrodes require involved thermal treatments in order to reduce the initial and sustaining glow discharge characteristics of operation, it is evident that material innovations in usual practices are necessary in order to meet the final requirements of the device in service. The correlation of the structure and techniques of manufacture have produced a device which overcomes the difficulties and the inherent restrictive factors imposed by the limits of space and magnitude encountered in the assembly.

One specific device in its final form has a length of 1¼ inches and a diameter of $\frac{5}{16}$ inch so that the electrodes, if the device is to be of the non-polarized type, must be of small size but of sufficient area to perform the functional characteristics of a glow discharge relay. To insure stability of operation and provide an active surface of constant breakdown potentiality in the discharge gap between the electrodes, it was found that electrodes of tubular form met the requirements in a most satisfactory manner and provided sufficient mechanical strength and low mass to eliminate stresses in the assembly. Accordingly, the electrodes comprise a pair of thin tubular nickel sleeves **10** and **11** which are mounted in parallel relation in a section of glass tubing having an internal diameter of .235 inch and an external diameter of .320 inch. The tubing forms a cylindrical container or vessel **12** which is provided with a constriction **13** near one end joined to a tubulation **14**. The pair of electrodes are formed of .005 inch wall nickel sleeves having a length of $\frac{21}{64}$ inch and a diameter of .0696 inch. The electrodes are mounted in parallel relation with a space or discharge gap of the order of 0.060 inch between the linear surfaces and the electrodes are sealed in the opposite end of the glass tubing by accurate alignment of a pair of conductors **15** and **16** which are attached to the electrodes respectively by pinching and welding the ends **17** and **18** around the conductors, as shown clearly in Fig. 3.

The accurate parallelism of the electrodes is assured by a sealing method which permits the plastic glass of the seal to collapse around the conductors without mechanical strains being imposed on the conductors which might alter their space relation in the completed seal. This is accomplished by anchoring the mounted electrodes in a holder or fixture in parallel relation to insure the required gap spacing of .060 inch. The glass tubing is held in a correlative fixture and surrounds the electrodes such that the glass may be converted to a plastic state in the desired relationship to the electrodes and conductors. The plastic glass collapses against the wires and flows into a mass or stem **19** which hermetically seals the conductors as the glass solidifies into the lobar shape as shown in Fig. 1. The strain-free seal secured by this method insures positive location of the conductors and electrodes in definite parallel space relation within the vessel **12** and also accurately spaces the electrodes **10** and **11** relatively in close proximity to the inner surface of the seal so that the limits of the unsupported length of the conductors **15** and **16** between the seal and the electrodes may be held to a small dimension and thereby aid in reducing the over-all length of the device. In a typical example, the distance between the electrodes and stem is less than the length of the electrodes, i. e., ¼ inch. The constriction **13** is provided to facilitate the final sealing of the device after processing and the tubulation **14** forms a connection to a suitable pumping and gas-charging system to complete the assembly of the device.

The parallel tubular electrodes **10** and **11** are coated exteriorly with electron emissive material **20**, to reduce the breakdown potential therebetween and to lower the work function of the bare metal electrodes across the discharge gap. This coating is preferably one or more alkaline earth compounds, for example, barium and strontium carbonates, which are easily decomposable to the active state in the final processing of the device, although other compounds and other types of emissive substances may be substituted for the active coating on the electrodes. The mixture of carbonates is combined with a carrier fluid or binder material, such as nitrocellulose and amyl acetate, and sprayed or painted on the cylindrical surface of the electrodes to form a uniform layer, approximately .77 milligram per square centimeter of active surface.

After the emissive coating is applied to the electrodes, a gas absorbing or getter material is affixed to the electodes to be vaporzed in the final pumping process of the device. Since the area within the vessel is limited, in accordance with a feature of this invention, the getter substance is introduced as an integral component of the electrodes and is flashed sequentially and selectively after the heat treatment of the electrodes in the device. This is accomplished by applying the getter substance in the form of a superimposed ring, layer, or bead **21** on the open or inner ends of the electrodes. A convenient method of application is to dip the ends of the electrodes in a viscous mixture of the getter composition suspended in a binder or carrier fluid which forms an agglutinous substance of the proper consistency to readily adhere to the ends of the metal electrodes. The ring or annulus **21** is superimposed over a limited area of the active coating on the electrodes and by the dipping process forms a thin annular bead around the cylindrical edge of the electrode, as shown in Fig. 5.

The getter composition has a high thermal flash point so that it is not materially affected during the heating cycles of the emissive coating on the exterior of the electrodes and, therefore, the activation of the getter substance may be selectively controlled in order to prevent substantial premature flashing thereof during the prior heating periods of the electrodes. The terminating bead **21** on the electrodes also serves an additional function during operation of the device, by preventing the spreading of the glow discharge to the inner surfaces of the electrodes, which might cause erratic behavior of the breakdown discharge in the operation of the device. After the getter is flashed to fix deleterious gases in the discharge space of the vessel, the spent residue of the rings **21** remains as a highly refractory insulating oxide which forms a stop or barrier at the open ends of the electrodes so that the glow does not creep along the inner surfaces of the electrodes.

In order to meet the stringent temperature conditions in the processing of the electrodes and in view of the fact that the getter is an integral component of the electrodes, the getter composition is formed of highly refractory ma-

terials having a flash point of 1025 to 1050° C. so that it will not be substantially affected by prior heating of the active coating on the electrodes. The getter composition is formed of barium beryllate 80 per cent and free metallic titanium 20 per cent, these ingredients being in fine particle or powder form. The mixture is suspended in a binder material of nitrocellulose and amyl acetate to make a viscous paste of creamy consistency so that a bead is readily formed on the ends of the electrodes when the electrodes are dipped into the mixture. In preparing the getter composition, the beryllate compound is formed initially by mixing barium carbonate and beryllium oxide in proportions of approximately 1 to 3 and heating to sintering temperature in a non-oxidizing atmosphere, such as hydrogen. The resultant beryllate compound is ground to a fine powder and mixed in the above-mentioned proportions with the free metallic titanium.

The tubulation 14 is sealed to a high vacuum pumping station and the glass vessel 12 is baked in an enclosing oven at a temperature of 350° to 475° C. to remove water vapor from the glass walls and release moisture from the electrodes and conductors within the bulb. The vessel is then evacuated to a low pressure of the order of 1×10^{-6} millimeters of mercury and while the vessel is still connected to the pumping system the preliminary high temperature heat treatment of the electrodes, in accordance with a feature of this invention, is performed to condition the low work function coating of the electrodes.

In order to completely convert the alkaline earth carbonates to the oxide state and enhance the low work function properties of the coating or film on the exterior of the electrodes, it is necessary to decompose or break down the carbonates to the oxides at a high temperature of the order of 1000° C. which is relatively close to the vaporization point of the thin nickel electrodes in the vessel. Furthermore, a prolonged heat treatment at the above temperature would not only result in considerable evaporation of the electrodes but the conduction of heat along the conductors 15 and 16 would set up serious strains in the glass seal 19 and generally result in cracks or fractures at the joint which would destroy the utility of the device in service.

In accordance with a feature of this invention, the breakdown process is performed by heating the electrodes inductively by high frequency current in intermittent flashes of transient periodic duration and cooling for like periods until the complete emissive coating is converted. This is accomplished by a pulsing procedure in which a high frequency coil surrounds the vessel in the vicinity of the active coating 20, preferably between the lower edge of the getter rings 21 on the top of the electrodes and the pinch on the bottom of the electrodes. The coil generates a high current heating effect by inductive interaction with the tubular electrodes to raise the temperature, almost instantaneously, to approximately between 1000 to 1025° C. The heating is applied intermittently by pulsing the current in uniform periodic steps of 1 to 2 seconds duration followed by a like period with the current off, to successively interrupt or segregate the heating cycle into short pulses of heating and cooling, generally 5 to 7 times, for the heating step so that the coating is completely decomposed to oxides. The pulsing periods, for example two seconds, are measured from the time of application of voltage to the coil and not from the instant when the electrodes attain the required temperature. During the heating period, the electrodes attain a temperature of approximately 1000 to 1025° C. for the short interval of heating so that the carbonates are decomposed to oxides by bombardment in intermittent flashes of heating energy. The current is disconnected for a similar period, to permit the electrodes to dissipate the heat energy mainly by radiation to the glass walls of the vessel and the heating is repeated in successive steps of current on and off for definite time intervals until the carbonates are completely broken down to the oxides matrix composition in the coating. The timing of the pulse periods may be performed manually by switching associated with the high frequency current source or it may be accomplished automatically by some suitable trigger timing circuit included in the current supply system.

While the electrodes attain a high temperature during the intermittent heating routine, the intervals are so short that the heat generated in the electrodes is not materially conveyed along the conductors by conduction but rather is expended as radiation heat energy to the surrounding space in the vessel and dissipated through the walls thereof. In this manner the seals are protected against fracture by prolonged heating which would detrimentally affect the glass hermetic joint.

When the emissive coating 20 is completely converted, the vessel is filled with an inert gas at a low pressure to form the ionizable medium in the discharge device. This gas may be argon, for example, and the vessel is filled to a pressure of 15 millimeters of mercury although this pressure may be varied within wide limits depending on the characteristics desired in the device. After the gas injection is completed, the tube is sealed off at the constriction 13 by fusion of the glass to form a sealing tip 22.

After the electrode coating is broken down to oxides the gaseous filling in the vessel is contaminated by deleterious gases evolved during the conversion of the emissive coating. These gases may be cleaned up or rendered impotent by the vaporization of the getter substance on the ends of the electrodes. This is accomplished by mounting a high frequency coil of a single turn around the vessel in line with the beads 21 on the ends of the electrodes and heating the annular beads 21 to the reaction temperature of approximately 1025° C. The beads readily attain the above temperature through the induction heating of the annular ends of the electrodes so that the getter rings are quickly heated to the temperature at which the titanium will react with the beryllate so that the barium is liberated and vaporized. The barium absorbs the deleterious gases in the vessel and when condensed on the interior wall of the vessel fixes the gases so that the inert gas filling is purified. Thus the barium will react with the impurities in the argon or other gas, which impurities may include nitrogen, carbon dioxide and particularly oxygen, both when the barium is a vapor and after it has condensed on the walls of the vessel.

After the getter rings 21 are flashed, the residue material is substantially beryllium oxide which is a highly refractory insulating substance. The reaction of the barium beryllate which is a complex with the metallic titanium yields the metallic barium which vaporizes, and a complex including titanium oxide and beryllium oxide which is a refractory material. The insulating rings, therefore, aid in forming a stop or barrier to prevent the glow discharge on the exterior surface of the

electrodes from spreading to the inner surfaces thereby stabilizing the discharge characteristics of the device in service.

The above steps complete the pumping procedure but further processing is required to condition the device for operating service. This comprises an activation process to prepare the electrode coating in the active state and produce the low work function properties of the coating on the electrodes.

A high voltage high frequency current of 4000 volts 30 megacycles source is applied, for a period of 1 to 2 minutes, to the conductors in series across the gaseous discharge gap within the vessel. The current source produces a high frequency steep wave front discharge between the electrodes which generates high frequency arcs between the scintillation points of the coating matrix and the arcing current produces high temperature at these minute points to reduce some oxide particles to free barium metal which is adsorbed on the surface and promotes high electron emission during the operation of the device. While the temperature of the scintillation points of the coating is extremely high, being of the order of 1000° C., the base metal of the electrode is not materially above a temperature of 500° C. during this activation step so that the electrode metal is relatively cool in comparison to the intensely heated coating. Therefore, practically no deleterious heat conduction obtains in the conductors to endanger the seal 19 and the highly refractory insulating coating 21 is substantially inert during this heating stage so that no further reaction occurs.

The construction of the device provides an assembly in which maintenance of gap spacing is held constant due to the low mass of the electrodes and the high resonant characteristic of their supports since they are close to the rigid seal 19 of the vessel. This produces a device having uniform electrical characteristics with regard to breakdown and sustaining potentials. The assembly is not easily affected by shock or vibration since the device can withstand an impact of a few hundred times gravity without adversely affecting the electrode spacing or the seal of the conductors in the stem. These attributes together with the processing treatments of the electrodes and the glow inhibiting barrier on the open ends of the electrodes materially enhance the functional operation of the device and increase the service life over a long period.

While the invention has been disclosed in connection with a specific example of a miniature type of device of particular construction, it is, of course, understood that the various aspects of the invention may be utilized in other types and constructions of discharge devices without departing from the scope and spirit of the invention as defined in the appended claims.

What is claimed is:

1. A glow discharge device comprising a vessel containing an ionizable gas at low pressure, a pair of parallel tubular electrodes mounted therein having an electron emissive coating thereon, and a getter composition on the open end of each electrode consisting of 80 per cent barium beryllate and 20 per cent titanium in a binder.

2. The method of processing glow discharge devices which comprises sealing a pair of tubular electrodes in an enclosing vessel of small diameter and length, said vessel being of a vitreous material said electrodes having an alkaline earth carbonates coating on the external surface and a composition coating on the open end thereof, said coating comprising barium berylliate and titanium evacuating said vessel, heating the electrodes periodically in short pulses to break down the carbonates coating to oxides, filling said vessel with an inert gas at low pressure, sealing said vessel, flashing said composition coating, and activating said oxides coating by high voltage glow discharge current.

3. The method of processing glow discharge devices which comprises sealing a pair of tubular electrodes in an enclosing glass vessel of small diameter and length, said electrodes having an alkaline earth carbonates coating on the external surface and a composition coating on the open end thereof, said coating comprising 80 per cent barium berylliate and 20 per cent free metallic titanium evacuating said vessel, heating said carbonates coating by high frequency pulsing current for approximately five repetitions of uniform duration, sealing said vessel, subsequently flashing said composition coating, and heating said electrodes to activate the converted coating.

4. The method of processing glow discharge devices which comprises sealing a pair of parallel tubular electrodes of predetermined length in one end of a tubular glass vessel, the distance between the electrodes and sealing point being of the order of the length of the electrodes, said electrodes having an alkaline earth carbonates coating on the external surfaces and a composition on the open ends thereof, said composition comprising barium berylliate and titanium, evacuating said vessel, heating said electrodes inductively in intermittent steps of substantially two seconds duration to prevent conduction of heat to said sealing point, filling said vessel with inert gas, sealing the opposite end of said vessel, heating the open ends of said electrodes locally by high frequency induction currents to flash said composition, and heating said electrodes in series by a steep wave front discharge current.

5. The method of fabricating a glow discharge device which comprises applying a ring of a composition to one end of a tubular electrode in the device, said composition comprising 80 per cent barium berylliate and 20 per cent free metallic titanium suspended in a nitrocellulose and amyl acetate binder, evacuating said device and heating said ring to a temperature sufficient to vaporize the barium and leave a glow inhibiting barrier ring substantially of a complex beryllium oxide.

GEORGE H. ROCKWOOD, JR.
ROBERT L. VANCE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,610,892	Skaupy	Dec. 14, 1926
1,661,235	Sarbey	Mar. 6, 1928
1,852,020	Metcalf	Apr. 5, 1932
1,873,730	Wiegand	Aug. 23, 1932
1,965,585	Foulke	July 10, 1934
2,057,183	Case	Oct. 13, 1936
2,173,258	Lederer	Sept. 19, 1939
2,173,259	Lederer	Sept. 19, 1939
2,213,182	Lederer	Aug. 27, 1940
2,223,977	Wamsley	Dec. 3, 1940
2,249,672	Spanner	July 15, 1941
2,403,745	Norton	July 9, 1946
2,443,633	Miller	June 22, 1948
2,474,335	Skellett	June 28, 1949