

Sept. 13, 1938.

E. A. LEDERER
GETTER FOR VACUUM TUBES

Filed March 18, 1936

2,130,190

Fig. 1

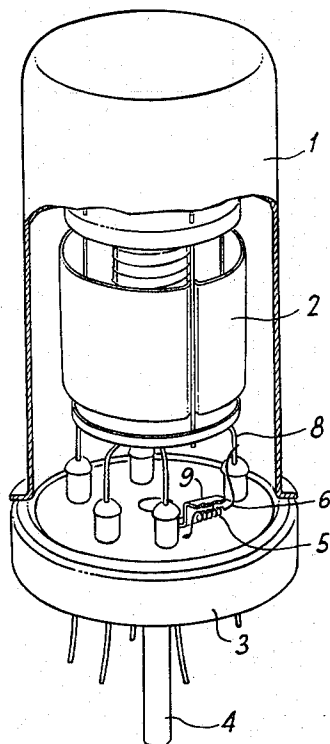


Fig. 2

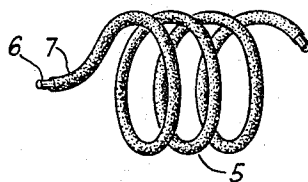


Fig. 3

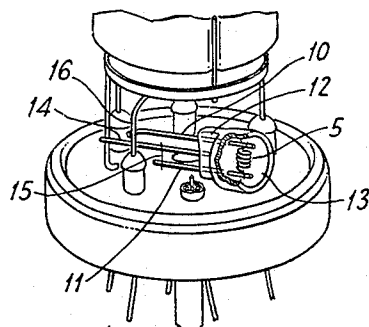


Fig. 4

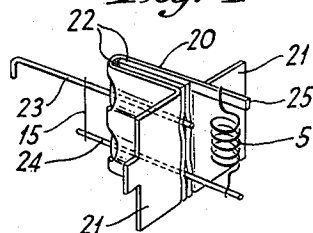


Fig. 5

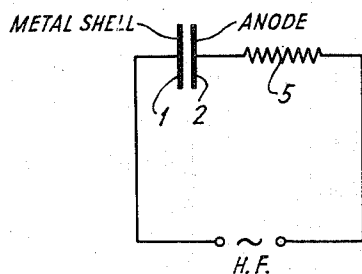
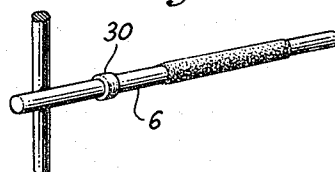


Fig. 6



INVENTOR
ERNEST A. LEDERER

BY *Charles McClain*
ATTORNEY

UNITED STATES PATENT OFFICE

2,130,190

GETTER FOR VACUUM TUBES

Ernest A. Lederer, Glen Ridge, N. J., assignor,
by mesne assignments, to Radio Corporation
of America, a corporation of Delaware

Application March 18, 1936, Serial No. 69,440

5 Claims. (Cl. 250—27.5)

This invention relates to vacuum tubes, such as electron discharge devices and the like, and more particularly to such devices evacuated by the aid of chemically active vaporizable clean-up agents which, either during or after mechanical exhaust, are vaporized to reduce the pressure of residual gases and vapors left in the device by the pumps.

It is common practice to use as a clean-up agent an active metal, such as an alkaline earth metal, introduced into the device in the form of a compound from which the metal may be liberated by heating and decomposing the compound. Various compounds of the active metal have been intermixed with a reducing agent, usually a powdered metal, which reacts with and reduces the compound with liberation of the active metal when the getter mixture is heated. Usually the reaction between the compound and the reducing agent is exothermic, and when the getter mixture is heated to a sufficient temperature the reaction proceeds with a sudden flash or explosion, and results in an uncontrollable liberation of the active metal and the production on the bulb wall of a film of active metal. This film appears to be more or less contaminated with reaction products and other impurities, and tests have shown that the active metal thus deposited is not in the most desirable and effective form.

The usual getters are relatively unsatisfactory when used in the conventional way in metal radio tubes, which at present are exhausted commercially by heating the metal shell or envelope of the tube by gas flames during the exhaust. Although the usual getter is placed in intimate contact with the metal shell at a spot which can be locally heated, difficulty is encountered in raising the getter mixture to the proper temperature for starting the flash without over-heating the wall of the metal envelope. Particular difficulty is encountered in evolving additional active metal after the getter mixture has once been flashed, although in many cases a controllable evolution of additional active metal, even after the tube has been sealed, is very desirable.

One object of my invention is to provide an improved getter of the active metal type by means of which a profuse and rapid yet easily controllable evolution of the active metal may be obtained.

Another object of my invention is to provide an improved method of gettering which is useful in all types of vacuum devices, particularly in

vacuum tubes with envelopes of metal, such as iron.

Still another object of my invention is to provide a metal radio tube of the oxide coated thermionic cathode type which has and maintains throughout its useful life a better vacuum than is feasible in similar tubes exhausted by the conventional methods now in use.

A more specific object of my invention is to provide a source of getter material for vacuum devices from which controllable supplies of active getter metal may be readily evolved at will before and after the device is sealed.

Further objects and advantages of my invention will appear from the following specification and detailed description.

In accordance with my invention the active getter metal is prepared as a compound, such as an oxygenous compound of the active metal, and placed in good thermal contact with or coated on a coherent body or core, such as a wire, of a metal which at elevated temperature reacts with the compound to evolve the active metal as vapor and produce reaction products which are stable and non-volatile in vacuum at the reaction temperature. I have found that by heating the core the evolution of active metal may at will be started by raising and stopped by reducing the temperature of the core, even though the reduction of the coating compound by the metal of the core is an exothermic reaction which would be expected to be uncontrollable when once started. For example, very pure clean barium, an active metal with a pronounced getter action in vacuum tubes, may be conveniently and copiously evolved at will from a coating containing barium oxide on a core of tantalum, the melting point of which is 2850° C. The getter film obtained on the inner wall of a vacuum tube with barium evolved in this way appears to be much cleaner and more effective than a barium film obtained by the conventional methods of gettering. I prefer to use for the coating a compound of an alkaline earth metal, such as barium carbonate, which is stable in air, and which when heated is partially or entirely converted into some oxide of the metal. The core or coating carrier is, according to one embodiment of my invention, made in the form of a resistance heating wire which is predominantly at its surface of a metal which at elevated temperature reacts with the coating material to release the active metal from that material. The coated wire is mounted in the envelope of an electron discharge device and its ends are connected to a current source to heat

the wire at will. By proper heating the barium carbonate may be converted into an oxide of barium and free metallic barium may then be evolved from the coating at will by controlling the heat applied to the core.

The novel characteristics of this invention may be more fully understood by reading the following specification in connection with the accompanying drawing in which:

Figure 1 shows an electron discharge device with a metal envelope and a getter made in accordance with my invention;

Figure 2 is a detailed view of a getter made in accordance with my invention;

Figures 3 and 4 show getter units with a fusible element and a vapor shield constructed in accordance with my invention;

Figure 5 shows schematically an arrangement for heating my improved getter; and

Figure 6 shows a novel fusible element made in accordance with my invention.

In the specific embodiment of my invention illustrated in Figure 1, which shows an application of my invention to metal tubes, I have shown a metal envelope 1 enclosing an electrode assembly 2 comprising the conventional activated oxide coated cathode, surrounded by a grid and an anode. The envelope is closed at the lower end by a header 3 having an exhaust tube 4 through which the tube is exhausted mechanically by pumps. For cleaning up residual gas after mechanical evacuation of the envelope, I use in one embodiment of my invention a getter 5 comprising a core or short piece of wire 6 covered, as best shown in Figure 2, with a coating of gettering material compound 7, and located in any desired position within the envelope. By way of example the getter is shown below the electrode assembly, with one end of the wire 6 connected to an electrode lead-in conductor 8 and the other end of the wire connected to the metal envelope. To shield the elements in the tube from any active metal which may be thrown off from the getter, a hood or deflecting plate 9 may be placed over the getter. After the pressure in the envelope has been reduced to a few microns by mechanical evacuation sufficient current is passed through the wire 6 for a sufficient time to drive off the required amount of getter vapor and clean-up residual gases in the envelope. The tube may then be sealed and based in the conventional manner. If after aging, gas is found in the tube, additional getter vapor may be liberated in the envelope merely by heating with a current by applying a voltage to the wire of the getter.

Certain alkaline earth metals, such as barium, have proven to be efficient gas clean-up agents for electron discharge devices, but being unstable in air and difficult to handle are usually prepared in a compound to protect the agents. It has been proposed, as in the British patent to Widell, No. 360,003, to evolve barium from a mixture of an oxygen compound of barium with a reducing agent such as powdered thorium, although other powdered metals, such as zirconium, titanium, hafnium, vanadium and tantalum powder, are suggested as alternative reducing agents. I have found that in such mixtures as barium oxide and powdered tantalum, the reduction of the oxide is by an exothermic reaction which is uncontrollable when once started and practically explodes the mixture, thereby throwing off objectionable particles, the metallic barium liberated being apparently contaminated and in a much less de-

sirable and effective state than barium liberated in accordance with my invention. I prefer to mix with a suitable binder, such as nitrocellulose or glycerine, a powdered compound such as barium carbonates containing the active metal to form a paste which may be sprayed or painted upon a core or carrier with a metal surface and which is convertible by heat into some oxide or similar salt reducible by heat into some oxide of the core. The reducing agent, however, is not mixed with the powdered compound of the active metal, but is according to my invention incorporated in the carrier or core upon which the powdered compound is placed. For this purpose I preferably draw a core, such as a round or flat wire, from a refractory metal having the necessary reducing properties. A core of tantalum has been found to readily evolve barium from the oxides produced by heating a deposited coating of barium carbonate, and to retain its shape at temperatures sufficient for copious evolution of free metallic barium. To insure a good bond between the tantalum core and its coating, I prefer to add a small amount of barium nitrate or of strontium nitrate to the barium carbonate. Tantalum at high temperatures, such as 1600° C., has such great affinity for oxygen that even as a wire or similar coherent body it acts as a powerful reducing agent on oxides intimately associated with it and readily draws the oxygen from the barium oxide in the coating. The reaction products, probably oxides of tantalum, have been found to be particularly stable and non-volatile in high vacuum at the reaction temperature, and, unlike the oxides of several other metals which will reduce barium oxide, are not set free in the envelope and do not reduce the vacuum or impair the emissivity of an activated oxide coated cathode. As the reducing agent is a coherent body or core the reaction between the reducing agent and the active metal compound is confined to the interface between the surface of the core and its coating. The reaction is easily started and stopped by controlling the temperature of the core, although the reaction of tantalum and barium oxide is exothermic. Apparently the rate of reaction is governed by the temperature of the core and by the rate at which the oxygen is drawn from the metal oxide through the interface of the core and its coating into the core. I have found the addition of strontium carbonate to the coating compound improves the mechanical properties of the coating at elevated temperatures, the melting point of strontium oxide being about 3000° C. which is well above the reaction temperature of barium oxide.

I have found that good results may be obtained by winding .005 inch tantalum wire into a coil about .05 inch in diameter, .08 inch long, and with a pitch of about 100 turns per inch, and coating the coil with about 2½ milligrams of barium-strontium-carbonate prepared by precipitating the double carbonate from a solution of barium and strontium nitrates by the addition of sodium carbonate. To 150 grams of the double carbonate is added 7½ grams of barium nitrate and 7½ grams of strontium nitrate in 200 to 300 cubic centimeters of water. To improve the spraying properties of the coating material, 1 to 2% glycerine may be added. This mixture is ball-milled sufficiently to insure thorough mixing and very small particle size and is applied to the coil by spraying or dipping, and dried in air.

The coated coil of tantalum wire is mounted in the envelope of the discharge device, and a

current passed through the coil to raise its temperature successively to 800°, 1000°, 1200°, and 1300° C. for periods respectively of six seconds each while the device is being mechanically exhausted. This series of heat treating steps has been found to convert the carbonate coating into a coating from which free metallic barium may be evolved at will. While the vacuum in the tube is maintained at a pressure of only a few microns the tube is sealed and the temperature of the coil is raised to a temperature above the reaction temperature of the barium oxide and below the melting point of strontium oxide, preferably about 1600° C., by passing about 1.6 amperes through it, and held at that temperature for about one minute, thereby driving off substantial quantities of free metallic barium, and strontium, when strontium is included in the compound. Electron discharge devices getterred in accordance with my invention have been found to be particularly free of residual gases, the gettering action in all cases being positive and resulting in extraordinarily low gas pressure. While tantalum as a core material has given good results and is preferred, zirconium has been successfully used, and columbium may be used. These metals may if desired be drawn or plated as a shell or cover on a refractory mandrel or wire of high melting point material.

Current may be supplied to the getter carrier or core through two auxiliary lead-in wires preferably sealed in the stem of the tube, or, where metal envelopes are used, one auxiliary lead-in wire may be added and the heating circuit completed through the metal of the envelope. However, my novel getter may be employed, according to another feature of my invention, without the addition of any auxiliary lead-in wires. According to this feature of my invention, the getter heating coil is connected in series with a fusible element between one electrode lead-in, say a filament heater wire, and another electrode lead-in wire, or the envelope of the tube, when the envelope is of metal. Upon completion of the gettering process, the circuit through the getter wire may be opened by melting the fuse with an excessive current. The getter heating coil, the fuse, and a shield for directing the vapor evolved from the getter may be conveniently assembled as a unit, one form of which is shown by way of example in Figure 3. The heater coil of getter 5 is connected between two support wires 10 and 11 sealed, as shown, into a press 12 at the end of a ceramic cylinder 13, of glass, aluminum oxide, or similar material. A third wire 14 sealed centrally in the press is welded to a bracket on the metal header and is electrically connected to support wire 11 by a short length of fusible wire 15, such as nickel, about .003 inch in diameter. Support wire 10 is connected to an electrode lead-in conductor 16 from which the necessary current may be obtained to heat the getter core. With .003 inch nickel fuse wire and .005 inch tantalum wire 1.6 amperes sufficiently heats the getter coil to drive off the free metallic barium, and a sudden current of 2.2 amperes melts the nickel wire. Thus upon completion of the gettering operation, the electrode lead-in conductor may be electrically disconnected from the metal header merely by increasing the current through the getter coil and the series connected fuse. The cup formed by the glass cylinder about the getter coil protects the electrodes from the discharged vapors which are directed outwardly against the envelope.

Figure 4 shows another getter assembly embodying my invention. A U-shaped metal tab 20 with outwardly extending vapor deflection plates 21 is compressed upon two sheets 22 of insulating material, such as mica, between which is clamped two wires 23 and 24. The getter coil 5 is connected between an ear or extension 25 of the tab, and wire 24. The fusible wire 15 is connected between conductors 23 and 24. By attaching the metal tab to the header or shell of a metal envelope and by connecting wire 23 to an electrode lead-in conductor, current may be sent through the fuse and getter coil in series and, as in the embodiment shown in Figure 3, may be heated to the gettering temperature and then electrically burned out.

Figure 5 shows another embodiment of my invention particularly adapted to metal tubes for heating the getter coil 5 without the addition of extra lead-in wires or without the use of a fuse. As shown diagrammatically, the heater coil 5 is connected at one end to the anode or to some other electrode which has an appreciable capacity with the metal shell of the envelope. By impressing a high frequency potential across the series getter heating coil and condenser formed by the metal shell and the anode, sufficient current may be passed through the coil to raise it to gettering temperature.

Another convenient method of electrically open-circuiting the getter heating coil is shown in Figure 6. About the heater wire 6 is placed a ring of nickel 30 which, it has been found, alloys with the tantalum and reduces its melting temperature so that the wire 6 at that point, upon increasing the current flow to a value above the necessary gettering value, melts and open circuits the wire at that point.

Many modifications may be made in my invention without departing from the spirit thereof, and I do not desire therefore to limit my invention to what has been shown and described except as such limitations occur in the appended claims.

I claim:

1. A getter consisting of a coherent body of metal which at temperatures at which the body is self-sustaining reacts with alkaline earth oxides to liberate the alkaline earth metals and produce reaction products stable and non-volatile at reaction temperature, and a coating composed of an alkaline earth reducible by said core metal and a refractory metal oxide with a melting point higher than said reaction temperature and in intimate contact with said core.

2. An envelope enclosing an activated oxide coated thermionic cathode and cooperating electrodes, a getter in said envelope comprising a metal core, and a coating containing barium oxide and strontium oxide on the core, said core being of a metal that reacts at a temperature below the softening point of the core with the barium oxide to liberate barium and produce reaction products having no appreciable effect on emissivity of the cathode.

3. The method of producing a gettering metal in an evacuated vessel which comprises introducing into said vessel a carbonate of a first alkaline earth metal and a carbonate of a second alkaline earth metal adherent to a coherent carrier of a metal capable of reacting with the oxide of the first mentioned alkaline earth metal at a temperature below the melting point of the oxide of the second alkaline earth metal to liberate the

- first alkaline earth metal copiously and produce reaction products which are stable and non-volatile in vacuum at reaction temperature, decomposing said carbonates to form on said carrier the oxides of said alkaline earth metals, and heating said carrier to a temperature below the melting point of the oxide of the second mentioned alkaline earth metal for a sufficient period of time to liberate the first alkaline earth metal.
4. A getter comprising a metal core, and a coating containing two alkaline earth compounds on said core, said core comprising a metal which reacts with one of said compounds to liberate the active metal of said one compound at a temperature below the melting point of the two compounds and produce reaction products which are stable and substantially non-volatile in vacuum

at reaction temperature and below the temperature at which said core softens.

5. The method of manufacturing envelopes containing electrodes and a gas clean-up agent having a refractory body with a surface containing a metal of the group consisting of tantalum, columbium and zirconium, and a coating composed of an alkaline earth oxide and strontium oxide, comprising mechanically exhausting said envelope, heating said electrodes, reducing said alkaline earth oxide by electrically heating said body, and then liberating sufficient free alkaline earth metal to clean up residual gases in the envelope by heating said body to a temperature between the vaporization temperature of the metal of the alkaline earth and the melting point of said strontium oxide.

ERNEST A. LEDERER.