

Sept. 19, 1939.

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2,173,259

ACTIVE METAL COMPOUND FOR VACUUM TUBES

Filed March 29, 1938

Fig. 1

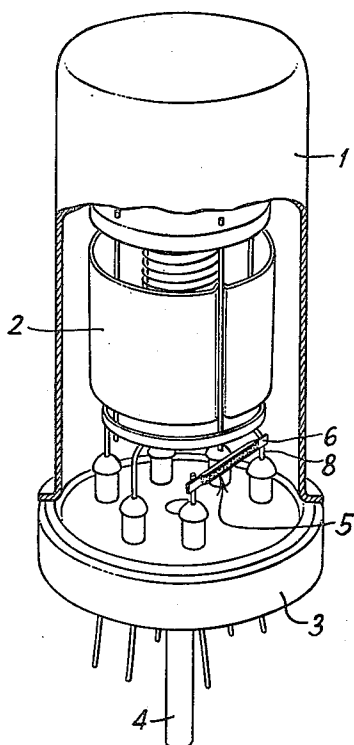


Fig. 2

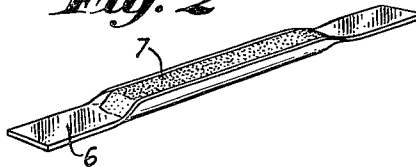


Fig. 3

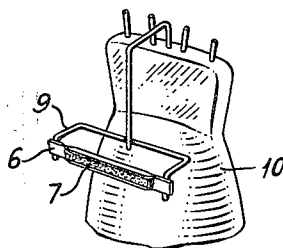
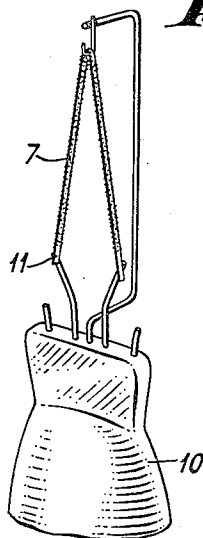


Fig. 4



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2,173,259

ACTIVE METAL COMPOUNDS FOR VACUUM TUBES

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Application March 29, 1938, Serial No. 198,620

6 Claims. (Cl. 250—27.5)

This invention relates to vacuum tubes, such as electron discharge devices and the like, and more particularly to the introduction into such devices of chemically active vaporizable substances or agents which, either during or after mechanical exhaust, are employed to reduce the pressure of the residual gases or to increase electron emission from cathodes.

The present application is a continuation in part of my co-pending application, Serial No. 176,825, filed November 27, 1937, and assigned to the same assignee as the present application.

It is common practice to use as a gas clean-up agent, for example, in envelopes an active metal, such as an alkaline earth metal, introduced into the device in the form of a compound that is stable in air and is decomposed with liberation of metal vapor when heated. The commonly employed carbon compounds of the alkaline earth metals, such as barium, unfortunately produce considerable quantities of products of decomposition such as carbonaceous gases including CO and CO₂ when the compound is heated. These undesired gases evolved in the presence of electrodes in the envelope to be exhausted contaminate the surfaces of the electrodes, load the pumps, and are difficult to remove even with prolonged degassing and pumping. Further, the undesired gases may so contaminate the emitting surface of the cathode, which is usually barium and barium oxide, as to impair electron emission. Various compounds for gettering residual gases and for activating cathodes have been proposed but none are known which do not produce considerable gas upon being heated.

An object of my invention is to prepare a stable source of alkaline earth metals free of objectionable amounts of gas.

Another object of my invention is to provide an improved getter of the active metal type which is stable in air and may be decomposed to liberate the active metal without producing undesired by-products of decomposition.

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 oxide coated cathodes.

The characteristic features of my invention may be easily understood by considering the specific embodiments of my invention described in the following specification and shown in the accompanying drawing in which—

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

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

Figure 3 shows one means for heating my improved getter; and

Figure 4 shows my new compound coated on a filamentary cathode.

In the specific embodiment of my invention illustrated in Figure 1, which shows an application of my invention to getters for 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 header 3 having exhaust tube 4, through which the tube is exhausted mechanically by pumps. For cleaning up residual gases after mechanical evacuation of the envelope I use in one embodiment of my invention a getter 5 comprising a core, such as a U-shaped strip of refractory metal 6 filled, as best shown in Figure 2, with my improved compound 7, and located in any desired position within the envelope. The getter may conveniently be heated with electricity by connecting one end of the strip 6 to electrode lead-in conductor 8 and the other end of the strip to the metal envelope or to a lead-in conductor. To shield the elements in the tube from any active metal which may be thrown off from the getter, the open side of the grooved strip is faced outward toward the bottom or side of the envelope. After the pressure in the envelope has been reduced to a few microns by mechanical pumping, sufficient current is passed through the strip for a time to drive off the required amount of getter vapor 35 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 the strip with a current by applying a voltage to the ends of the getter strip. If desired, the getter may be flashed and most of the barium liberated after seal-off.

Certain alkaline earth metals, such as barium, have proven to be good electron emitters and efficient gas clean-up agents for electron discharge devices, but being unstable in air and difficult to handle are usually prepared in a stable compound to protect the agents. I have proposed in my co-pending application, mentioned above, to prepare a barium-beryllium compound and coat the compound on a refractory reducing core. This compound consists of an oxide of an alkaline earth metal, such as barium, strontium, 55

calcium or magnesium, and beryllium oxide, free of water of crystallization, which I believe is a beryllonate compound of the alkaline earth, such as BaBeO_2 . I have found that a coating of barium-beryllium compound when decomposed on a tantalum core in an evacuated envelope produces only 1½ to 4% of the amount of gas produced by an equivalent coating of barium strontium carbonate, and that at about 1200–1400° C. free metallic barium is copiously liberated, leaving a hard, stable residue which appears to be beryllium tantalate with low vapor pressure.

While the precise chemical reaction in my improved getter is not known, it is believed that the reducing properties of the core serve to draw the oxygen from the coating compound and liberate the active metal of the coating. Zirconium, titanium, hafnium, vanadium, columbium, tungsten or molybdenum are refractory metals with the necessary reducing properties and may be substituted for tantalum.

The barium-beryllium compound of my invention has been prepared by dry ball-milling 216 grams of commercial barium carbonate and 66 grams of commercial beryllium oxide for two to three hours. The powder mixture is then fired in nickel boats for thirty to sixty minutes in hydrogen at 1065° C. ± 20° C. At this temperature the barium carbonate is converted first to barium hydroxide by the action of the hydrogen and the barium hydroxide then reacts with the beryllium oxide forming a barium-beryllium compound, BaBeO_2 . To sinter the mass and increase its density it is then fired in a Denver fireclay crucible for 250 minutes at 1250 to 1300° C. The product is then ball-milled dry or otherwise pulverized to the desired fineness after cooling in air. A coating or spraying solution is then prepared of the powdered compound by mixing it with an organic binder, such as a solution of nitrocellulose in dimethyl phthalate.

Good results have been obtained with my barium-beryllium compound as a getter by coating about 2.5 milligrams of the compound in a groove on a tantalum strip .0008 inch thick, .037 inch wide, and .65 inch long. A current of about 2.8 to 3 amperes heats the strip to a temperature of about 1300° C. and liberates more than 50% of the barium present in the compound.

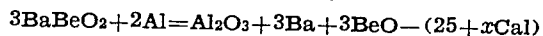
Although my new barium beryllonate compound has been specifically described and its use indicated as a getter in which the compound is coated upon a reducing core, my new compound may, if desired, be reduced by mixing a powdered reducing agent, such as aluminum tantalum or silicon, with the compound and coating upon a refractory core of metal such as iron or nickel. The powdered reducing metal may if desired consist of columbium tungsten, molybdenum or thorium and the core may be of any refractory metal such as columbium, chromium, nickel-iron-chromium alloy, molybdenum, tungsten or alloys of molybdenum and tungsten.

Alternatively my barium beryllonate may be mixed with a powdered reducing agent and with a binder and molded into pellets which may be heated in the conventional manner with high frequency in the envelope to be gettered. Good results have been obtained by mixing 2.5 grams of commercially pure aluminum powder screened through a 150 to 400 mesh sieve with 23 grams of barium beryllonate of about the same particle size, and pressing into pellets of about 30 milligrams in weight and heating to reaction temperature in the standard envelope of the ra-

dio tube commercially known as the 6L6. To apply my improved mixture to an electrically heated core a mixture of aluminum powder and barium beryllonate, in the proportions mentioned above, is prepared in a creamy paste with a nitrocellulose binder. When applied to a refractory core of metal such as molybdenum, iron or nickel and heated to a temperature of 1050 to 1100° C. copious quantities of barium are liberated, giving a clean barium deposit on the wall of the envelope. Good results have been obtained by placing 3.5 milligrams of the paste in a channel formed from a strip of molybdenum, nickel or iron .001 inch thick, .050 inch wide and ¾ inch long. The reaction was quiet and completely controllable by the current flowing through the channel. Increasing the amount of aluminum was found to shift the temperature of reaction to higher levels.

It would appear that the reaction between the aluminum and the compound would be exothermic because of the high heat of combustion of aluminum, but I have found the reaction is not self-sustaining and will continue only if heat is supplied to the mixture, probably because of the high specific heat of the compound containing beryllium oxide. As a result the evolution of barium may be controlled accurately merely by controlling the heating current flowing through the channel.

I believe the chemical reaction which takes place may be represented by—



where x represents the amount of heat required to split the compound and to heat the beryllium oxide to the temperature of reaction. This amount of heat has been found to vary between 37 and 40 calories per gram-molecule.

My new compound may, if desired, be coated upon a filamentary cathode, such as shown at 11 in Figure 4, or on an indirectly heated cathode, and reduced by material in the cathode core or by material mixed in the compound, to produce an electron emissive layer rich in barium. I have found, for example, that barium-beryllonate prepared in accordance with my invention and sprayed upon a tantalum or molybdenum filament can be activated in vacuum at about 1400° C. without any appreciable evolution of gas. With an input of about six watts per square centimeter to a tantalum filament coated with my new compound, I have obtained an electron emission of about 20 milliamperes per square centimeter. The coating has a dark gray appearance and when activated may be exposed to the air and again activated in a vacuum by aging. Because of the ruggedness of this type of cathode it is particularly useful for indirectly heated cathodes in large transmitter tubes.

My improved compound is economical to manufacture, easy to prepare, mold or coat upon its core, is stable in air, and when heated in a vacuum liberates copious quantities of free metallic barium without the evolution of undesired products of decomposition.

I claim:

1. An electron emissive source of barium consisting of an oxygen compound of barium and beryllium, and a reducing agent for said compound in intimate contact with said compound, said agent consisting of a metal which does not react exothermically with the compound.

2. A source of barium comprising a refractory core of metal, and a coating on said core consist-

ing of a reducible oxygen compound stable in air of barium oxide and beryllium oxide, a powdered reducing agent intimately admixed with said compound, said compound being non-hygrosopic and containing an excess of beryllium oxide.

3. A gettering device comprising a refractory core of a metal of the group consisting of tantalum, tungsten, iron, nickel molybdenum, columbium, chrome-iron and tungsten coated with a mixture of aluminum and an oxygen compound stable in air of barium and beryllium.

4. A source of barium comprising a core of a refractory metal included in the group consisting of iron, nickel, columbium, chrome iron, nickel-iron-chrome alloy, molybdenum and tungsten, and a coating on said core consisting of a mixture of a reducible oxygen compound of barium oxide and beryllium oxide, and a powdered metal of the group consisting of aluminum,

columbium, tungsten, molybdenum, thorium, tantalum and silicon, said powdered metal being mixed in said coating in the proportions of about ten parts of said compound to one part of said powder.

5. A getter for an electron discharge device comprising a pellet composed of a mixture of one part of aluminum powder and ten parts of an oxygen compound of barium and beryllium.

6. In combination, a source of barium comprising a mass of a powdered reducible oxygen compound of barium oxide and beryllium oxide and a powdered metal of the group consisting of aluminum, columbium, tungsten, molybdenum, thorium, tantalum and silicon, said powdered metal being intimately mixed with said compound, and a support upon which said mass may be heated.

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