July 23, 1940. D. H. WAMSLEY 2,208,692

ACTIVE METAL COMPOUND FOR VACUUM TUBES

Filed March 23, 1939

Fig. 2

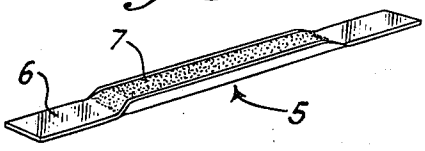


Fig. 1

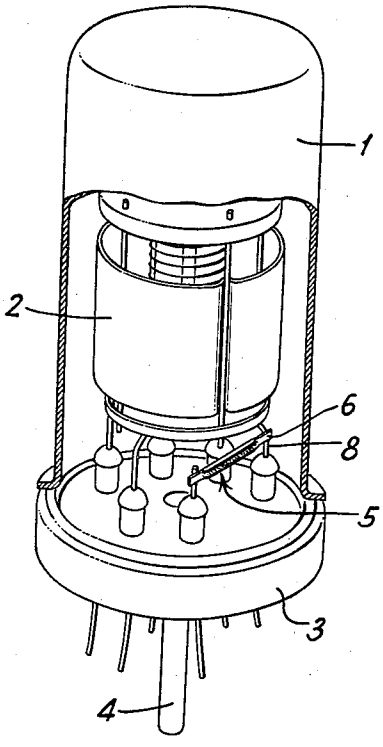


Fig. 3

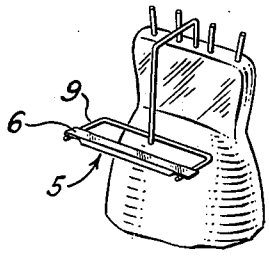
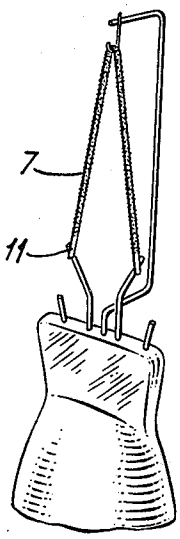


Fig. 4



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ACTIVE METAL COMPOUND FOR VACUUM TUBES

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Application March 23, 1939, Serial No. 263,629

12 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 are employed either during or after mechanical exhaust to reduce the pressure of residual gases or to increase electron emission from cathodes.

A new oxygen compound of beryllium and an alkaline earth metal, such as barium, described in the co-pending application of Ernest A. Lederer, Serial No. 176,825 filed November 27, 1937 and assigned to the RCA Manufacturing Company, Inc. has been used commercially as getter material with good results as it yields copious quantities of free metallic barium with little gaseous by-products when heated in vacuum. However, this compound as handled in the factory and exposed for long periods to a more or less humid atmosphere is not entirely stable and tends to deteriorate, as apparently it tends to hydrolyze in a humid atmosphere.

An object of my invention is to provide a stable compound of oxygen, beryllium and alkaline earth metals which is free of objectionable amounts of gas, will yield copious quantities of active metals, and which is substantially unaffected by long exposure to a humid atmosphere.

The characteristic features of my invention are defined with particularity in the appended claims and one preferred embodiment is described in the following specification and illustrated 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.

While my improved stable compound is specifically described here as a getter material, it may be used as cathode material from which good electron emission is obtained. In the specific embodiment of my invention illustrated in Figure 1, I have shown an envelope 1 enclosing an electrode assembly 2 comprising the conventional activated oxide coated cathode surrounded by a grid and anode. The envelope shown is of metal and is closed at the lower end by a header 3 having an exhaust tube 4 through which the envelope is exhausted mechanically by pumps. For fixing residual gas after mechanical evacuation of the envelope, the getter material is heated to evolve the active metal. The getter material may be pressed into pellets and placed on a getter tab in the conventional way but for practical reasons, and particularly for gettering metal tubes, I prefer to heat a thin layer of the meterial on an electrically heated core. In one preferred embodiment a getter 5 comprises a carrier or core such as a grooved strip or channel 6 of refractory metal which is located in any desired position in the envelope, and which, as best shown in Figure 2, carries the getter material 7. The getter may conveniently be heated electrically 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 second lead-in conductor. In glass tubes high frequency induction heating may be employed by closing the conductive loop 9 with the getter strip as shown in Figure 3. To shield the elements in the tube from active metal which may be thrown off from the getter, the open side of the grooved strip is faced outward toward the side of the envelope as shown in Figure 1 or downwardly as shown in Figure 3 so that the getter deposit is localized at the bottom of the envelope. After the pressure in the envelope has been reduced to a few microns by mechanical pumping, the strip 6 is heated for a time sufficient 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 again heating the strip. If desired, the getter may be flashed and most of the active metal liberated after seal-off.

In manufacture short refractory metal strips 6 are formed into shallow troughs substantially as shown and my improved getter material mixed with a binder into a thin paste, is deposited in the channels or troughs by a machine. In factory production the material must be prepared in large quantities and is unavoidably exposed to the atmosphere for considerable periods of time before it is sealed in the tube envelope.

After extensive experimentation with different combinations of the alkaline earth metals and their oxides in an attempt to obtain a gas free compound from which large quantities of the metal could be easily liberated and which was stable for factory use under adverse atmospheric conditions, I found that a double berylliate of alkaline earth metals, such as barium, strontium, calcium and magnesium, preferably an oxygenous compound of beryllium, barium and strontium is excellent for the purpose. This compound is a

double salt of barium and strontium in which the beryllium oxide acts as the acid radical for the barium and the strontium.

An indication of the extent to which my new alkaline earth compound stands up in factory use and the extent to which the single berylliate of barium deteriorates as getter material when exposed to the atmosphere is given by the amount of gas that can be driven from the material by heating in vacuum at about 700° C. Barium berylliate, strontium berylliate or mechanical mixtures of these two berylliates have been found to produce per milligram of the berylliate more than one thousand liters of gas at a pressure of one micron of mercury after standing for a few hours in an atmosphere of 70% relative humidity at 30° C. My improved oxygen compound of barium, strontium and beryllium however has been found to give off less than eight liters microns of gas per milligram after standing eleven days in an atmosphere of 70% relative humidity at 30° C. Under such atmospheric conditions which are usual in the summer months, the moist single berylliate compounds behave much like popcorn and puff to several times normal size when heated.

Several conventional tests for identifying materials show my material to be a true compound of barium, strontium, beryllium and oxygen. The index of light refraction, determined by the oil immersion method with a petrographic microscope, of my material is found to lie between the index of barium berylliate and of strontium berylliate, and the petrographic microscope test shows distinct hexagonal crystals that are different from either the crystals of barium berylliate or strontium berylliate. It can be shown, further, by X-ray defraction analysis that there is a definite compound of barium, strontium, beryllium and oxygen.

My new material is a double berylliate of barium and strontium and to the best of my knowledge and belief may be correctly indicated in the molecular proportion $BaO \cdot SrO \cdot 6BeO$ or

$$BaSrBe_6O_8$$

While the sum of the weights of the two metals must be in definite proportion to the acid radical of the compound, BeO, the ratio of the two metals, barium and strontium, may be widely varied. To increase the barium strontium yield, the getter material may be prepared with barium oxide and strontium oxide in excess of the amount required by the formula $BaSrBe_6O_8$.

While the technique of preparing my new compound may be varied, I have obtained good results in manufacturing large batches of the material for factory use by ball-milling and firing together barium and strontium carbonates and beryllium oxide. Specifically my getter material comprising barium-strontium-beryllium compound with about a 20% excess of BaO and SrO, has been prepared by ball-milling 1480 grams of commercial barium-strontium carbonate and 520 grams of commercial beryllium oxide for four to fifteen hours. The powder mixture leveled to a depth of 1¼" in flat nickel boats is then fired for thirty to sixty minutes in hydrogen at 1065° C.±20° C. At this temperature a barium-strontium-beryllium compound, $BaSrBe_6O_8$, is formed probably by conversion of the carbonates to the hydroxides by the action of the hydrogen, and reaction of the hydroxides with the beryllium oxide. The compound thus formed is sintered and its density increased by firing in air in a Denver fireclay crucible for four hours at 1200 to 1250° C. The sintered product is then ball-milled dry or otherwise pulverized to the desired fineness after cooling in air.

The powdered compound is preferably applied as a coating or spraying solution made by mixing it with an organic binder. A thin paste-like coating material suitable for filling the channels of the ribbon getter cores of Figure 2 may be made by mixing 400 grams of barium-strontium berylliate prepared as described above with 95 cc. of liquid binder comprising commercial butyl carbitol, nitrocellulose and natural or synthetic camphor. For large scale manufacture I have prepared the binder by mixing 1000 cc. of the butyl carbitol with 39 grams of nitrocellulose and 10 grams of camphor. In some cases the camphor may to advantage be replaced with a commercial plasticizer, such as that commercially known as "plasticizer 3GH".

Good results have been obtained with my barium-strontium-beryllium compound as a getter by coating about 2.5 milligrams of the compound in a groove on a tantalum strip .001 inch thick, .040 inch wide, and .65 inch long. A current of about 3.8 to 4 amperes heats the strip to a temperature of about 1300° C. and liberates more than 75% of the barium and strontium present in the compound. Little gas is given off upon decomposition and the residue is hard, refractory and non-volatile.

The tantalum strip core has been found to readily reduce the barium-strontium berylliate and to give good results, but, if desired, a reducing agent for the compound, such as a powdered metal, may be mixed with the compound. Good results have been obtained by mixing 16.5% by weight of titanium powder with 83.5% of barium-strontium berylliate and coating it on a molybdenum strip. Zirconium, vanadium, hafnium or colombium, as well as titanium or tantalum, are refractory metals with the necessary reducing properties to liberate the active metals and may be used as core material or powdered and mixed with the compound. While the precise chemical reaction of my improved getter is not known, it is believed the oxygen is drawn from the compound by the reducing agent, in the core or in the admixed metal powder, and the active metal liberated.

My new compound 7 may, if desired, be coated upon a filamentary cathode, such as shown in Figure 4 at 11, 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-strontium berylliate 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 and to mold or coat upon its core, is non-hydroscopic and particularly stable in humid 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. A source capable of evolving alkaline earth metals comprising barium oxide and strontium oxide chemically compounded with beryllium oxide.

2. A source of alkaline earth metals comprising a chemical compound of said alkaline earth metals, oxygen and beryllium.

3. A source of alkaline earth metals comprising a double berylliate of barium and strontium.

4. A source of alkaline earth metal comprising a double salt of barium and strontium with beryllium oxide.

5. A source of alkaline earth metals consisting of a reducing agent and a chemical oxygenous compound of the alkaline earth metals and beryllium in intimate contact with said agent.

6. A getter for an electron discharge device comprising barium oxide, strontium oxide and beryllium oxide, the barium oxide and strontium oxide being present in an amount in excess of the amount required by the chemical formula $BaSrBe_6O_8$.

7. A source of alkaline earth metals free of products of decomposition consisting of oxygen chemically compounded with barium, strontium and beryllium and a refractory core capable of reducing the compound to free said metals, the compound being coated upon said core.

8. An electron emissive source of barium consisting of oxygen, barium, strontium and beryllium chemically combined in a compound, and a reducing agent in intimate contact with said compound.

9. A source of alkaline earth metal comprising a core of tantalum and a coating on said core consisting of a reducible oxygen compound stable in a humid atmosphere of barium oxide, strontium oxide and beryllium oxide.

10. A getter device comprising a metal of the group consisting of tantalum, molybdenum, colombium, titanium, zirconium, hafnium and vanadium and an oxygen compound stable in air of barium, strontium and beryllium, said metal being in contact with said compound.

11. A source of active metals comprising a refractory core, a coating of an oxygen compound of barium, strontium and beryllium chemically combined on said core, and a powdered reducing agent for said compound mixed in the coating.

12. A getter device comprising a refractory core of molybdenum, a coating on said core consisting of an oxygen compound stable in air of barium, strontium and beryllium mechanically admixed with titanium powder.

DELOS H. WAMSLEY.