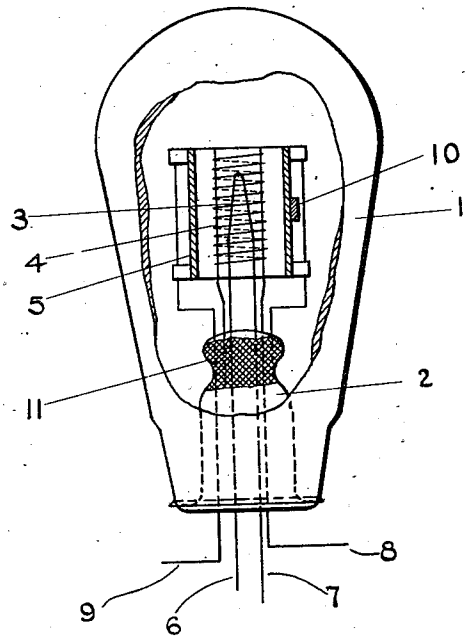
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METHOD OF CLEANING UP RESIDUAL GASES

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METHOD OF CLEANING UP RESIDUAL GASES.

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This invention relates to a vacuum electric device and more particularly to a method of evacuating such a device, cleaning-up the residual gases contained therein and activating the electron-emitting element thereof.

This invention is especially adapted to the production of high vacuums in radio tubes and similar apparatus employing an oxide coated filament. It is not limited to this type of device, however, but may be applied for the cleaning-up of residual gases in devices employing other forms of filaments, such as pure tungsten or thoriated tungsten filaments.

In radio tubes it is desirable, in order that uniform results may be obtained and in order to prevent arcing between the electrodes and consequent destruction of the filament, that a high vacuum be produced and maintained therein. Some gases, moreover, such as carbon dioxide and oxygen act to destroy the emissivity of the filament and have other detrimental effects. The gases usually present in the tube after it has been exhausted to a moderately high vacuum are water vapor and carbon dioxide given off by the glass and by the decomposition of the coating on the filament, residual air, oil vapor from the pumps, and carbon monoxide and hydrogen given off by the plate.

It is not practical to remove completely these various gases and vapors by means of pumps since such operation is very long and expensive and the pumps suitable for this purpose are very costly.

It is the usual practice, therefore, in the manufacture of radio tubes, to exhaust the devices to a moderately high vacuum by means of rotary oil pumps and to clean-up the residual gases and vapors by metallic clean-up agents such as magnesium, aluminum, misch metal, etc.

In application Serial No. 636,510 of Ralph E. Myers, filed May 3, 1923, and entitled Evacuated devices and method of exhaust, is disclosed the use of magnesium as a clean-up material. The use of misch metal as a clean-up material shown and described in application Serial No. 679,489, Marden et al., filed December 8, 1923, and entitled Clean-up and activation by misch metal and the rare earth metals, and in application Serial No. 586,261, Rentschler, filed August 16, 1922, entitled Vacuum devices and methods of exhausting the same, there is disclosed the use of aluminum as a clean-up agent. All of these cases are assigned to the Westinghouse Lamp Company.

Briefly, the method employed in using these clean-up materials, is to place a small quantity of such metal on the plate or other metal part of the device before the same is sealed into the bulb and after exhausting and sealing-off the tube, vaporizing such material by heating the same inductively by high frequency currents or otherwise to render it in a condition in which it will react with the gases to produce solid compounds thereof.

While excellent results are obtained with the use of a metal getter alone, I have found that higher emissivity and greater life may be obtained by combining therewith, a basic getter material such as calcium oxide. This is particularly true in the manufacture of radio tubes employing oxide coated filaments.

In the production of oxide coated filaments, it is desirable to apply the oxides, which may be a combination of barium and strontium oxides, to the filament in the form of a coating of the carbonates of these substances and subsequently decompose the carbonate to produce the oxide in accordance with the method disclosed in application Serial No. 587,270, MacRae, filed September 11, 1922, entitled Electron-emitting devices and method of making, and assigned to the Westinghouse Lamp Company.

The use of the carbonates of barium and strontium as the coating material is extremely advantageous since this material may be readily applied to the filament and baked thereon by the ordinary equipment in use in coating incandescent lamp filaments and other wires. Moreover, on decomposition, the character of the oxide coating obtained, is such as to give the filament higher emission than when other known means of producing oxide coated filaments are used. This appears to be due to the porous and spongy character of the oxide coating produced in this way.

In decomposing such a coating from the carbonates of the oxides, a large quantity of carbon dioxide is liberated which must be eliminated from the device in some manner. Heretofore, in order to render possible the use of filaments coated with carbonates of barium and strontium and to eliminate from

the tube, the carbon dioxide liberated on decomposition of the coating, it has been proposed to decompose the coating during the exhausting of the device and while it is still on the pumps. This procedure, however, requires the use of a special type of very low pressure mercury pump combined with a complicated electrode treatment during the exhaust operation. The operation moreover, is relatively slow and expensive and the results obtained are not as uniform as with the present invention.

One of the objects of this invention is to provide a method of obtaining high vacuums in devices containing oxide coated filaments without necessitating the use of extremely low pressure pumps and which is adaptable for factory operation on rotary oil vacuum pumps.

Another object is to provide a method of obtaining high vacuums in tubes employing oxide coated filaments which will permit the coating to be applied to the filament in the form of a carbonate of the coating materials and to be decomposed to the oxide subsequent to the exhaust operation.

Another object is to provide a method of evacuating an electron emission device by which the life of the device and the emission of the electron-emitting element will be increased.

Another object is to provide a method of evacuating radio tubes which will be effective to decrease the plate resistance thereof.

Another object is to provide a method of cleaning-up residual gases in a vacuum device which will be effective to maintain said vacuum throughout the life of the device.

Other objects and advantages will hereinafter appear.

In accordance with this invention, radio tubes or other devices are evacuated to a moderately high vacuum by any suitable means such as rotary oil vacuum pumps and the residual gases retained therein are cleaned up by a metallic getter such as magnesium in combination with a non-metallic or basic material such as calcium oxide. The calcium oxide serves to clean-up the gases capable of reacting with it to form solid compounds such as carbon dioxide and water vapor and the metallic clean-up agent removes the hydrogen, oxygen and carbon monoxide from the tube and also assists in cleaning up the carbon dioxide and water vapor. It is believed that the calcium oxide also occludes or absorbs the argon gas present but I do not desire to restrict myself to such action since the same is not fully understood.

This invention is not limited to calcium oxide as a basic clean-up material, since other alkali oxides or alkaline earth oxides may be used for this purpose, if desired.

The magnesium or other metal clean-up material is introduced into the device by attaching it to one of the metal parts of the tube, preferably the plate in the case of radio tubes and the calcium oxide is preferably introduced in a water suspension, painted or otherwise coated on the stem or other glass part of the tube.

After the device has been evacuated and tipped off the barium and strontium carbonates on the filament are decomposed to the oxides, in a manner which will hereinafter appear, with a liberation of large quantities of carbon dioxide which is partially or entirely cleaned up by the action of the calcium oxide. The plate and other metal parts are then heated by high frequency induction to vaporize the magnesium secured thereto and to liberate the gases occluded in such parts. The volatilized magnesium will clean up those gases, such as hydrogen, oxygen, carbon monoxide, etc., not eliminated by the lime and the excess magnesium forms a coating on the surface of the bulb. The tube is then given a seasoning treatment by heating the filament with voltage on the plate and grid so as to ionize any gases contained in the tube or given off by the filament and render them active so that they may be readily absorbed by or combined with the magnesium or lime.

In order that this invention may be more fully understood, reference may be had to the accompanying drawing in which the single figure is a side view partly in section, of a radio tube adapted to be treated in accordance with this invention.

The radio tube comprises a bulb or envelope 1, a stem 2 sealed therein, a filament 3, grid 4 and plate 5. The filament, grid and plate, are carried by the stem 2 in the usual manner of constucting radio tubes and suitable leading-in wires 6, 7, 8 and 9 sealed through the stem are joined to the electrodes in the ordinary manner. The filament 3 is preferably of the oxide coated type and may be prepared by first coating a platinum-iridium ribbon or wire of the desired size with a mixture of barium and strontium carbonates prepared by making an aqueous suspension of a mixture of pure powdered barium carbonate in pure powdered strontium carbonate in approximately the proportions of 9 grams of the former with 10 grams of the latter and about 18 c. c. of water added gradually to form a suspension of proper consistency for coating. This suspension may be applied to the wire in any suitable manner and baked thereon in an electric tube furnace in an atmosphere of carbon dioxide to prevent decomposition of the carbonates.

The plate 5 has secured thereto, before being sealed into the bulb, a small piece of magnesium 10 or its equivalent metal clean-up material. This material may be attached by welding, soldering, pasting, crimping or

otherwise. The amount of magnesium used may be very small weighing not more than a milligram. With even this small amount of magnesium there will be an excess thereof in the bulb which, after vaporization, will form a coating on the inside surface of the bulb and serve throughout the life of the device to maintain the vacuum therein.

The stem 2 of the tube has applied thereto, a coating 11 of calcium hydroxide applied thereto in any suitable manner prior to the sealing-in operation. Calcium hydroxide is preferably applied in the form of a water suspension produced by slaking a quantity of calcium oxide or lime with a small amount of water in a mortar, breaking up the calcium oxide with a pestle, adding additional water and grinding to a paste-like consistency. The calcium hydroxide so formed, may be painted or otherwise coated on a suitable glass part of the device such as the stem. It is preferable to use the mixture fairly soon after it is made up within from say 10 to 20 hours, as it absorbs carbon dioxide from the atmosphere. For the same reason, it is advisable to exhaust the device reasonably soon after the stem has been sealed therein. If desired, the calcium oxide may be applied directly to the stem in the form of an alcoholic suspension; however, the former method is preferable.

In the sealing-in and exhaust operation, the bulbs are baked at a fairly high temperature and the metal parts heated by high frequency induction to drive off any gases occluded in the glass or metal parts thereof and during this baking operation, it is believed that the calcium hydroxide is partially or entirely converted to calcium oxide. It is preferable, however, not to completely dehydrate the material since a slight amount of moisture will render the same more active.

After sealing in the stem and exhausting the bulb to as high a vacuum as is practical in factory production, the carbonate coating on the filament is decomposed to the oxide with the liberation of carbon dioxide and water vapor. The decomposition of the coating of the filament may be accomplished by passing a current of sufficient strength through the filament to heat it to the decomposing temperature of the carbonates thereon. I have found that a current of .4 amperes through the filament for a period of about 30 seconds will decompose substantially all of the carbonates.

The calcium oxide on the stem will absorb a large part of the carbon dioxide and water vapor given off by the filament, the carbon dioxide combining with the lime to form calcium carbonate and the water vapor to form calcium hydroxide. The lime may act at the same time to absorb or occlude the argon gas contained within the tube.

The calcium oxide, however, does not appear to be effective for cleaning-up hydrogen, oxygen, carbon monoxide, oil vapors, etc. In order to eliminate these latter gases and any carbon dioxide and water vapors not combined with the lime, the magnesium is vaporized from the plate preferably by heating the same inductively by high frequency current. The vaporized magnesium reacts with substantially all of the residual gases within the tube except argon, to form solid compounds thereof and forms a deposit on the bulb which serves throughout the life of the tube to absorb any gases formed therein.

After the vaporization of the magnesium, the tube is seasoned for about 5 minutes at approximately .3 amperes through the filament and about 60 volts across the plate and filament. A potential of about 1.5 volts is also impressed on the grid. The gases driven off during this period are ionized and rendered active so that they will react with the magnesium on the bulb and form solid compounds. If desired, the magnesium may be vaporized before the decomposition of the coating on the filament.

It will be noted that by using a combination of a metallic clean-up agent and a basic clean-up agent, that barium and strontium may be applied to the filament in the form of carbonates and after tipping off the device, the carbonates decomposed into the oxides, thus eliminating the expensive and troublesome operation of decomposing the coating on the pumps. Moreover, the tube need not be evacuated by the pumps to as high a vacuum as when no clean-up material is used or when lime alone is used, since the magnesium is very effective for cleaning-up large quantities of gas. The process, therefore, permits the use of rotary oil vacuum pumps and renders the same commercially practical.

While the exact manner in which the lime acts in the tube is not clearly understood aside from its clean-up effect on the carbon dioxide and water vapor, I have found that a much better emission and longer life is obtained when using this material in combination with magnesium or other metal getter than when either of these materials are used separately.

I have found that by using lime in combination with the magnesium, an increase in emissivity of the filament of substantially 100% over the use of magnesium alone, may be obtained. I have also found that this combination of getters decreases to a very large extent the plate resistance of the tube and increased considerably the life of the device.

In order that the improved results obtained by using the combination of lime and magnesium getters, may be more fully appreciated, the following tabulation of actual

test on tubes with and without lime, is submitted. In these tests all conditions were made as nearly identical as possible with the exception of the addition or omission of the lime.

Tube	Plate resistance	Emission
W. D. 12 average of 9 tests without lime	17917	5.44
W. D. 12 average of 8 tests with lime	15756	31.2
W. D. 11 average of 14 tests without lime	15954	20.
W. D. 11 average of 15 tests with lime	13247	36.

It is thought that the improved results are obtained because of the action of lime in absorbing those gases which destroy emission and because of the liberation from the lime of hydrogen, which in minute quantities in a free condition in the tube, appears to have a beneficial action. This hydrogen may be liberated as free hydrogen or in the form of water vapor which is decomposed by the magnesium, the oxygen being absorbed thereby and the hydrogen liberated.

I do not desire to be limited to any particular theory of operation of the clean-up materials described herein, or to the exact materials for and method of carrying the invention into effect, but desire it to be understood that many changes may be made in the process without departing from the invention.

What is claimed is:

1. The method of cleaning up residual gases and vapors in a partially evacuated envelope containing an electrode coated with oxides of the alkaline earth metals comprising absorbing said gases and vapors by the combined action of a vaporizable metal and an alkaline earth oxide.

2. The method of cleaning up residual gases and vapors in a partially evacuated envelope containing an electrode coated with oxides of the alkaline earth metals comprising absorbing said gases and vapors by the combined action of a metallic clean-up agent and line.

3. The method of producing a high vacuum in a discharge device employing an electrode coated with the oxides of alkaline earth metals which comprises evacuating said device to a commercially obtainable vacuum by a suitable pump and cleaning up the residual gases and vapors by the combined action of magnesium and calcium oxide.

4. The steps in the method of producing an electron discharge device which comprise coating the filament of said device with an alkaline earth carbonate, evacuating and sealing the device, subsequently decomposing the carbonate to produce an oxide of said alkaline earth and absorbing the residual gas within said device and the gas liberated by said decomposition by the combined action of calcium oxide and a vaporizable metal.

5. The steps in the method of producing an electron discharge device which comprise coating the filament of said device with an alkaline earth carbonate, evacuating said device, sealing the same, decomposing the carbonate to produce an alkaline earth oxide and cleaning up the gases contained in said device by the combined action of a vaporizable metal and calcium oxide.

6. The method of activating an electron-emitting element having an alkaline earth carbonate applied thereto which consists in heating said element in an evacuated container and absorbing the residual gases contained in said container and the gases and vapors liberated from the element by a vaporizable metal and an alkaline earth oxide.

7. A discharge device comprising an evacuated container having therein an anode, a cathode coated with alkaline earth oxides, a quantity of metallic clean-up material and a quantity of an alkaline earth oxide clean-up material.

8. A discharge device comprising an envelope having therein an anode, a cathode coated with alkaline earth oxides, a quantity of magnesium and a quantity of calcium oxide.

9. A discharge device comprising an evacuated container having a stem sealed therein, a plurality of electrodes supported by said stem, one of said electrodes having a coating of alkaline earth oxides thereon, a film of metallic clean-up material disposed over the inner surface of the container and a coating of an alkaline earth oxide clean-up material on said stem.

10. A discharge device comprising an evacuated container having a stem sealed therein, a plurality of electrodes supported by said stem, one of said electrodes having a coating of alkaline earth oxides thereon, a film of magnesium disposed over the inner surface of the container and a coating of calcium oxide on the stem.

In testimony whereof, I have hereunto subscribed my name this 29th day of October, 1924.

ANDREW ERNEST LYLE.