Patented Feb. 5, 1935 1,990,204

UNITED STATES PATENT OFFICE

1,990,204

MANUFACTURE OF THERMIONIC CATHODES FOR ELECTRIC DISCHARGE DEVICES

John Turton Randall, Ruislip, England, assignor to General Electric Company, a corporation of New York

No Drawing. Application July 3, 1933, Serial No. 678,989. In Great Britain July 22, 1932

9 Claims. (Cl. 250—27.5)

This invention relates generally to the manufacture of thermionic cathodes for electric discharge devices and more particularly the invention relates to the manufacture of cathodes of the type consisting of a self-supporting mass containing alkaline earth oxides, generally rod-like in shape, heated by means, for example a tungsten spiral, which does not contribute materially to the rigidity of the mass. Cathodes of this type are to be distinguished from those in which the oxides form a layer on a metallic core which supports them and by which they are heated; they are most widely employed in gaseous electric discharge lamps.

Cathodes of this type are usually prepared by forming a mass of the appropriate shape from some compound of the alkaline earth metals which is later converted into the oxide by heat. The carbonate is the compound most generally used. It is a necessary consequence of this process that the resulting mass is porous and less dense than a truly compact mass of the oxide. This porosity is disadvantageous for several reasons; for example, it permits air to penetrate into the interior of the mass, if the mass is exposed to air for a short time to disintegrate the mass by the formation of hydroxide and carbonate. The porosity can be reduced somewhat by sintering the mass after the carbonate has been decomposed, but it is not easy by this means to produce a rod of the necessary compactness.

The object of the present invention is to provide a compact electrode of the above type which does not disintegrate when exposed to air. A further object of the invention is to provide an electrode of the above type which is less porous and more readily compacted by sintering than those now known in the art. Still further objects and advantages attaching to the device and to its use and operation will be apparent to those skilled in the art from the following particular description.

We have discovered that less porous masses, more readily compacted by sintering, can be produced if the peroxide is used instead of the carbonate for the starting material. We are aware that it has been proposed to produce thermionic cathodes by converting the peroxide of the alkaline earth metals into oxides, but only when the cathode has the form of a layer on a support, not when it has the form of a self-supporting mass. When the cathode is a layer on a support the qualities that we have found to result from the substitution of the peroxide for the carbonate are of little or no importance.

According to the invention a thermionic cathode of the type specified is produced by forming a mass out of materials in which the alkaline earth metals are present as peroxide, and decomposing the peroxide by heat.

Since the main feature of the invention is the substitution of peroxide for the usual carbonate, any characteristics of known cathodes of the type specified that are not necessarily affected by the substitution can be adopted in cathodes according to the invention without exceeding its scope. Thus metal powder, particularly tungsten powder, is often mixed with the alkaline earth carbonates and remains in the resulting oxide. Such admixture is permissible also in cathodes made in accordance with the invention.

The original mass of the desired shape is often prepared by squirting the material mixed with a small quantity of binder. We have discovered that not all binders suitable for use with carbonate are equally suitable with peroxide; thus gum tragacanth is not a suitable binder for peroxide. On the other hand a suitable binder is a 10% solution of nitro-cellulose in amyl acetate, 4 to 5 grams of this solution being mixed with 20 grams of barium peroxide. Since the quality of nitro-cellulose differs markedly among different samples, the exact composition and amount of the binder must be adjusted by trial to the particular sample.

The heat treatment of the squirted mass consists of two main stages. In the first stage the binder and then the peroxide are decomposed leaving the oxide. In the second the oxide is sintered so as to be rendered more compact. The first stage is preferably conducted in a vacuum, that is to say at as low a pressure as the evolution of gas during this stage will permit. The temperature during this stage need not exceed 1000° C., though 1150° C. is sometimes preferable; this is a temperature that can be attained in a vacuum furnace of the usual type. The rate at which the temperature is raised must be slow until the binder is decomposed, thereafter it may be more rapid. The second stage is not conveniently conducted in a vacuum, since the temperature required is too high for vacuum furnaces of the usual type, but it may be conducted in hydrogen or other gas neutral to the oxide.

In one example of the process according to the invention, a mixture of barium peroxide with the binder above-mentioned is squirted into rods 4.5 mm. in diameter. The rods are placed in a vacuum furnace and the temperature is raised

to 125° C. over a period of 30 minutes; it is then raised from 125° C. to 250° C. over a further period of 30 minutes, by the end of which period the binder is decomposed. The temperature of the vacuum furnace is now raised from 250° C. to 1150° C. over a period of about 90 minutes, during which period the peroxide is decomposed; the completion of this stage is indicated by the fall of pressure when the evolution of gas ceases. The rods are now removed from the vacuum furnace and placed in a molybdenum boat lined with tungsten with a furnace filled with hydrogen; the temperature is raised to 1620° C. over a period of 30 minutes and held at this temperature for about 10 minutes. They are then removed, cooled and inserted in the electric discharge device. The use of a tungsten-lined boat is necessary because barium oxide is very corrosive at these high temperatures. Magnesia is a possible substitute for tungsten. The temperature to which it is desirable to heat the oxide in the second stage is limited mainly by the resistance of the boat to attack, higher temperatures would probably be desirable if boats to stand them could be obtained.

While the above described method includes the step of squirting the mass into desired shape it will be understood, of course, that we contemplate the step of pressing the mass into desired shape, either by compacting it in a mold or by any other method of applying pressure thereto. When a mold is used the mass is left therein during the carrying out of the process, or not, as desired, the mold forming a support for the mass during the process and in the lamp in which the completed electrode is incorporated. The mold, of course, consists of material capable of withstanding the high temperatures of the process, such as tungsten or magnesia. It will be understood, of course, that the electrode leads are inserted and sintered in the mass during the process, when desired. When the mass is pressed into shape, as by compacting it into a mold, a binder can frequently be dispensed with, particularly where the mold is retained thereon during the process. When no binder is used the steps in the process necessary to decompose the binder are modified accordingly. The resulting electrode as stated has been found to be a highly efficient one when used as the cathode of gaseous electric discharge lamps and the like.

What we claim as new and desire to secure by Letters Patent of the United States is:—

1. The method of manufacturing a thermionic cathode which comprises the steps of mixing alkali earth metal peroxide with a binder consisting of a solution of nitro-cellulose in amyl acetate, shaping the mass of such material and decomposing the peroxide by heat.

2. The method of manufacturing a thermionic cathode which comprises the steps of mixing alkali earth metal peroxide with a binder consisting of a solution of nitro-cellulose in amyl acetate, shaping the mass of such material and heating the shaped mass in a vacuum to the decomposition temperature of the peroxide.

3. The method of manufacturing a thermionic cathode which comprises the steps of mixing alkali earth metal peroxide with a binder consisting of a solution of nitro-cellulose in amyl acetate, shaping the mass of such material, heating the shaped mass in a vacuum to the decomposition temperature of the peroxide and then raising said mass to the sintering temperature thereof.

4. The method of manufacturing a thermionic cathode which comprises the steps of mixing alkali earth metal peroxide with a binder consisting of a solution of nitro-cellulose in amyl acetate, shaping the mass of such material, heating the shaped mass in a vacuum to the decomposition temperature of the peroxide and then raising said mass to the sintering temperature thereof in an atmosphere of neutral gas.

5. The method of manufacturing a thermionic cathode which comprises the steps of mixing alkali earth metal peroxide with a binder consisting of a solution of nitro-cellulose in amyl acetate, shaping the mass of such material, heating the shaped mass in a vacuum to the decomposition temperature of the peroxide, placing said mass on a tungsten support and then raising said mass to the sintering temperature thereof in an atmosphere of neutral gas.

6. The method of manufacturing a thermionic cathode which comprises the steps of mixing alkali earth metal peroxide with a binder consisting of a solution of nitro-cellulose in amyl acetate, shaping the mass of such material, heating the shaped mass in a vacuum to the decomposition temperature of the peroxide, placing said mass on a magnesia support and then raising said mass to the sintering temperature thereof in an atmosphere of neutral gas.

7. The method of manufacturing a thermionic cathode which comprises the steps of forming a mass of desired shape out of materials in which alkaline earth metals are present in the form of their peroxide, decomposing the peroxide by heat and then raising said mass to the sintering temperature therof.

8. The method of manufacturing an electron emitting electrode which comprises the steps of mixing alkali earth metal peroxide with a binder having a lower decomposition temperature than the peroxide, shaping the mass of such material and decomposing first the binder and then the peroxide by heat.

9. The method of manufacturing an electron emitting electrode which comprises the steps of mixing alkali earth metal peroxide with a binder having a lower decomposition temperature than the peroxide, shaping the mass of such material, heating the shaped mass to the decomposition temperature first of the binder and then of the peroxide and then raising said mass to the sintering temperature thereof.

JOHN TURTON RANDALL.