# United States Patent [19]

**Koppius**

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[54] **IMPREGNANTS FOR DISPENSER CATHODES**


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[52] **U.S. Cl.**.....**313/346 DC,** 313/311, 313/346 R

[51] **Int. Cl.**.....**H01j 1/14,** H01j 19/06

[58] **Field of Search**.....313/346 R, 346 DC, 311



[56] **References Cited**

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| | | | |
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| 2,813,807 | 11/1957 | Levi | 313/346 R X |
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[57] **ABSTRACT**

A dispenser cathode suitable for use as an electron emitter for microwave tubes and the like. The dispenser cathode is constituted by a porous body of refractory material such as tungsten, impregnated with a fused mixture of barium oxide, and at least one oxide of a rare earth metal, such as holmium oxide, terbium oxide, thulium oxide or yttrium oxide.


**4 Claims, 7 Drawing Figures**

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FIG. 1.




FIG. 2.




FIG. 3.

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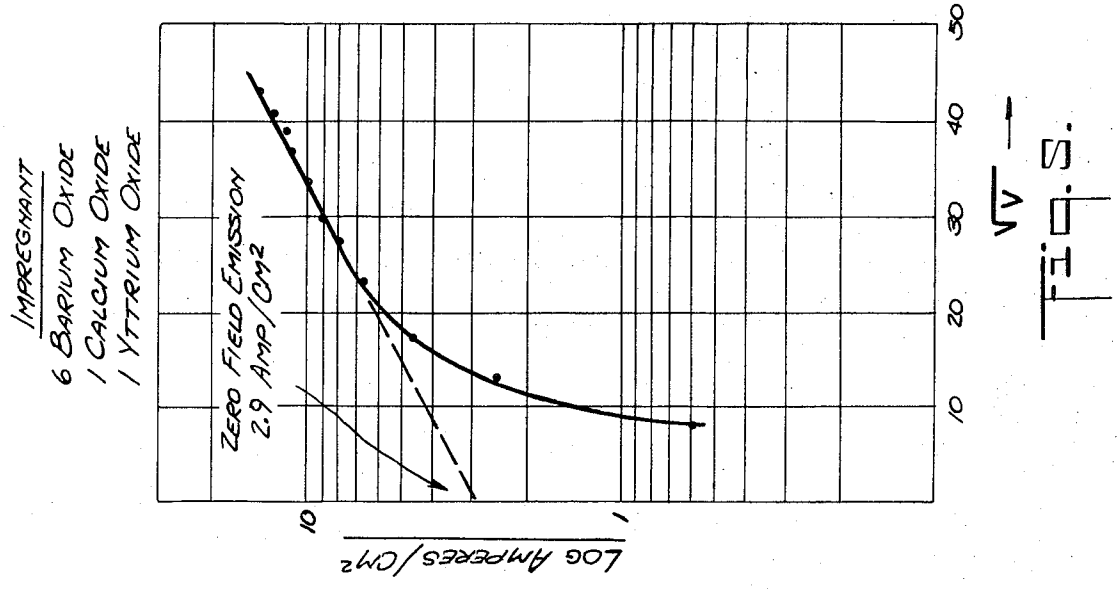


FIG. 3.

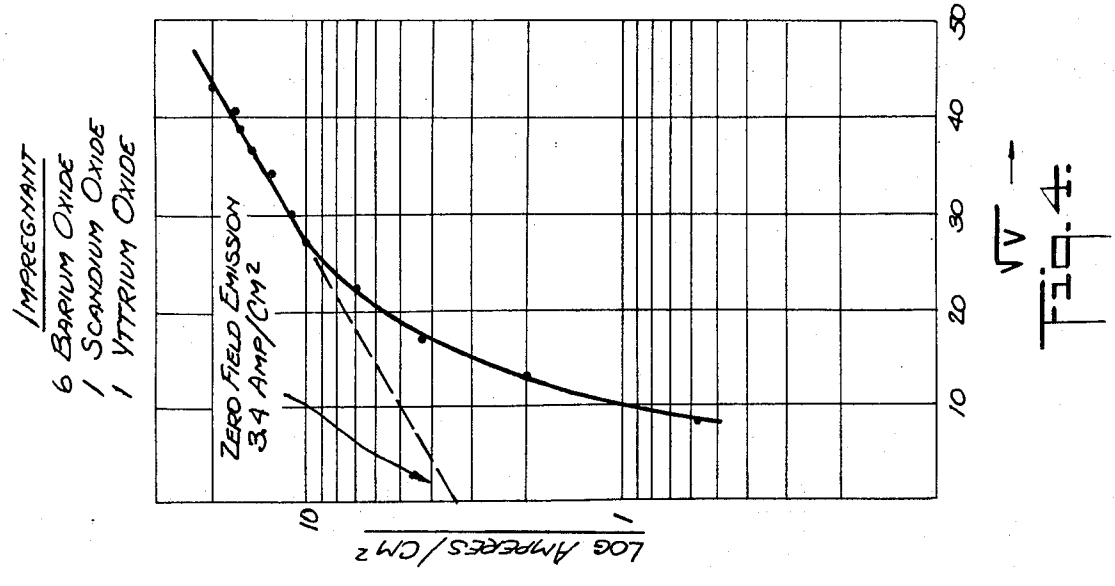


FIG. 4.

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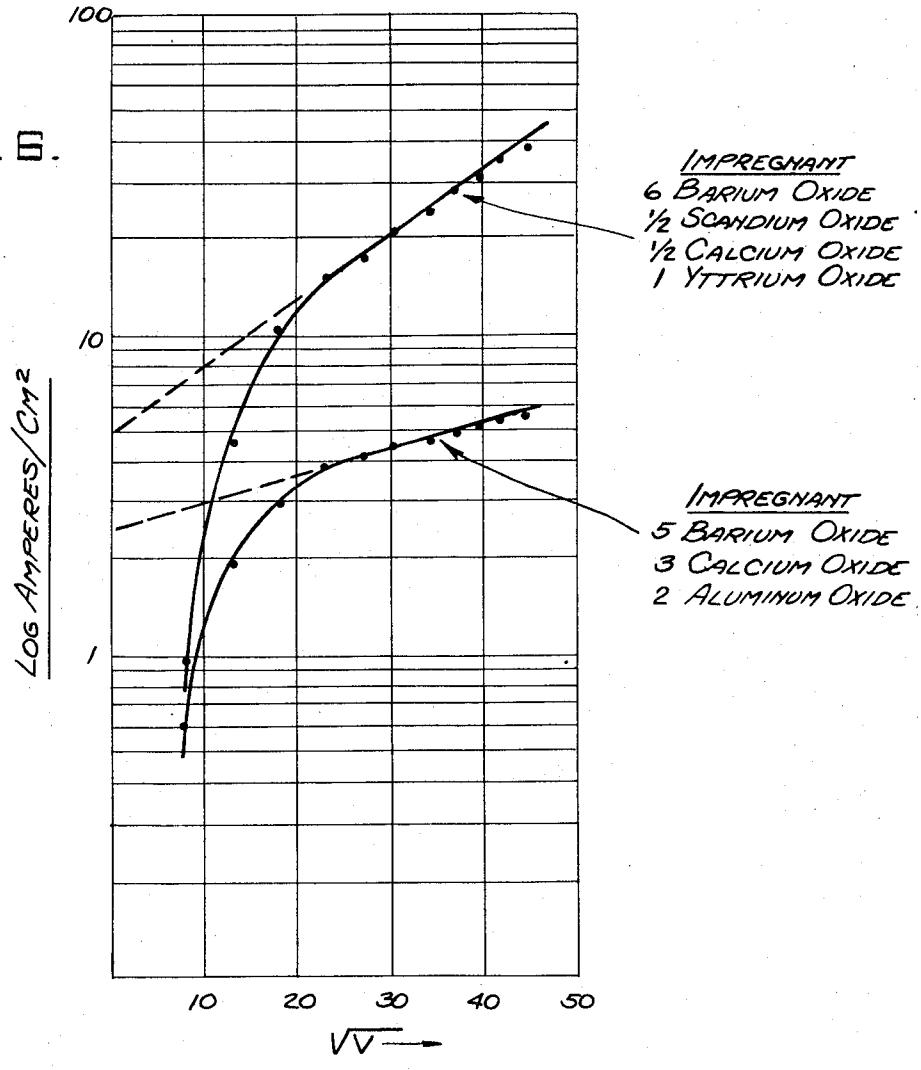
Fig. 6.



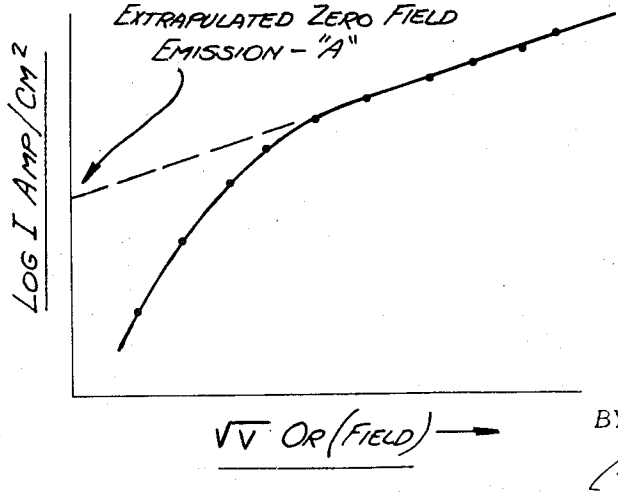




Fig. 7.

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# IMPREGNANTS FOR DISPENSER CATHODES

## BACKGROUND OF THE INVENTION

The present invention relates generally to dispenser cathode structures, to methods for fabricating such structures and to improved impregnants therefor.

Dispenser cathodes are known in which a porous body of a refractory metal such as tungsten is impregnated with a supply of an alkaline earth composition capable of furnishing free alkaline earth metal to the cathode surface. In the U.S. Pats. Nos. 2,700,000, 2,813,807, 3,118,080 and 3,201,639, there are disclosed dispenser cathodes in which a preformed porous body of refractory metal is impregnated from a melt with a fused mixture of barium oxide and one or more other metal oxides. During operation of the cathode, the mixture reacts with the refractory metal to supply free barium to an emissive surface of the cathode.

The refractory metal body of such cathodes may be formed by compressing a finely divided powdered metal to form a green body and heating the body to an elevated temperature at which the particles sinter together and form a cohesive mass which is dense yet porous. To work this dense, hard, porous mass of refractory material into intricate bodies suitable for commercial microwave tube structures adapted to deliver moderate to high power in the megawatt range, I prefer to use the technique described in my prior U.S. Pat. No. 3,538,570.

The pores in such a body thus obtained may now be filled with an alkaline earth composition. The alkaline earth metal composition is first heated to a temperature at which the composition melts in a neutral or reducing atmosphere. The porous body is then brought into intimate contact with the molten material, as by immersing the porous body in the molten material, or by placing the material on the body and converting it to a molten state. While in the molten state, the material flows or diffuses into the pores of the body and completely fills all voids within the porous body.

After cooling, the body is mounted in an evacuated envelope and activated by heating to a temperature at which the alkaline earth composition reacts with the refractory metal to supply alkaline earth metal which covers the surface of the body. The cathode is now ready for operation as an electron emissive device.

As the refractory metal, tungsten is preferred, but molybdenum, hafnium, tantalum, niobium, and rhenium may be used.

The alkaline earth metal composition is the most critical material for the formation of high quality electron emitting cathode structures. The exact manner in which each component of the alkaline earth metal composition plays in the role of an electron emitter is unknown. Presently in widespread commercial use are dispenser cathodes of the type disclosed in the Levi U.S. Pat. No. 3,201,689 wherein the impregnant is a fused mixture of barium oxide and at least one oxide selected from the group consisting of aluminum oxide and boron oxide.

## SUMMARY OF THE INVENTION

The main object of the invention is to provide a dispenser cathode whose impregnant is constituted by a composition containing barium oxide and an oxide of a rare earth element.



Quite unexpectedly, I have found that impregnant compositions containing barium oxide and the oxides of the rare earth elements, produce dispenser cathodes which are exceptionally good electron emitters and which perform better than those which are now commercially available.

The chemical elements grouped with lanthanum in the periodic table — numbers **57** through **71**, are traditionally referred to as rare earth elements. In recent years, the term, "rare earth elements" has been extended to include two outlying elements, namely scandium (element **21**) and yttrium (element **39**), which fall in the same group (IIIB) of the periodic table. The term "rare earth" is really a misnomer, for the elements in the group are not rare as compared to gold or platinum, and they are not earth, but true metal.

In order of increasing atomic number, the rare earths are scandium (symbol Sc); yttrium (Y); lanthanum (La); cerium (Ce); praseodymium (Pr); neodymium (Nd); promethium (Pm); samarium (Sm); europium (Eu); gadolinium (Gd); terbium (Tb); dysprosium (Dy); holmium (Ho); erbium (Er); thulium (Tm); ytterbium (Yb); and lutetium (Lu).

More specifically, it is an object of the invention to provide an improved impregnant for a dispenser cathode which consists of a fused mixture of barium oxide and an oxide of a rare earth metal.

Briefly stated, these objects are attained in a thermionic dispenser cathode, comprising a porous body of refractory material, preferably tungsten, having at least one surface portion adapted to afford an electron emission surface provided with a large number of small passageways connecting the interior of said body to said surface.

Dispersed within the body is an impregnant constituted by a fused mixture of barium oxide and at least one rare earth oxide in a mole ratio providing relatively high emission.

## OUTLINE OF THE DRAWING

For a better understanding of the invention as well as other objects and further features thereof, reference is made to the following detailed description to be read in conjunction with the accompanying drawing, wherein:

FIG. **1** is a graph showing the emission of a dispenser cathode whose impregnant includes holmium oxide;

FIG. **2** is a graph showing the emission of a dispenser cathode whose impregnant includes terbium oxide;

FIG. **3** is a graph showing the emission of a dispenser cathode whose impregnant includes thulium oxide;

FIG. **4** is a graph showing the emission of a dispenser cathode whose impregnant includes scandium oxide and yttrium oxide;

FIG. **5** is a graph showing the emission of a dispenser cathode whose impregnant includes calcium oxide and yttrium oxide;

FIG. **6** is a graph showing the emission of a dispenser cathode whose impregnant includes scandium oxide; calcium oxide and yttrium oxide; and

FIG. **7** is a plot illustrative of the emission test procedure.

## DESCRIPTION OF THE INVENTION

Promethium and Lutetium are not commercially produced in any quantity and have not therefore, been

tested in cathode structures. The commercially available rare earth oxides which were tested are Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, and Ytterbium. The oxides of Yttrium and Scandium were tested as carriers for barium oxide in cathodes.

Each of the above-mentioned oxides were mixed with barium oxide in the mole ratio of 3:1, i.e., (3 BaO: 1 Rare Earth). Such compositions were mechanically mixed, calcined at 1,200° C to remove the carbon dioxide, reground, then melted in a neutral or reducing atmosphere, and again reground. The final reground impregnant was stored in a vacuum dessicator until used. Each of the above-mentioned impregnants were used as an electron emissive material.

A small amount of the impregnant material was placed on a test cathode porous tungsten body and impregnated by melting as described previously. The theoretical density of the porous tungsten body was 82 percent in all tests. The impregnation time was 2 minutes. Such test cathodes were mounted in a suitable diode structure, evacuated, and tested for electron emission capabilities as will be described later.

All rare earth oxide elements tested in such a manner were electron emitters, some were better than others, and some had different degrees of evaporation of the metal barium. Of the available rare earth oxides, I prefer to use Holmium oxide, Terbium oxide, and/or Thulium oxide. These gave exceptionally good electron emission, long life, and a very low metal barium evaporation. The emission curves are shown in FIGS. 1, 2, and 3.

FIG. 1 is a graph showing the emission of a dispenser cathode impregnant which is a fused mixture of 3 moles Barium oxide and 1 mole Holmium oxide; FIG. 2 is a graph for an impregnant which is a fused mixture of 3 moles Barium Oxide and 1 mole Terbium oxide; FIG. 3 is a graph for an impregnants which is a fused mixture of 3 moles Barium oxide and 1 mole thulium oxide.

The zero field emission at 1,000° C Br (Brightness) was found to be 3.3, 2.9 and 2.6 amps/cm² respectively for the three different impregnants. The melting point of the impregnants are 1,790° C, 1,750° C, and 1,800° C respectively. Test cathodes made with Scandium oxide gave high emission, good life, but the amount of barium evaporation was much too high. The melting point of 3 BaO: 1 $Sc_2O_3$ composition was 1,710° C. Cathodes made from Yttrium oxide gave good emission, low barium evaporation, but were difficult to impregnate. The melting point of 3 BaO: 1$Y_2O_3$ mixture was 1,950° C. Such a high melting point complicates other procedures which make a cathode attractive commercially. Many cathode structures need a potted heater and the high melting point of the impregnation step causes undue shrinkage of the heater potting material.

A combination of barium oxide, scandium oxide and yttrium oxide was made and tested. The mole combination was:

6 Barium oxide

1 Scandium oxide

1 Yttrium oxide.

The melting point was found to be 1,790° C. The impregnation time was 2 minutes. The zero field emission was 3.4, as shown in the graph in FIG. 4, and the amount of metallic barium evaporation was moderate.

A combination of barium oxide, calcium oxide, and yttrium oxide was made and tested. The mole combination was:

6 Barium oxide

1 Calcium oxide

1 Yttrium oxide.

The melting point was found to be 1,730° C. The impregnation time was 2 minutes. The zero field emission was 2.9, as indicated by the graph in FIG. 5 and the amount of metallic barium evaporation was very low. It is to be noted that each of these impregnants has a zero field emission better than the one now used commercially, the published value of which is 2.5 amps/cm² at 1,000° C Br. Further it is to be noted that the addition of scandium oxide and/or calcium oxide reduced the melting point of the barium oxide/yttrium oxide combination to values that are practical, i.e., to a melting point of about 1,800° C or lower.

A combination of barium oxide, calcium oxide, scandium oxide and yttrium oxide gave surprising results. The optimum mole ratio combination was found to be:

6 BaO (barium oxide)

½$Sc_2O_3$ (scandium oxide)

½CaO (calcium oxide)

1 $Y_2O_3$ (yttrium oxide)

i.e., 6 BaO; ½$Sc_2O_3$:½CaO: 1 $Y_2O_3$ where the number of moles of barium oxide can vary between 5 and 7. The melting point of these combinations are 1,740° C; 1,680° C and 1,690° C for 5,6, and 7 moles of barium oxide, respectively, with the other components remaining fixed.

The impregnation time can vary between 30 sec. and 2 min. with 1 minute being optimum for full impregnation. The melting point of all three combinations is well within practical limits for the performance of other procedures that must be accomplished for producing commercially acceptable cathodes. Additionally, I was surprised to find that cathodes made with this impregnant gave unusually high zero field emission of about 5 amps/cm² at 1,000° C. In addition, the evaporation of metallic barium from the cathode is very low and the emission life is in excess of 2,000 hours.

The graph in FIG. 6 shows the pulsed emission test data of the new impregnant as compared to a commercially used type containing barium oxide, aluminum oxide, and calcium oxide in about a mole ratio 5:2:3. The zero field emission of the new impregnant is about a factor of two better.

In addition, there is one other surprising difference between the two impregnants. The pulsed electron

emission of the new impregnant has a very much higher slope at high field strength than the other. ( $\sqrt{V}$ is proportional to Field Strength). The performance of the new cathode impregnant was found to be much better in devices which require a high field strength at the cathode. Most magnetron tubes and some ion gas laser tubes require such a cathode characteristic for maximum performance.

I shall now describe the emission procedures developed in connection with my new impregnants.

Conventional planar test diodes were made to determine the emission characteristics of the new electron emissive impregnants. Also, conventional Schottky plots were made for each cathode under pulsed conditions. The zero field emission at any given temperature represents a figure of merit of a cathode. It is a value whereby one can compare performance data. The method by which it is determined will be given presently.

The diodes were simple glass bulbs containing a molybdenum plate and the test cathode along with a suitable cathode electrical heater. These were mounted on a glass stem having molybdenum feed-through leads. A barium getter was positioned on one lead in such a way that when flashed it would not interfere with the tests. The plate-to-cathode spacing was 0.75 mm. This device was thoroughly evacuated, baked, and sealed from the pumping system. Life tests of the cathode were run at 1,050° C Br. with sufficient plate voltage to run the plate red hot. Evaporation of metallic barium could be observed with time from a darkening of the glass bulb. Also emission data could be taken as a function of time and temperature.

The standard Schottky equation relates the emission from the cathode with the applied plate voltage (or Field). The Schottky equation equates the Richardson emission equation with the voltage or field enhanced emission. For high plate voltages and for a fixed temperature the equation approaches a straight-line equation of the form $y = a + bx$; where $b$ is the slope and $a$ is the $y$ intercept when $x = 0$. The Schottky equation becomes:

$$\log I = A + B \sqrt{V}$$

where $A$ is related to the Richardson emission and is a constant for a fixed value of the cathode temperature, and $B$ is the slope of the straight line portion. It is a constant for a fixed value of the cathode temperature. I is the emission current in amperes/cm$^2$.

Thus an extrapolation of the straight line portion to zero plate voltage gives the intercept $A$, which value represents the emission of the cathode at zero field (plate voltage). A typical plot has the appearance shown in the graph illustrated in FIG. 7. The Schottky equation is:

$$\log I = \log \left( AoTc^2 e^{\frac{-e\phi}{kTc}} \right) + \frac{(300\sqrt{e10^7})}{(kTc\sqrt{d})} \cdot \sqrt{V}$$

Constant A Constant B

$$\log I = A + B\sqrt{V} \qquad \text{(At constant } Tc\text{)}$$

where Field $= \sqrt{v/d}$ $\quad I =$ amperes/cm.$^2$

Pulsed emission test data were taken at 1,000°C Br. on each cathode. The pulser applied a 60 microsecond pulse 60 times per second to the test diode. The total emission current in amperes/cm$^2$ was measured as a function of the square root of the plate voltage.

Data were plotted for each test cathode on semilogarithm paper. These are shown on the attached graphs along with the zero field extrapulated intercept in amperes/cm$^2$.

While there have been shown and described preferred embodiments of impregnants for dispenser cathodes in accordance with the invention, it will be appreciated that many changes and modifications may be made therein without, however, departing from the essential spirit of the invention.

I claim:

1. A thermionic dispenser cathode comprising a porous body of refractory metal having at least one surface position adapted to afford an electron-emission surface, and provided with a large number of small passageways connecting the interior of the body to said surface, and an impregnant disposed within said body and constituted by a fused mixture of barium oxide, yttrium oxide and at least one rare earth oxide selected from the class consisting of calcium oxide and scandium oxide in a mole ratio providing relatively high emission.

2. A cathode as set forth in claim 1, wherein said fused mixture consists essentially of 6 moles barium oxide, 1 mole calcium oxide, and 1 mole yttrium oxide.

3. A cathode as set forth in claim 1, wherein said fused mixture consists essentially of 6 moles barium oxide, 1 mole scandium oxide, and 1 mole yttrium oxide.

4. A cathode as set forth in claim 1, wherein said fused mixture consists essentially of 6 moles barium oxide, one-half mole scandium oxide, one-half mole calcium oxide, and 1 mole yttrium oxide.

* * * * *