

UNITED STATES PATENT OFFICE

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VACUUM ELECTRIC TUBE

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This invention relates to vacuum electric tubes and particularly to electron-emitting cathodes of the oxide coated type. These cathodes of say platinum or platinum-iridium are usually coated with oxides of calcium, barium or strontium for example, or a mixture of such oxides. In practice a common method is to apply a coating of a compound of the metal, usually the nitrate, with an organic binder, by painting or dipping the cathode; which binder is subsequently removed by heating in an oxidizing atmosphere and the compound decomposed to the oxide.

According to this invention an electron-emitting cathode of the type above referred to is produced in the following manner. The cathode is first coated with the metal, or a mixture of the metals of the compounds which form the electron-emitting coatings, and the metal surface is then converted to the compound desired by suitable means. For instance, a cathode consisting of a sheet, wire or filament of suitable material may be coated with an alkaline earth metal, such as calcium, barium or strontium, or a mixture of these metals in any desired proportion and the surface then oxidized by contact with, or heating in, air or oxygen. The cathode base or support for the coating may consist for example of tungsten, molybdenum, platinum, platinum-iridium alloy, or carbon. The coating metal may be applied to the support by electro-deposition, by precipitation or deposition from a compound which readily decomposes into the metal on heating, or by deposition by means of cathode sputtering in vacuum. In the latter case the alkaline earth coating metal may be volatilized on to the metal base by placing the base over or near to the alkaline earth metal, which is then heated in a vacuum; or alternatively the alkaline earth metal may be sputtered on to the base by means of a glow discharge.

In the preferred method of carrying out the invention an alkaline earth metal is applied to the support or base by electro-deposition. Preferably the metal is deposited from a solution of the iodide in acetone using the support or base as the cathode for electrolysis. The metal is then converted to oxide by heat-

ing in air, or alternatively it may be totally or partially oxidized while it is still immersed with the support in the acetone solution, the support or base being heated subsequently in air.

The invention will be particularly described by way of example, in its application to coating a cathode of platinum or molybdenum with the oxides of alkaline earth metals. As hereinbefore stated, preferably the alkaline earth metal is deposited on the filament by electrolysis of an acetone solution of the iodide. To prepare the electrolytic solution in one method a quantity of one of the alkaline earth metal iodides is placed in a distilling flask and heated in a current of hydrogen to a temperature between 180° C. and 200° C., for a period of at least two hours, in order to secure complete dehydration. The dehydrated iodide is then mixed with pure acetone and the solution is made up with acetone to about half normal strength. In another method of preparing the electrolytic bath, the iodide of an alkaline earth metal is dissolved in acetone and the resulting solution is dried over anhydrous sodium sulphate or calcium chloride for two or three days.

The cathode of platinum is first cleaned by placing it in concentrated nitric acid followed by ammonia or by boiling in caustic soda solution, with subsequent washing in water. If tungsten or molybdenum is employed for the cathode, then it is cleaned in the case of wire by heating in hydrogen; or in the case of sheet or tube by dipping it into molten sodium or potassium nitrate, which is finally carefully removed from the cathode by washing. The cathode is then lowered into the electrolytic depositing bath. It is obvious that a number of cathodes may be coated at the same time, and that they may be in any suitable form, such for example as hairpin loops. The metal is electrolytically deposited on the filament to the required thickness, and for this purpose the voltage effecting deposition is advantageously continuously raised from a low to a high value during deposition; sometimes it is found that 100 volts are finally necessary to keep the deposition current fairly constant. The filament is advantageously

coated with a mixture of alkaline earth metals rather than with a single alkaline earth metal. This may be effected by two electrolytic deposition processes employing solutions of strontium iodide and barium iodide. The filament is placed alternately in each electrolytic bath thus coating it with alternate layers of strontium and barium; or it may be coated with two layers only. The metals deposited alloy with each other when the filament is subsequently heated. Or a mixture of barium and strontium may be deposited from a single electrolytic bath containing a solution of mixed barium and strontium iodides.

After coating, the filament with the desired alkaline earth metal is removed from the bath and the metal coat is converted to oxide. This may be effected in various ways. For example it is sufficient to leave the filament in dry air, but it is preferable to heat it to a temperature between 600° C. and 700° C. in air for half-an-hour to two hours. By this means the coated metals are alloyed with each other, converted to oxides and the oxide coating firmly bonded to the filament.

The oxide coat produced by any of the above described processes may then be converted if desired to a carbonate coat. A filament with a carbonate coating can be handled with ease, and can be left in a moist atmosphere without injury, before its subsequent assembly in a valve, whereas an oxide coated filament often requires a further protective coating. The carbonate coating is produced by heating the oxide coated filament to a dull red heat in carbon dioxide and permitting it to cool in an atmosphere of the same gas. In this method of preparation the filament is heated to between 600° C. and 700° C. in air, for about 10 minutes, after removal from the depositing bath, and is then heated in a stream of carbon dioxide for about 30 minutes, the filament being left cold in the carbon dioxide for a further 30 minutes. On assembly within the valve the carbonate is reconverted to oxide by heating.

The coat may be oxidized while it is still in the depositing bath by permitting a little water to be present. The coating is deposited as metal and is then oxidized by the water present in the solution, the cathode subsequently being heated. The exact action of the water is not known, but it appears that a complex oxygen compound is formed probably combined with acetone. Although this method of production is not preferred it may sometimes be employed for coating special cathodes.

When the supporting base consists of a material which is capable of alloying with the alkaline earth metals at a temperature below the volatilizing point of said metals, such for example as platinum, then the alkaline earth metal may be alloyed thereto by heating out

of the presence of oxidizing gases before the oxidizing process is effected. For instance, a platinum filament coated with a mixture of barium and strontium metal may be heated for a few moments in pure hydrogen, whereby subsequently a more homogeneous and a more firmly bonded coat is obtained. It will be realized, however, that this alloying process cannot be carried out when metals such as molybdenum or tungsten form the supporting base.

Although it is better to heat the filament in an inert or non-oxidizing atmosphere when it is desired to alloy it to the supporting base, it is not necessary for if the base is clean and the metal coat is not very porous, small but appreciable alloying will occur if the filament is flashed in air. Preferably in this case the filament is flashed for a moment or two to a temperature of say 1100° C. to 1200° C. after which period it is baked in the usual manner.

For some purposes it is desirable however that the barium and strontium metal should not be alloyed to the base, since often the subsequently produced oxides are found to have eaten in to the base, thus making it brittle. If the base is in the form of a thin filament, the uniformity of its resistance is thus destroyed.

If the supporting base consists of a strong refractory metal, such as molybdenum or tungsten then after being coated it is preferably not heated in air, since oxidation of the molybdenum or tungsten takes place and the coating falls off. In this case, the coated tungsten or molybdenum is heated for about ten minutes at a dull red heat in hydrogen of commercial purity. There is sufficient oxygen or oxygen containing material such as water present in the hydrogen and in the metal support to effect partial or complete oxidation of the alkaline earth metal deposits. The coating may then be converted to carbonate if desired in the manner described above.

By the use of this invention cathodes of tungsten and molybdenum may be coated with an adherent coating of alkaline earth oxides or a mixture of these; and it is particularly applicable to cases in which the cathode is not filamentary such for example, as when it consists of a sheet or tube of tungsten or molybdenum.

It is understood that the invention may be applied generally to the coating of cathodes with compounds or mixtures of compounds of any metal for obtaining a desired electron emission, and is not limited to the processes described by way of example.

I claim as my invention:—

1. The method of making electron-emitting cathodes for vacuum electric tubes by coating a suitable support with at least one metal, converting said coating into a compound which has desired electron-emitting

properties, and then converting said coating to a carbonate by heating in an atmosphere of carbon dioxide, whereby the cathode can readily be handled before assembly.

5 2. The method of making an electron-emitting cathode of the oxide-coated type, which consists in producing on a metal cathode a coating of at least one alkaline earth metal and substantially simultaneously oxidizing
10 said coating.

3. The method of making an electron-emitting cathode of the oxide-coated type, which consists in depositing on a metal cathode a coating of at least one alkaline earth metal
15 and substantially simultaneously oxidizing said coating.

4. The method of making an electron-emitting cathode of the oxide-coated type, which consists in electrolytically depositing on a
20 suitable support a coating of at least one alkaline earth metal from a solution thereof in acetone containing a trace of water.

5. The method of making an electron-emitting cathode of the oxide-coated type, which
25 consists in producing on a metal cathode a coating of at least one alkaline earth metal and substantially simultaneously oxidizing said coating while out of contact with atmospheric air.

30 In testimony whereof I have hereunto subscribed my name this ninth day of May, 1924.

ERNEST YEOMAN ROBINSON.

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