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COLD CATHODE AND METHOD OF PREPARING SAME

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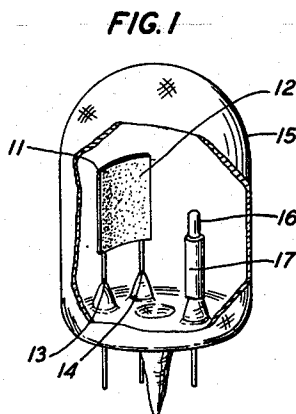


FIG. 2

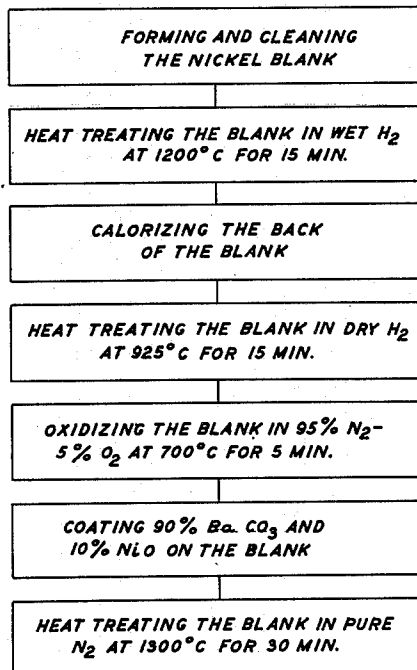
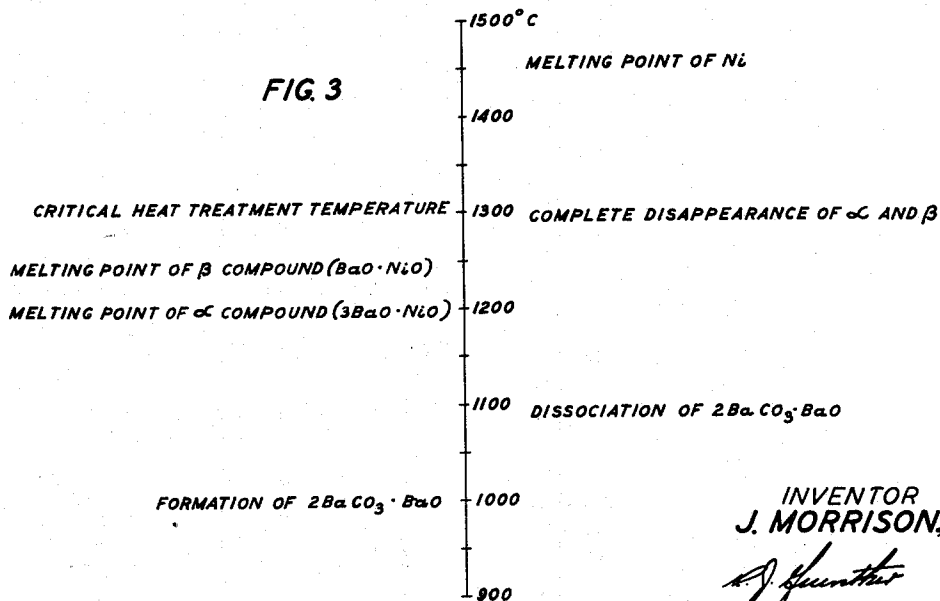


FIG. 3



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COLD CATHODE AND METHOD OF
PREPARING SAME

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This invention relates to electron emissive cathodes and more particularly to the preparation of activated surfaces for cold cathodes especially suitable for use in gaseous discharge devices.

Gaseous discharge devices of the cold cathode type are often used in switching operations, as in telephone circuits. In such circuits they are mainly unattended and must have a long operating life expectancy. Prior coatings on the cathode of such devices have greatly limited the life expectancy of the device. These prior coatings, generally of alkaline earth, for example barium and strontium, oxides on a nickel cathode blank, were necessarily too thin for long life expectancy. The thin coating was required by the activation process which comprised application of a series of condenser discharges through the device with peak currents of many amperes. During this process, tiny arcs play over the cathode surface converting the appearance and organization of the surface. However, the activation will not proceed smoothly if the coating thickness is greater than about 1 milligram per square centimeter. Since this activation process dislodged particles of the coating and during the course of life the coating is slowly sputtered off, the life, of course, being dependent upon the amount of coating present, the method of activation prevented attainment of a long life cathode.

Not only is a long life required of such devices but in most operations a low sustaining voltage is prerequisite. Thus, in many uses a sustaining voltage of below 70 volt is required. The sustaining voltage of the final coating is dependent both on the composition of the coating and on the temperature, and hence technique, of activation.

It is an object of this invention to provide an improved cathode coating.

It is another object of this invention to provide a thick surface coating.

It is a further object of this invention to provide such a coating having a long life and a low sustaining voltage.

In accordance with a feature of this invention, the cold cathode surface consists essentially of a mixture of 90 per cent barium carbonate and 10 per cent nickelous oxide by weight sprayed on a nickel surface and heat treated at about 1300° C. for thirty minutes.

It has previously generally been the trend to decrease the temperature of the heat treatment required for activation by the appropriate choice of the composition percentages and particularly by increasing the percentage of nickel. It is a

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feature of this invention, however, that particular percentages of barium carbonate and nickelous oxide when heated to particular critical high temperatures produce a cathode coating having a calculated operating life of forty years and a sustaining voltage of less than 70 volts, which critically high temperature runs counter to the general trend and teaching of the art.

It is a feature of this invention that an initial thick coating of 90 per cent barium carbonate and 10 per cent nickelous oxide be placed on a nickel blank and heat treated above 1300° C.

It is a part of the discovery of this invention that when nickelous oxide and barium carbonate are heated, various compounds and eutectics are formed.

It is thus a further feature of this invention that the heat treatment be carried on so that an eutectic of barium carbonate and barium oxide be formed during the heat treatment and then be dissociated.

It is thus a further feature of this invention that the temperature of the heat treatment be such as to cause compounds formed in the BaO-NiO system to disappear, the temperature being about 1300° C.

It is a still further feature of this invention that the activated cathode surface be of barium oxide with about 2 per cent of very finely dispersed nickel, the surface having a velvety brown coloration.

A complete understanding of this invention and of the various features thereof may be gained from consideration of the following detailed description and the accompanying drawing, in which:

Fig. 1 shows a gaseous discharge device employing the cathode coating of this invention;

Fig. 2 lists the steps in the process of preparing the cathode surface; and

Fig. 3 is a temperature diagram illustrating the changes in the cathode surface during the heat treatment activation.

Referring now to the drawing, Fig. 1 shows one cold cathode gaseous discharge device wherein the coating of this invention may be utilized. A cathode 11 having the activating coating 12 of this invention thereon is supported by two leads 13 and 14 in an evacuated glass envelope 15. A wire anode 16 having a ceramic insulating cylinder 17 around its lower portions is positioned opposite the cathode 11.

The cathode 11 is prepared in accordance with the steps outlined in Fig. 2. A nickel cathode blank is degreased by rinsing in trichloroethylene and then heat treated in wet hydrogen for fif-

teen minutes at 1200° C. The heat treatment is to clean and degrease the surface since the trichloroethylene rinse has been found to be not wholly effective. The back of the cathode blank is then rendered inactive so that there will be no glow discharge on this part of the cathode, as by being sprayed with a suspension of aluminum in amyl acetate solution, though other glow deterrents may be employed. The calorized blanks are then heat treated in dry hydrogen for fifteen minutes at 925° C. and this treatment sinters and oxidizes the aluminum on the nickel, there being a sufficient impurity of oxygen present in the system to oxidize the readily oxidizable aluminum. The blanks themselves are then oxidized by heating for five minutes at 700 degrees in a mixture of 95 per cent nitrogen, 5 per cent oxygen in order to increase the ability of the fused coating to wet the surface. It has also been found that this light oxidation is a sensitive and efficient method for indicating the presence of surface impurities. The cathode blanks are now ready for the application of the coating material.

The coating consists essentially of a mixture of 90 per cent barium carbonate and 10 per cent nickelous oxide by weight sprayed on the nickel surface using pyroxalin in amyl acetate solution as a vehicle. In one specific embodiment, the nickelous oxide used is passed through a 400 mesh sieve before mixing with the barium carbonate. In this particular embodiment, the mixture of barium carbonate-nickelous oxide in amyl acetate solution was sprayed on the prepared cathode blank by an air brush to a coating weight of 3.3 milligrams per square centimeter.

The cathode blank with this surface is then processed by heat treatment in pure nitrogen for thirty minutes at substantially 1300° C. The furnace, in one specific technique, may be at 700° C. with purified nitrogen flowing there-through when the cathode blank is introduced. The temperature is then raised in about twenty minutes to 1300° C. where it is held for thirty minutes. The cathode is allowed to cool in the furnace until the temperature is below 600° C. when it may be removed. After removal it should be kept in an evacuated container until ready for use in a device, such as shown in Fig. 1. It has been found very advantageous in this processing that pure nitrogen be employed as any oxygen impurity in the gas will tend to fuse the coating to the extent that it will become molten and run off the nickel base.

The cathode surface following this heat treatment at 1300° C. will be in an active state. Following its incorporation in a device such as shown in Fig. 1, the cathode surface is brought to a uniform state of activation by drawing a higher than normal current density for a period of one to two hours. The normal or operating current density of the tube will depend on the geometry of the tube and the activating current may be twice this value.

Referring now to Fig. 3, the coating material has been found to undergo several changes from the time it is placed in the furnace tube at 700° C. to the end of its half hour treatment at 1300° C., which have definite bearing on the determination of 1300° C. as the critical temperature for the optimum results with the specifically determined percentages of initial compounds. There is a low temperature melting observed at 1000° C. to 1050° C. which is, it is believed, due to the formation of a eutectic with the probable com-

position $2\text{BaCO}_3\cdot\text{BaO}$. This eutectic disappears with the dissociation of the barium carbonate between 1050° C. and 1100° C. A second stage of melting is observed in the temperature range between 1200° C. and 1300° C. In this range, with the dissociation of BaCO_3 priorly complete, the melting is due to products of NiO and BaO. The NiO itself decomposes without melting at 1450° C. in 10^{-4} atmospheres of oxygen and without melting at 2000° C. in air. Moreover, melting of BaO alone would not be observed since its melting point is 1923° C. It has been found that there are two compounds which are formed at temperatures above the dissociation of the $2\text{BaCO}_3\cdot\text{BaO}$ eutectic and which cause this second stage of melting. A compound $3\text{BaO}\cdot\text{NiO}$, called α , has a melting point at about 1200 degrees and a compound $\text{BaO}\cdot\text{NiO}$, called β , has a melting point at about 1250 degrees.

Partial fusion of the mixture of these compounds takes place and this is followed by gradual solidification of the mixture since in pure nitrogen at 1300° C. the NiO is reduced. It is thus apparent that it is essential that the temperature of the heat treatment be raised to about 1300 degrees in order to remove traces of these undesirable compounds.

In order to attain the high temperature heat treatment at 1300° C., it is not essential that the eutectic between BaCO_3 and BaO be formed at 1000° C. Thus if the temperature of the heat treatment were first brought to 950° C. and maintained there for a sufficient period of time, such as five or ten minutes, there would be a complete decomposition of the carbonate in the nitrogen atmosphere. Further heating into the 1000° C. through 1050° C. range would produce no signs of melting nor formation of this eutectic. However, it has been found highly advantageous that the temperature of the heat treatment be raised to about 1300° C. in such steps as will insure the formation and subsequent disappearance of the $2\text{BaCO}_3\cdot\text{BaO}$ eutectic.

This heat treatment is carried on entirely at atmospheric pressures, to which these melting points refer. The nickel blank itself, it is to be remembered, will melt at 1455° C. It has been found that the blank is deleteriously affected when the temperature is raised to 1400° C. Therefore for these particular percentages and compounds, which are necessary for the multiple beneficial results obtained, the range of possible temperatures of heat treatment is about 1300° C. to 1400° C. It has been found however, that for optimum results treatment at 1300° C. is most advantageous.

It is believed that the various compounds formed during the processing of the cathode blank are important for the preparation of the active surface. Thus the fusion is believed to be necessary for the proper incorporation of the nickel as an impurity in the BaO lattice, resulting in a coating of higher electrical conductivity. Therefore the heat treatment must be carried beyond such temperatures and in such a manner as will insure the formation of the compounds. However, while it is a part of the discovery of this invention that these compounds have performed a beneficial role in the changes occurring in the orientation, composition and lattice structure of the coating, the heat treatment must further be carried out in such a manner and in such a way as to dissociate and remove them.

Cathodes prepared in the manner of this invention have been tested in order to determine

the final constituents. Within the limits of X-ray analysis, the final surface is indistinguishable from pure BaO. Chemical analysis, however, shows that there is still 1 to 3 per cent of nickel in the active coating. The coating itself has a velvety brownish coloration which is quite different from the pure white of the BaO, and its electrical properties in a gas discharge are also observed to be different. It can, therefore, be concluded that the coating consists of about 98 per cent BaO with about 2 per cent of very finely dispersed nickel which is not readily detected by X-ray analysis. This nickel, some of which may be in solid solution in the BaO lattice, apparently modifies the electrical properties of the BaO so as to give an active cathode surface.

These cathodes prepared in the manner of this invention may have coatings of any desired thickness and still retain the other advantageous features of the activated coating and the low sustaining voltage. Certain exemplary cathodes have been prepared with final coatings having thicknesses but little below the initial coating of 3.3 milligrams per square centimeter, and a sustaining voltage of below 62 volts, which values are illustrative.

The choice of the base material is important, as having an integral part in the processing and the nickel blank, prepared in the manner specified above, has been found to be most advantageous for this purpose.

The cathode surface, as mentioned above, undergoes a partial fusion during this process. This fusion produces a dense surface material on the cathodes of velvety brown appearance. In the absence of this fusion, as when the heat treatment temperature is below 1300° C., the surface of the coating is very porous with poor adherence to the oxidized nickel base. The surface hydrates readily, turning to a grey or in extreme cases a white surface which will drop off the base material. If too great a fusion takes place, as by having too high an oxygen content in the nitrogen atmosphere, the surface will have a black metallic appearance. Under these conditions the coating passes through a fluid state and a large portion of the coating runs off the nickel surface.

While various modifications may be made by those skilled in the art without departing from the spirit and scope of the invention, certain aspects are important to the preparation of an activated cathode surface having the properties of a long life, a thick surface, a uniformly distributed and partially fused surface and a low sustaining voltage. Thus to produce the resultant surface of this invention it is important that the initial composition be 10 per cent nickelous oxide and 90 per cent barium carbonate and that the coating applied to the cathode blank be heated to at least substantially 1300° C., and advantageously not more than 1400° C., but it is to be understood that the other above-described arrangements are merely illustrative of the application of the principles of the invention.

What is claimed is:

1. An electron emissive cathode comprising a nickel blank and a thick electron emissive velvety brown surface thereon, said surface consisting essentially of substantially 98 per cent barium oxide and 2 per cent nickel in solid solution in the barium oxide lattice and having a sustaining voltage of less than 70 volts.

2. The method of preparing an electron emissive cathode for glow discharge devices which

comprises coating a mixture of 90 per cent barium carbonate and 10 per cent nickelous oxide on a nickel cathode blank, heat treating said blank in an atmosphere free of oxygen and at atmospheric pressure to first form a BaCO₃.BaO eutectic and then to dissociate said eutectic, continuing said heat treatment to form a plurality of compounds of nickelous oxide and barium oxide, and then maintaining said heat treatment at a temperature between 1300° C. and 1400° C., whereby said compounds are converted to barium oxide and finely dispersed nickel.

3. The method of preparing an electron emissive cathode for glow discharge devices which comprises coating a mixture of 90 per cent barium carbonate and 10 per cent nickelous oxide on a nickel cathode blank, and heat treating said blank in a nitrogen atmosphere at atmospheric pressure, said treatment comprising heating said blank to 1050° C. to form a BaCO₃.BaO eutectic, raising the temperature to dissociate said eutectic, raising the temperature to 1300° C. and maintaining the heat treatment at 1300° C. for 30 minutes to convert the 3BaO.NiO and BaO.NiO compounds formed during said heating to barium oxide and finely dispersed nickel.

4. The method of preparing an electron emissive cathode for glow discharge devices which comprises cleaning nickel cathode blanks, oxidizing said blanks in 95 per cent nitrogen and 5 per cent oxygen for 5 minutes at 700° C., coating said blank with 90 per cent barium carbonate and 10 per cent nickelous oxide, then placing said blanks in a furnace at 700° C., raising the temperature of said furnace in steps to form and then dissociate a BaCO₃.BaO eutectic and then to 1300° C., and maintaining said furnace at 1300° C. for 30 minutes, the heating being done in an atmosphere of nitrogen at atmospheric pressure.

5. The method of preparing an electron emissive cathode for glow discharge devices comprising coating a mixture of 90 per cent barium carbonate and 10 per cent nickelous oxide onto a nickel cathode blank and heat treating said blank in an atmosphere free of oxygen and at atmospheric pressure, the heat treatment comprising raising the temperature of said blank in steps to a temperature sufficient to form compounds of the BaO.NiO group, raising said temperature to about 1200° C. to cause melting of a first one of said compounds, raising the temperature to about 1250° C. to cause melting of a second one of said compounds, and then maintaining the temperature at between 1300° C. and 1400° C. for a time sufficient to assure complete conversion of said compounds to barium oxide and finely dispersed nickel.

6. The method of preparing an electron emissive cathode for glow discharge devices which comprises cleaning a nickel cathode blank, oxidizing said blank in a slightly oxidizing atmosphere, coating said blank with 3.3 milligrams per square centimeter of a mixture of 90 per cent barium carbonate and 10 per cent nickelous oxide, raising the temperature of said blank in an atmosphere free of oxygen and at atmospheric pressure to a temperature sufficient to form compounds of the BaO.NiO group, raising said temperature to about 1200° C. to cause melting of the compound 3BaO.NiO, raising the temperature to about 1205° C. to cause melting of the compound BaO.NiO, and then maintaining the temperature at between 1300° C. and 1400° C.

for a time sufficient to assure complete conversion of said compounds to barium oxide and finely dispersed nickel.

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