Dec. 6, 1955 H. NELSON ET AL 2,726,178

THERMIONIC CATHODE WITH THORIA COATING

Filed Nov. 17, 1950 3 Sheets-Sheet 1

HEATING COMMERICAL THORIA TO FORM AGGLOMERATES OF SOLID PARTICLES OR TO FORM A SOLID MASS

BALL MILLING THE AGGLOMERATES OR SOLID MASS TO POWDER FORM HAVING A PARTICLE SIZE PEAKING AT FROM .05 TO .10 MICRONS DIAMETER

APPLYING THE BALL MILLED POWDERS TO A BASE OF REFRACTORY METAL BY SPRAYING RELATIVELY DRY TO PROVIDE AN ADHERET COATING ON THE BASE

HEATING THE COATED BASE TO SINTER THE COATING PARTICLES TO PROVIDE A COATING HAVING A RELATIVELY HIGH APPARENT DENSITY FOR LONG EMISSION LIFE

Fig. 1.

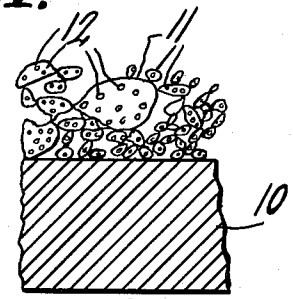


Fig. 6.

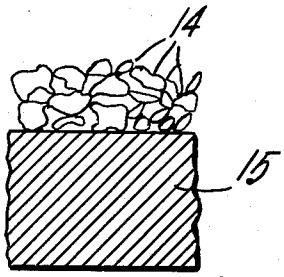


Fig. 7.

Fig. 4.

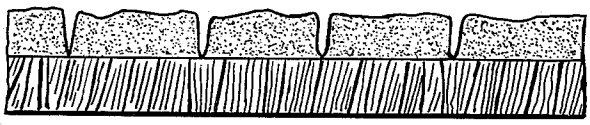
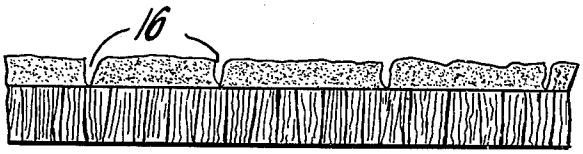


Fig. 5.

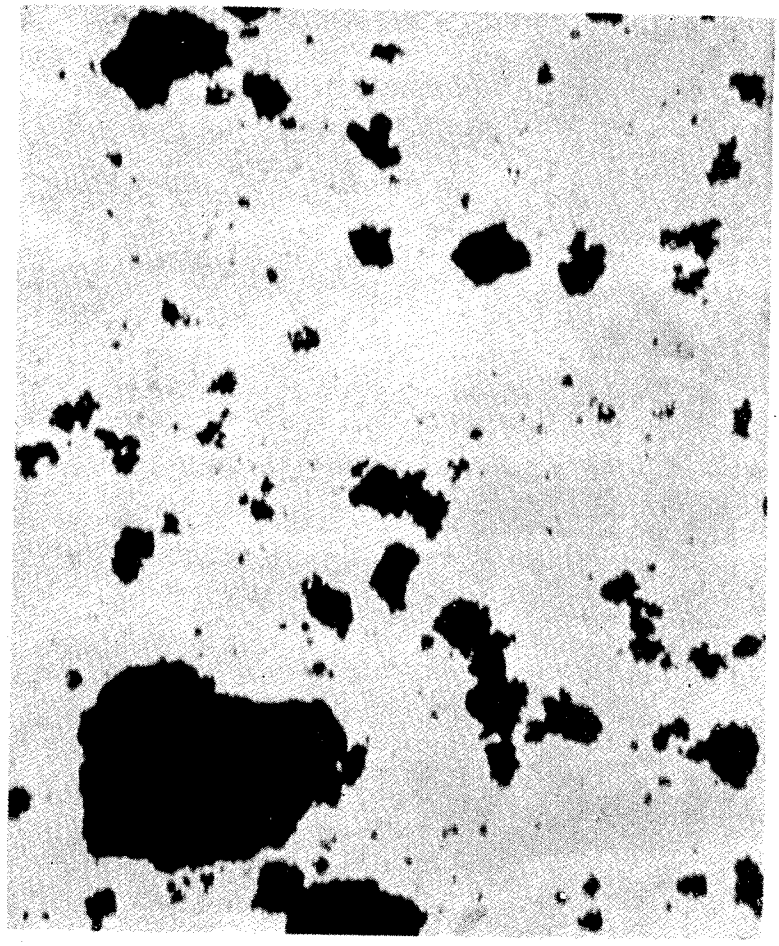


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Filed Nov. 17, 1950 3 Sheets-Sheet 2

Fig. 2.



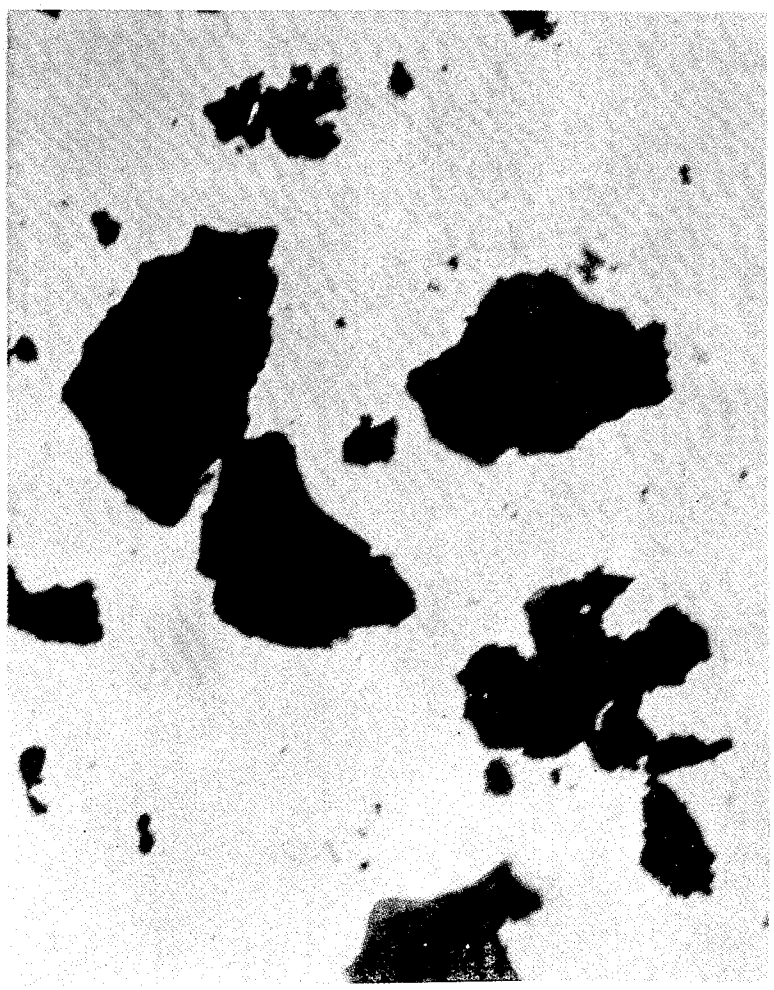
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THERMIONIC CATHODE WITH THORIA COATING

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Fig. 3.



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THERMIONIC CATHODE WITH THORIA COATING

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Application November 17, 1950, Serial No. 196,158

8 Claims. (Cl. 117—220)

The present invention relates to thermionic cathodes and more particularly to directly heated cathodes comprising a base of refractory metal having thereon a coating of thoria.

The thoria coated filamentary cathode was developed to meet the demands for a cathode supplying long life emission at relatively high current densities and relatively high anode voltage, as compared with the conventional barium-strontium coated indirectly heated cathode, and the directly heated thoriated tungsten filamentary cathode.

One of the difficulties in securing long life and high emission resides in the fact that high emission requires a high operating temperature of the cathode. While a barium-strontium coated cathode requires a lower operating temperature for a given magnitude of emission than a thoria coated filament, at high emission its coating evaporates rapidly, resulting in a relatively short life as compared with the life of the thoria coated filament. A conventional thoriated tungsten filament requires a higher temperature of operation than a thoria coated filament for providing a given emission and such higher temperature shortens the life of the cathode so that it is less than that of the thoria coated filament for a given emission.

The thoria coated filamentary cathode, though superior to the tungsten and barium-strontium coated filament at high emission levels, is however, also subject to deterioration at high operating temperatures. At the high temperatures required for desired high emission levels, life is seriously shortened due to excessive loss of thoria by the process of evaporation. For example, after as short period as 100 hours all thoria may be lost from a particular filament with consequent loss of emission.

Attempts have heretofore been made to lengthen life by increasing the amount of material applied per unit area of the filament surface and thus prolonging the time required for total loss of the thoria coating by evaporation. These attempts, however, have not been entirely successful chiefly because they have led to loss of coating by peeling and also indirectly, because of excessive change in the electrical characteristics of electron tubes in which the filaments have been used. The first named difficulty is experienced when the amount of material is increased by applying the thoria on the filament surface in a layer having high apparent density. This densely packed thoria layer tends, upon heating, to sinter into a continuous ceramic-like layer. As a result of a difference in its thermal expansion from that of the underlying base, this layer tends to separate from the base surface during heating and cooling cycles.

To avoid this particular difficulty attempts were made to increase the amount of material per unit area by greatly increasing the thickness of the layer, keeping the apparent density of the layer low. In this manner there was obtained a layer that was not a continuous ceramic-like body, but was composed of a plurality of individual thoria blocks sintered to the base metal. As a consequence, we could apply a greater amount of thoria

while maintaining sufficient adherence of the thoria to the base for practical applications.

However, this thick layer, because of its low apparent density, tends to shrink as a result of further sintering which takes place during use of the coated filament in a tube. Therefore, the separation between the outer surface of the layer and an adjacent electrode in a tube tends to increase, to materially affect tube characteristics. For example, a thoria layer of this type initially may have a thickness of 6 mils which may decrease to about 3 mils after a relatively short life. In some tube types 3 mils is a relatively large portion of the spacing between a cathode and an adjacent electrode. This second-named difficulty is particularly acute since the present trend is toward closer spacings between cathodes and adjacent electrodes.

By the expression "apparent density," as used herein is meant mass per volume, wherein the volume includes spaces not actually occupied by the mass, such as the spaces between the particles, and pores in the particles. This is distinguished from absolute density wherein the volume is that actually occupied by the mass and includes no free space.

While a thick coating applied loosely or in a fluffy manner by the well known "dry" method of application, is better adherent than a thin and denser coating applied by the "wet" method, it is characterized by the difficulties mentioned of rapid depletion of the emitting material and shrinkage, the latter affecting tube characteristics. This improved adherence of a fluffy coating results from cracks formed in the coating during processing. A "wet" or densley applied coating, on the other hand, does not permit the formation of cracks therein during processing, so that expansion strains during use cause peeling of the coating from its base. Furthermore, a "wet" coating is usually relatively thin, and lacks thickness uniformity. This causes exposure of portions of the base metal on evaporation of the thinner portions of the coatings resulting in increased heat or "hot spots" at such portions. Such "hot spots" cause runaway peeling incidents of the coating.

It is apparent from the foregoing that a desirable coating should have the characteristic of loose packing together with the features of high apparent density. With commercial thoria powders this combination is not feasible. This is because the pores in the particles of such powders as well as the particle size range and the particle size distribution peak in said range, limit the apparent density of a coating made from such powders.

Accordingly it is the object of the invention to provide a directly heated thoria coated cathode suitable for use at relatively high temperatures with a relatively long life of good emission.

Another object is to provide a thoria coated, directly heated cathode in which the thoria coating combines the advantage of good adherence that is characteristic of a loosely packed coating, with the advantage of a large reservoir of emitting material provided by a densely packed coating.

A further object is to provide thoria powder of a predetermined particle size for providing a coating having the desired apparent density when applied loosely to a base.

A further object is to provide a thoria coated cathode wherein the coating is of uniform thickness to prevent hot spots.

Another object is to provide a thoria coating material having a novel particle size distribution for increasing the apparent density of the material for long emission life of a coating in which it is used when the coating is loosely packed for good adherence on a base.

Another object is to provide a novel method of making an improved thoria coated cathode that includes processing the coating material to secure a desired particle size distribution for high emission and long life of the cathode.

A further object is to provide a novel method of processing thoria powder for securing a loosely packed coating having a relatively high apparent density.

According to one way of practicing the invention, commercial thoria powder is treated for the purpose of increasing its apparent density, prior to inclusion in a mixture for application as a coating. This treatment involves heating the commercial thoria powder to either sinter the powder particles to form relatively large agglomerates of the solid thoria, or to fuse the powder to form a solid mass. The resultant agglomerates or solid mass are then ball-milled under controlled conditions to provide a powder having a particular size of from 0.01 to 1.5 microns in diameter, with most of the particles intermediate the limits of the range.

A coating made from the thoria powder treated as aforementioned includes the advantage of having a relatively high apparent density, although applied to a base in a relatively loosely packed manner. We have found that a coating including our novel thoria powder and loosely packed for improved adherence will have a thickness of 4.56 mils when applied at 50 milligrams per square centimeter. A coating including commercial thoria powder and applied in the same manner was found to have a thickness of 6 mils when applied at 50 milligrams per square centimeter.

According to our invention therefore a relatively thin cathode coating may be employed where necessary, such as in ultra high frequency electron tubes, and yet have the required reservoir of emitting material and good adherence for long life of such tubes. A further advantage of the greater apparent density of our novel coating is that it evaporates less rapidly than coatings of the prior art having a lower apparent density. Our coating therefore inhibits the formation of hot spots that cause eventual peeling of the coating from the base, and contributes to a long life of high emission of a device in which it is used.

Further objects and features of the invention will become apparent as the present description proceeds.

Referring to the drawing for a better understanding of the invention,

Figure 1 is a flow chart illustrating one way in which the method of the invention may be practiced;

Figure 2 is a microphotograph of commercially available thoria powder magnified 20,000 times;

Figure 3 is a microphotograph of thoria powder as prepared by a practice of the method of the invention, magnified 20,000 times;

Figure 4 is a line drawing of a photograph of a cross-section of a cathode having a coating of thoria thereon, according to the prior art and magnified 100 times;

Figure 5 is a line drawing of a photograph of a cross-section of a cathode having a coating of thoria thereon applied in accordance with the method of the invention and magnified 100 times;

Figure 6 is an enlarged fragmentary schematic view partly in cross-section of the cathode shown in Figure 4 and shows the porous character of the coating particles applied in accordance with prior methods; and

Figure 7 is an enlarged fragmentary schematic view partly in cross-section of the cathode shown in Figure 5 and depicts the solid character of the particles of thoria coating processed and applied in accordance with the method of the invention.

Several factors are desirable in a cathode having an emitting coating. One of these factors is freedom from peeling of the coating. A recourse availed of in the prior art for reducing peeling incidents is to apply the coating in a relatively loose or fluffy manner. The reason for this type of application is that a fluffy or loosely applied coating permits cracks to form therein during manufacture of a cathode. These cracks serve to relieve strains in the coating caused by different expansions of the coating and the base during use in an electron tube.

Another desirable factor is a sufficient reservoir of emitting material in the coating for long life of the cathode. However, such reservoir is best provided in a relatively densely packed coating.

A further desirable factor in a coated cathode is the availability of a relatively thin coating where space requirements are critical, such as in high frequency electron tubes where the cathode is relatively close to an adjacent electrode.

It is apparent that the foregoing factors are mutually opposed. Thus a loosely applied coating for preventing peeling is deficient in its supply of emitting material. And a thin coating lacks both fluffiness for good adherence as well as a required reservoir of emitting material for long life.

We have found that the failure of the prior art to provide a coating of thoria that is characterized by all the factors of good adherence, large reservoir of emitting material and high density, is due partly to the nature of commercially available thoria powders.

Commercial thoria (thorium oxide) is usually prepared by subjecting a thorium compound such as thorium oxalate to one or more heat treatments to reduce it to the oxide form and mechanically working the resultant oxide to powder form.

When commercial thoria is prepared from the oxalate form, the reaction is as follows:

$$Th(C_2O_4)_2.6H_2O + heat = ThO_2 + 2(CO) + 2(CO_2) + 6(H_2O)$$

During the reaction, the CO and the CO_2 escape as gases and the H_2O as water vapor. The escape of the CO and CO_2 leaves a plurality of pores in the resultant thoria particles which persist after the subsequent mechanical working operation.

The presence of the pores pereferred to in the thoria particles reduce their apparent density. This results in a reduction in the apparent density of a coating made by the particles, as well as in the reservoir of emitting material in the coating. A further reduction in apparent density of the coating results from a loose or fluffy application of the coating. When the coating is applied thinly, the reduction in apparent density caused by the pores in the particles results in a relatively short life of the cathode due to the small reservoir of emitting material in such coating.

Commercial thoria is also characterized by a particle size range and distribution that further contribute to reduction in apparent density of a coating formed thereby. Commercial thoria is usually made up of particles varying in size from slightly above zero to 1.5 microns in diameter. The size distribution usually peaks at a size very close to zero in diameter. Since the particles are usually ragged edged, the relatively large number of particles in a given volume, results in a relatively large number of spaces between the particles when formed into a coating, thus contributing to a further reduction in the apparent density of the coating.

According to the invention, a thoria coating and method of application to a base, are provided that avoid the aforementioned difficulties. The method of the invention includes a step for increasing the apparent density of commercially available thoria particles and a further step for confining the sizes of the particles to a predetermined range and for causing the particle size distribution to peak at a predetermined portion of this range. As a result of this method a thoria coating is formed from commercial thoria that may be applied loosely for improved adherence and yet possess the required reservoir of emitting material for long life. When applied thinly and loosely

it also has adequate emitting material for a relatively long life due to the increased apparent density of the coating particles and to the increased density of the coating resulting from the particle size range and particle size distribution.

A physical characteristic of a coating formed in accordance with the method of the invention is the substantial absence of pores in the particles forming the coating.

The processing of commercial thoria powder in accordance with the invention involves a controlled heat treatment of the powder for softening the particles thereof sufficiently to cause substantially all the pores therein to collapse. After the heat treatment, therefore, each particle is a solid mass of thoria. The method also involves a controlled mechanical working step whereby the size of the particles is confined to a predetermined range and the particle size distribution is caused to peak at a predetermined portion of the range. This latter step conditions the powder in such a way that it is capable of forming a coating having increased apparent density.

As shown by the flow chart of Figure 1, the method of the invention starts with commercially available thoria and culminates in a coating having increased apparent density as compared with coatings of thoria applied by prior art methods.

The first step of the method involves heat treating the commercial thoria. The heat treatment should be carried out at a temperature sufficiently high to cause the smaller particles to merge in relatively large agglomerates and to cause substantially all the pores in the individual particles to collapse.

We have found that a temperature as low as 1200° centigrade, brightness temperature, causes appreciable sintering of the smaller particles to form agglomerates, and results in collapse of some of the pores in the particles. At this temperature therefore some increase in the apparent density of the powder results. An increase in the temperature of the heat treatment results in the formation of more strongly coherent agglomerates and in more complete collapse of the pores in the particles. At a temperature as high as 3000° centigrade, brightness temperature, which is the fusion temperature of thoria, a solid mass is formed. While a temperature above 3000° centigrade, brightness temperature, can be used in practicing the method of the invention, it is not necessary.

While the thoria powder acquires greatest apparent density when heat treated at a temperature of 3000° centigrade, brightness temperature, another factor involved in the practice of the invention renders a lower temperature more suitable. This factor is present in the subsequent mechanical working step. Thus, if the powder is fused, as when heated to a temperature of 3000° centigrade, brightness temperature, to form a solid mass, it is more difficult to break up the mass to particles of a size suitable for mechanical working.

We have found, therefore, that a temperature of about 1700° centigrade, brightness temperature, during the heat treatment step is best for a practice of the invention. At this temperature agglomerates are formed having good cohesion and the porosity of the agglomerates and individual particles is reduced. Agglomerates formed at this temperature are more easily broken up than those formed at higher temperatures.

However, while the invention is most advantageously practiced using a heat treatment temperature of about 1700° centigrade, brightness temperature, some advantages also accrue when other temperatures within the range of from 1200° centigrade, brightness temperature, to 3000° centigrade, brightness temperature, are used, as indicated before herein.

The heat treating operation according to the invention may be performed in air or hydrogen. According to one example, 100 grams of commercial thoria powder known as Lindsay 112 was heated in a molybdenum boat of 100 grams capacity in hydrogen at a temperature of 1700° centigrade, brightness temperature, for one hour. This provided a desired sintering action resulting in a reduction of pore volume. According to another example, the powder was heated in air at a temperature of about 1200° centigrade, brightness temperature, for two hours. Less coherent agglomerates were formed and reduction of pore volume was not as complete as under the higher temperature condition. Generally, when the operation is performed in hydrogen, a lower temperature may be used than when it is carried out in air. The heat treatment at 1700° centigrade, brightness temperature, therefore, if carried out in air should be continued for more than one hour to about 1¼ hours. The heat treatment at 1200° centigrade, brightness temperature, would require a time slightly less than 2 hours if carried out in hydrogen. If the heat treatment is performed at 3000° centigrade, brightness temperature, a shorter period than in the two examples referred to is required. At this temperature the powder will form a solid mass within about ½ hour.

After the commercial thoria powder is heat treated in the manner indicated above, it is subjected to a preliminary mechanical working operation. The purpose of this operation is to break up relatively large agglomerates, or the solid mass, that may have been formed during the heat treatment step, to render them suitable for the subsequent mechanical working step. When the powder has formed a solid mass, the solid mass may be broken up by a jaw crusher, or by passing the mass when hot into cold water to cause it to shatter. When the heat treatment temperature is not high enough to form a solid mass, but sufficiently high to form agglomerates, the agglomerates may be broken up by grinding in a glass mortar for a few minutes.

After the preliminary working operation referred to is completed, the resultant powder is screened through a 10 mesh sieve.

The screened powder is then subjected to the basic mechanical working step of the invention. The purpose of this step is to give the particles of the powder a size range and size distribution for forming a suspension capable of being applied to an object by the spray process. This further mechanical working step is performed on the powder after it has been mixed with a suitable binder.

According to a specific example of the mechanical working step, 50 grams of thoria powder heat treated, worked and screened as aforementioned, is mixed with 12.5 cc. of a nitrocellulose binder made up in a batch including 4 grams nitrocellulose (½ second viscosity—dry) 80 cc. diotol and 20 cc. diethyl oxalate; and 37.5 cc. diotol. The resultant mixture is ball-milled for 8 hours in a ball mill of one quart capacity and containing 400 grams of flint pebbles ranging in size from ½ inch to 1 inch in diameter. The ball mill is operated at a velocity of 100 R. P. M.

A portion of the ball-milled mixture was used in a test to determine the apparent density and the particle size distribution, of the thoria particles in the mixture. To this end the binder was first removed from the portion referred to of the mixture, leaving the thoria powder in a dry state. The dry thoria powder was then weighed and it was found that it had an apparent density of 1.81 grams per cubic centimeter. The powder was then examined under an electron microscope at 20,000 magnification. Figure 3 shows the thoria powder so examined. A careful measurement of the particles indicated that 30 per cent were from .01 to 0.5 micron in diameter, 50 per cent were from .05 to .10 micron diameter, and 20 per cent were from .10 to 1.5 microns in diameter.

The results obtained from this examination were compared with the results of a similar examination of commercial thoria powder known as Lindsay No. 112. A portion of this powder was weighed and was found to have an apparent density of 1.45 grams per cubic centimeter. The powder was then examined under the electron microscope at 20,000 magnification. The powder so magnified

is shown in Fig. 2. The powder particles were carefully measured and it was found that 90 per cent were from slightly above zero to .05 micron in diameter, 8 per cent were from .05 to .10 micron in diameter, and 2 per cent were from .10 to 1.5 microns in diameter.

It will be appreciated from the foregoing that thoria powders treated according to the invention are characterized by greater apparent density than untreated commercial thoria powder, and have a particle size distribution peaking in a larger size range than is the case in commercial thoria powder. Both of these characteristics of thoria powder treated according to the invention contribute to increased apparent density of a coating made from such treated powder.

Another portion of the mechanically worked mixture of thoria powder and binder referred to before herein, was used in the application of a coating on a base. The mixture was sprayed on a base by means of a Paasch type H airbrush held at a distance of approximately 2 inches from the base. The airbrush was operated at a pressure of from 30 to 35 lbs. per square inch. The fluid opening of the brush was adjusted to provide a spray for forming a coating having a mass of 50–60 milligrams per square centimeter for each 30 to 40 minutes of application, including drying time.

The coating was sprayed in a plurality of passes of one second duration each. After continuous application of 30 passes, the coating was dried under a small infra-red lamp for one-half to one minute and the process repeated until the required thickness of coating was obtained. Rough measurements indicate the coating thickness was from .001 to .0015 inch at 20 mgs. per square centimeter.

A base coated in accordance with the foregoing procedure and using thoria powder treated according to the invention, is shown in Fig. 5.

In Fig. 4 is shown a coating made from untreated commercial thoria powder. The mass of the coating per square centimeter is substantially the same as that shown in Fig. 5. However, it will be noted that the thickness of the coating is much greater than that shown in Fig. 5. This clearly indicates that the apparent density of a coating made according to the invention is much greater than that of a coating made according to the prior art from untreated commercial thoria powder. Moreover, a coating according to the invention had cracks therein shown at **16** in Figure 5, which relieve strains in the coating due to different expansion characteristics of the base and coating.

Fig. 6 is a fragmentary view of the coated base **10** of Fig. 4 and shows the coating formed of particles **11**, having pores **12** therein. It also shows that the particle size distribution peaks at a relatively small size, with a consequent increase in the number of particles for a given volume. This increase in the number of particles also increases the number and overall volume of the spaces between the particles. The pores in the particles and the relatively large number of spaces between the particles contribute to reduction in the apparent density of a coating formed by the particles.

The coating particles **14** on base **15** shown in Fig. 7, on the other hand, which were processed according to the invention, have no pores and have a size distribution peaking in a larger size range than do the untreated powders forming the coating shown in Fig. 6. The absence of pores in the particles and the reduced number of spaces between the particles, contribute to increased apparent density of a coating made from the particles.

It will be appreciated from the foregoing that we have provided a novel coating of thoria having the measurable characteristics of substantially increased apparent density over coatings of the prior art. We have also provided a novel thoria powder in which the particles thereof are substantially free from pores and have a size distribution peaking in a novel sub-range of the size range. In addition, we have provided a novel method for making a thoria coating that includes the novel steps of heat treating commercial thoria powder under predetermined conditions and mechanically working the heat treated powder to provide a predetermined size distribution of the particles thereof.

A coating made from our novel thoria powder and in accordance with our method, may be applied loosely for improved adherence and yet possess a relatively large reservoir of emitting material for long life. Moreover, the coating may be applied relatively thin for advantageous use in high frequency devices without closely packing the coating, for good adherence, and still possess appreciably more emitting substance than thinly applied coatings of the prior art. Since the life of an electron tube is in large measure related to the emission life of the cathode employed therein our invention is of substantial significance in prolonging the life of electron tubes.

Various modifications departing from the exact parameters referred to may be made in practicing the invention without departing from its spirit and it is desired to include such modifications within the scope of the appended claims.

We claim:

1. A long life high emission cathode comprising a filament having thereon a coating consisting of substantially non-porous thorium oxide particles sintered together and having a particle size distribution from .01 to 1.5 microns in diameter, said size distribution peaking at a particle size of from .05 to .10 micron in diameter.

2. A cathode comprising a filament having thereon a coating of thoria particles sintered together, said thoria particles having a size distribution ranging from .01 to 1.5 microns in diameter, with about 50% of said particles having a size distribution of from .05 to .10 micron in diameter, said coating having a density of 50 milligrams for a volume of one square centimeter 4.56 mils thick, whereby a relatively thin coating is provided having a relatively large reservoir of emitting material.

3. A cathode including a filamentary base and a coating of thoria particles sintered on said base, said coating being formed from a thoria powder consisting of particles having a size range from .01 to 1.5 microns and a size distribution wherein about 30 per cent of said particles have a size from 0.01 to 0.05 micron, about 50 per cent of the particles have a size from 0.05 to 0.10 micron and the remainder of said particles range from 0.10 to 1.5 microns, said size range and size distribution contributing to increased apparent density of said powder.

4. A cathode including a filamentary base and a coating consisting of thoria particles sintered on said base, said coating being formed from a thoria powder having a particle size distribution for increased apparent density of said coating for providing a relatively large reservoir of emitting material on said cathode, said particle size distribution disposing about 30 per cent of the particles in a range from 0.01 to 0.05 micron diameter, about 50 per cent of the particles in a range from 0.05 to 0.10 micron in diameter, and the remainder of the particles in a range from 0.10 to 1.50 microns in diameter.

5. A cathode including a filamentary base and a coating consisting of thoria particles sintered on said base, said coating being formed of a thoria powder consisting of thoria particles having a size ranging from the lower limit of .01 micron to the higher limit of 1.5 microns of a size range, said size range consisting of thirty subranges having equal gradients, about 30 per cent of said particles by weight being included in one of said sub-ranges extending from the lower limit of said size range, about 50 per cent of said particles by weight being included in another of said sub-ranges extending from the first-named sub-range and the remainder of said particles being included in the remaining twenty-eight of said sub-ranges, said size distribution of said particles in said range contributing to an increase in apparent density of said coating.

6. A cathode including a filamentary base and a coating of thoria particles sintered on said base, said coating being

formed of a thoria powder consisting of thoria particles having a size ranging from the lower limit to the higher limit of a size range extending from .01 to 1.5 microns in diameter, said size range consisting of thirty sub-ranges of equal gradients, about 30 per cent of said particles by weight being included in one of said sub-ranges adjacent the lower limit of said size range, about 50 per cent of said particles by weight being included in another of said sub-ranges adjacent the first-named sub-range and the remainder of said particles being included in the remaining twenty-eight of said sub-ranges, said size distribution of said particles in said size range contributing to an increase in apparent density of said coating, said sintered particles being free from pores therein for further increasing the apparent density of said coating.

7. A cathode including a filamentary base and a coating of thoria particles sintered thereon, said coating being formed of a thoria powder consisting of particles having a size ranging from a lower limit of .01 micron in diameter to a higher limit of 1.5 microns in diameter, said lower limit being spaced from said higher limit by a series of equal gradations, about three-tenths of said particles by weight having a size in a range extending from said lower limit and including 3⅓ per cent of said gradations, about one-half of said particles by weight having a size in an upper range adjacent said last-named range and including 3⅓ per cent of said gradations, and the remainder of

said particles having a size in a range adjacent said higher limit and including 93⅓ per cent of said gradations.

8. Method of applying to a filamentary base a thoria coating having a relatively high apparent density and good adherence to said base, comprising spraying said base under conditions to provide a fluffy coating with a coating mixture consisting of substantially poreless thoria particles having an overall size range of from .01 to 1.5 microns in diameter and with about 50% of the particles included within a sub-size range of from .05 to .10 micron in diameter.

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