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THERMIONIC CATHODE FORMING PROCESS USING
ELECTROSTATIC CHARGE ATTRACTION
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3,342,635

FIG. 1

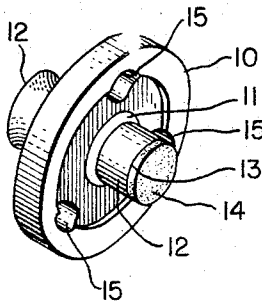


FIG. 2

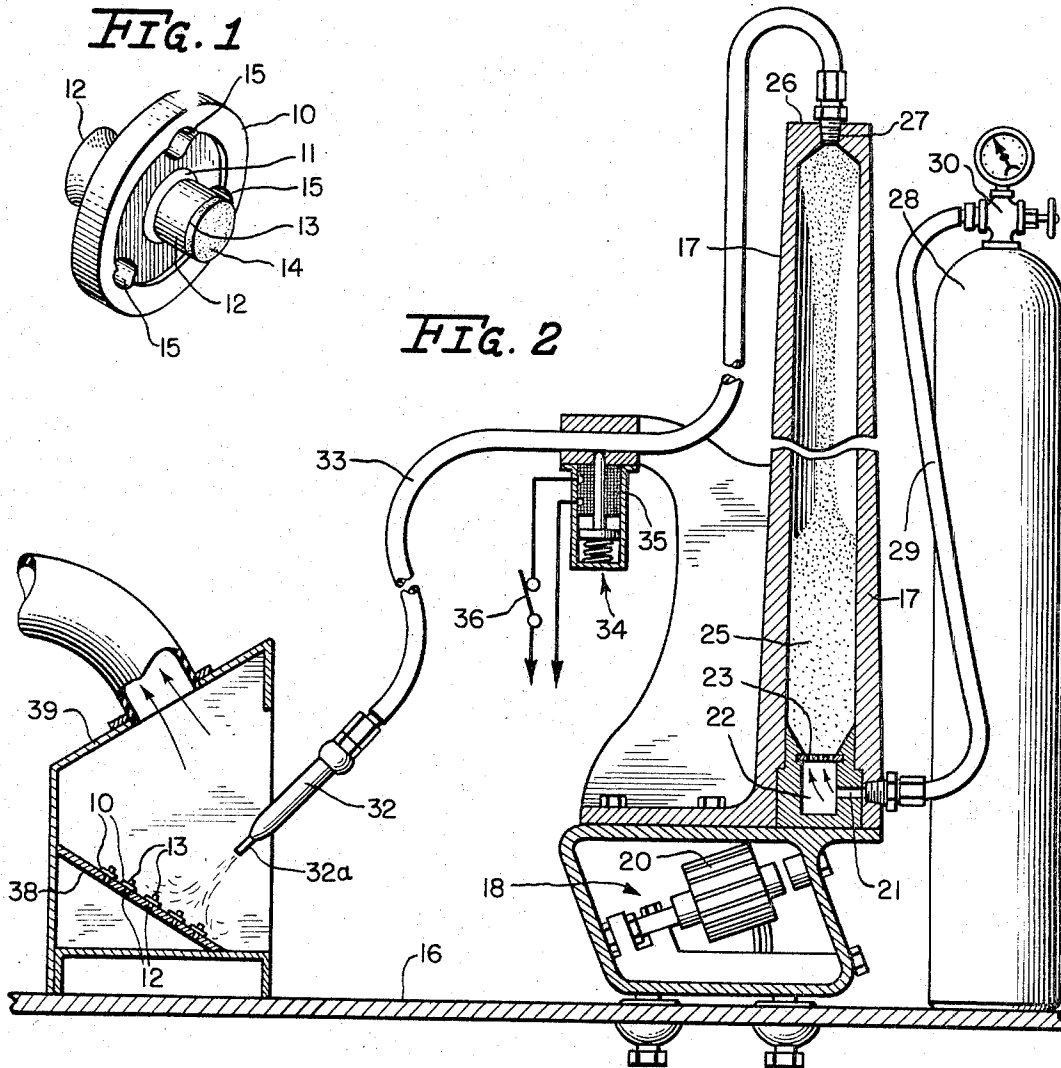


FIG. 4

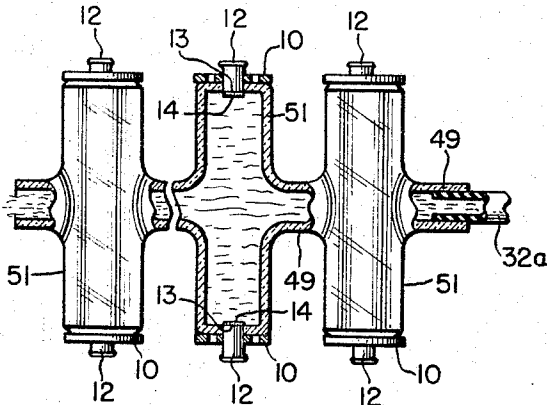
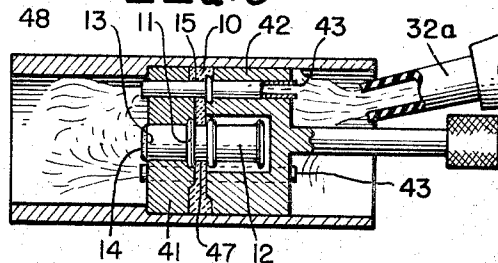


FIG. 3



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**THERMIONIC CATHODE FORMING PROCESS
USING ELECTROSTATIC CHARGE ATTRAC-
TION**

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4 Claims. (Cl. 117—223)

This invention relates to electron tubes and more particularly to thermionic cathodes and the preparation of such cathodes.

In many applications, and particularly in cathode-ray tubes such as television picture tubes, electron guns with very narrow grid-to-cathode spacings are employed to obtain the required high transconductance. In such applications, it is customary to use specially prepared oxide cathodes of high density and high surface smoothness. Conventionally, the thermionically emissive cathode surface is formed by spraying or otherwise depositing in a wet condition a mixture of barium carbonate or barium and strontium carbonates with a nitrocellulose binder to a metal substrate such as a nickel cathode sleeve; the requisite high degree of smoothness may be obtained by mechanically shaving the carbonate coating before activation, or by the use of centrifuging or cataphoretic deposition techniques in applying the carbonate coating to the substrate. In any event, the provision of thermionic cathodes of increased surface smoothness permits the use of closer grid to cathode spacings with resultant substantial increases in transconductance, and increased density of the thermionically emissive material is desirable for the improvement of cathode emission cathode life and for the provision of increased beam currents leading, in a television picture tube, to increased image brightness and contrast.

In the formation of oxide cathodes, it is necessary to activate the cathode by baking the carbonate coating during tube exhaust to reduce the carbonate or carbonates to an oxide or oxide complex. When a nitrocellulose binder is employed, as in most conventional processes, the nitrocellulose is decomposed during the baking out of the carbonate coating, and this often leads to the evolution of deteriorating gases as well as partial carbonization of the resultant oxide material, both of which are detrimental to emission efficiency and tube life.

Accordingly, it is a principal object of the invention to provide a new and improved thermionic cathode, as well as a new and improved process for making thermionic cathodes.

Another object of the invention is to provide a method of producing thermionic cathodes with increased surface smoothness as compared to that obtained by the use of even the best prior art processes.

A further object of the invention is to provide a new and improved cathode, and a process for producing such a cathode, which provides a substantial improvement in emission efficiency and in cathode life.

Still a further object of the invention is to provide a new and improved thermionic cathode, and a process for producing such a cathode, which avoids certain of the limitations and disadvantages of prior art cathodes and processes.

In accordance with the invention a new and improved process for the preparation of a thermionically emissive coating on an electrically conductive substrate comprises the steps of exposing the substrate to electrostatically charged particles of dry cathode-forming pulverulent material comprising an alkaline earth carbonate whereupon said charged particles are bound to said substrate by electrostatic charge attraction to form a coating of the cathode-forming material on the substrate and thereafter heat-

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ing the substrate with its coating of cathode-forming material to provide a thermionically emissive coating on the substrate.

The features of the present invention which are believed to be novel are set forth with particularity in the appended claims. The invention, together with further objects and advantages thereof, may best be understood by reference to the following description taken in connection with the accompanying drawing, in the several figures of which like reference numerals identify like elements, and in which:

FIGURE 1 is a perspective view of a thermionic cathode assembly of a type employed in television picture tubes, embodying a thermionically emissive cathode constructed in accordance with the present invention;

FIGURE 2 is a side elevational view, partly in cross-section, showing illustrative apparatus for producing thermionic cathodes in accordance with the invention;

FIGURE 3 is a side view, partly in cross-section, showing a modification of a portion of the apparatus of FIGURE 2; and

FIGURE 4 is a side view, partly in cross-section, of an alternative modification of a portion of the apparatus in FIGURE 2.

The cathode assembly of FIGURE 1 is of a type commonly employed in the electron gun of a television picture tube. More particularly, a ceramic insulating disc 10 is provided with a central circular aperture 11 which receives a metal tubular cathode sleeve 12, the end surface 13 of which constitutes a substrate for a thermionically emissive coating 14. A plurality of apertures 15 may be provided in disc 10 for reasons to become apparent. In accordance with the invention, thermionically emissive coating 14 is composed of any suitable thermionically emissive material such as barium oxide, or a mixture of complex of barium and strontium oxides or barium, strontium and calcium oxides all of which are derived from cathode forming material in the alkaline earth carbonate family. The chemical composition of the cathode coating is not, however, of the essence of the present invention, and accordingly other materials known in the art may be employed.

Thermionically emissive cathode coating 14 does differ materially from prior art thermionic cathode coatings in exhibiting a markedly greater surface smoothness, and in many instances a substantially higher density than even the best of the oxide cathodes prepared with conventional wet deposition techniques, such as spraying, centrifuging or cataphoretic deposition. These highly desirable improvements are obtained by impacting the dry cathode-forming material (usually barium carbonate or an equi-molecular mixture of barium and strontium carbonates) on the cathode substrate 13 without the use of nitrocellulose or other wet binders or bonding agents. This may be accomplished with the use of a high-velocity gas jet in a manner to be more fully described. This process is disclosed and claimed in a concurrently filed application of Serge Pakswier, Ser. No. 354,252, entitled Impaction Process for Forming a Thermionic Cathode, and assigned to the present assignee. The carbonate coating so applied to the cathode substrate 13 is found to adhere to the substrate, without the use of nitrocellulose or other binder, sufficiently well to permit normal handling and mechanical gauging and jiggling employed in the usual assembly of an electron gun, without flaking or peeling. When the completed electron gun or other assembly including the prepared carbonate coated substrate has been assembled within the ultimate tube envelope, the further processing including baking during exhausting of the envelope to reduce the carbonate coating to a thermionically emissive oxide may be carried out in an entirely conventional manner.

Oxide cathodes produced in accordance with the invention of the above Pakswar application are superior to prior art cathodes, not only as to surface smoothness and high density of the emissive material, but also in tube life and emission efficiency because the ordinarily used nitrocellulose binder has been eliminated. Accordingly, carbonization often encountered when a nitrocellulose binder is employed, and the resultant deterioration of the emissive material, are entirely avoided. Moreover, since no binder is employed, there is no residuum of extraneous binder or decomposition products from the binder which, in conventional cathode forming processes, constitute potential sources of extraneous gas released during subsequent tube operation; thus, ion bombardment of the cathode is materially reduced.

A preferred apparatus for impacting the pulverulent dry particles of barium and strontium carbonates or other cathode-forming material on substrate 13 is illustrated in FIGURE 2. This apparatus includes a base 16 which supports a mechanism for suspending the pulverulent cathode forming material in a high-velocity gas stream. A cylindrical vertically oriented fractionating tower 17 is mounted on a vibrator 18 comprising an actuating solenoid device 20 for vibrating the attached column structure. The bottom portion of fractionating tower 17 includes an inlet port 21 which enters a chamber 22 capped by a wire-mesh screen 23. On top of screen 23 is placed a predetermined amount of pulverulent cathode-forming material 25 in a dry state. Fractionating tower 17 is capped by a plug 26 which includes a centrally located output port 27.

A source of pressurized gas such as nitrogen is supplied to inlet port 21 by a pressure tank 28. Other types of gas may be used if non-reactive with the cathode-forming material. A coupling hose 29 connects the inlet port 21 to the outlet valve 30 of the tank, the valve including means for regulating the output pressure. Outlet port 27 of the fractionating tower 17 is connected to a nozzle 32 by a rubber connecting hose 33. A rubber extension tip 32a serves as the output orifice of the nozzle. A valve assembly 34 is located at the midpoint of the hose 33 to open and close the hose to control the passage of material through it. The valve is schematically indicated to include a solenoid device 35 which is remotely operated by a switch 36.

Still referring to FIGURE 2, a plurality of cathode sleeves 12, preassembled in their ceramic supporting discs 10, are retained in a fixture plate 38 which is supported within a vented enclosure 39.

In carrying out the process fractionating tower 17 serves to separate the particles of cathode-forming material according to their size and weight, permitting only the smaller and lighter particles to reach outlet port 27. As the pressurized gas is blown through the pulverulent cathode-forming material 25, the lighter and smaller particles tend to collect near outlet port 27, while the heavier particles and any agglomerated clumps remain near mesh 23 at the bottom of the column. This, of course, necessitates periodic removal of the residue material and replenishment of cathode-forming material 25. The size of the fractionating tower 17 may be varied to control the size of the particles contained in the gas jet delivered by the apparatus; the taller the tower, the greater the fractionating effect.

Impacted cathodes have been produced with a fractionating tower 17 twelve inches in height with an internal diameter of approximately two inches. Approximately two teaspoonfuls of an equimolecular mixture of barium and strontium carbonates with particle sizes in the 250-500 mesh range were placed in the bottom of the tower. Nitrogen at a pressure of approximately 130 pounds per square inch was supplied from valve 30 to inlet port 21. A nozzle extension 32a, having an internal diameter of $\frac{1}{16}$ of an inch, was held approximately one inch from the cathode substrates 13.

Switch 36 is then operated, actuating valve 34 to open hose 33 and allow a momentary release of gas. The cathode-forming material 25 rises in the column of tower 17 as shown with the finer particles rising to the top and eventually being emitted in suspension with the jet of gas escaping through nozzle 32. Vibrator 18 is continuously actuated to minimize agglomeration of the cathode-forming material.

Nozzle 32 is directed at cathode substrate 13 and produces a high-velocity gas stream carrying the pulverulent dry cathode-forming material which impinges at high speed upon substrate 13. This impingement causes the particles to impact into the surface of the substrate and thus produce permanent adherence of the cathode-forming material to the substrate. Several factors determine the effectiveness of the adherence of the cathode-forming material to the substrate; namely, the pressure used, the distance of nozzle 32 from cathode sleeve 12, the size of the nozzle diameter, and the size and shape of the particles themselves. The latter, of course, is determined by the initial fineness of the pulverulent cathode-forming material 25 and, in addition, the height of fractionating tower 17. While a single jet may be employed, it has been found preferable to apply the particles with several successive jets of shorter individual duration.

The use of finely divided particles of cathode-forming material is critical if a uniform and densely packed emissive surface is to be produced. For example, a larger size particle or agglomerated bunch will, if blown through nozzle 32, tend to produce an uneven surface if it adheres to the substrate or alternatively may cause a flaking of the previously deposited material. Moreover, it is important that the carbonate particles be kept dry at all times during the process of applying them to the substrate.

The carbonate coated cathode sleeves 12 are then subjected to further processing in accordance with any of the known techniques, being handled in the same manner as cathode sleeves which have been carbonate coated with the use of a nitrocellulose binder. More particularly, the carbonate coated cathode sleeve is assembled with the other tube elements in its associated envelope which is baked during exhaust through an appropriate temperature-time cycle to reduce the carbonates to a thermionically active oxide coating. The resultant coating is, however, much smoother and more compact than that obtained with prior techniques and, as previously pointed out, is much freer of occluded gases and carbon residue.

It has been found that the thickness of the thermionically emissive layer which may be applied to a metal substrate by the jet impacting technique of the present invention is somewhat limited, owing to an observed tendency of the first-applied cathode-forming material to peel or flake under the impact of subsequent layers once a relatively small thickness has been exceeded. In fact, the maximum thickness which can be obtained by the application of a single layer of cathode-forming material by jet impaction is less than that required to provide adequate emission life or adequate beam current in a modern-day television picture tube. In accordance with the invention, it has been found that a jet-impacted layer of cathode-forming material such as barium and strontium carbonates in equimolecular proportions may be built up in thickness without sacrificing the greatly improved density and surface smoothness of the jet-impacted cathode by employing a somewhat different procedure on the second and subsequent layers or passes. It has been observed, in experimentation with the jet-impacted cathodes of the Pakswar application, that the barium and strontium carbonate particles carried by the high velocity jet acquire a positive electrostatic charge as they come into contact with insulating materials. It has further been observed, in accordance with the invention, that when such charged carbonate particles are deposited on the metal cathode

substrate they adhere to it, partly as a result of the charge and partly as a result of impact velocity. Moreover, the adherence has been observed to be much stronger when the charged particles impact on a previously deposited layer of the same carbonate materials, rather than on the metal substrate itself.

In accordance with another feature of the invention, an improved thermionic cathode of substantially any desired layer thickness may be produced by first forming only a thin layer of cathode-forming material on the metal substrate by the use of a direct high velocity jet, and thereafter depositing the remainder of the pulverulent cathode-forming material by blowing the powder stream past an insulating surface before contacting the precoated metal substrate.

For the application of subsequent carbonate layers by electrostatic charge attraction, a somewhat different jig or fixture for supporting the cathode sleeve is employed, as shown in FIGURE 3.

The cathode sleeve 12 and its supporting ceramic insulator ring 10 is placed in a tubular enclosure 48, and a pair of mating jigs 41 and 42 are provided within enclosure 48 to shield the cathode sleeve 12 from direct impingement by the powder jet. Three venting tubes 43 of insulating material such as glass extend through jig portions 41 and 42 and through apertures 15 in the ceramic supporting ring 10 in which cathode sleeve 12 is mounted. Nozzle extension 32a of the jet forming apparatus of FIGURE 2 is directed to the end of tubular enclosure 48 which accommodates the rear end of cathode sleeve 12, so that the high-velocity carbonate powder particles are blown through insulating tubes 43 and acquire a positive electrostatic charge. Upon emerging from venting tubes 43, in relatively close proximity to the previously jet-impacted carbonate coating on the end surface 13 of the cathode sleeve 12, the positively charged powder particles are attracted to the previously formed first layer on the cathode sleeve and are held there by electrostatic charge attraction. The thickness of the carbonate layer may be built up to the desired thickness, to provide emission efficiency and cathode life equivalent to or superior to those achieved with conventionally produced cathodes. Moreover, it has been determined that the adherence attributable to electrostatic charge attraction is sufficiently strong to withstand normal handling and gauging operations, and that the smoothness and density of the cathode produced in this manner is also superior to those obtained with wet processes such as spraying, cataphoretic deposition or centrifuging as employed in the prior art.

An alternative jig or fixture which may be employed for the electrostatic deposition of dry powder carbonates on the cathode substrate is shown in FIGURE 4, in which nozzle extension 32a of the jet producing apparatus of FIGURE 2 is inserted in a glass tube 49 which is provided with a plurality of laterally extending glass chambers 51 for individually receiving a metal cathode sleeve 12 having a previously applied jet-impacted carbonate layer. The dry pulverulent carbonate or other cathode-forming material, in passing through tube 49, acquires a positive electrostatic charge, and a substantial portion of this material is attracted into the lateral chambers 51 which contain the exposed end surfaces of the cathode sleeves. The charged cathode forming material is attracted to the substrate and its preliminary jet-impacted coating, and a carbonate coating of a desired thickness may be formed by appropriately timing the duration of this supplemental process step.

While the jet impacted cathode-forming material, and that retained by electrostatic charge attraction, adheres to the metal substrate sufficiently well to withstand most normal handling and even mechanical-contact gauging and jiggling, there may be applications in which additional adherence is required or desired. Such additional improvement in adherence can be obtained by precoating the car-

bonate or other cathode-forming material with a thin layer of dry plastic material. For example, an equimolecular barium and strontium carbonate powder may be mixed with a solution of a low molecular weight styrene resin in acetone and evaporated to dryness. The dry residue is then pulverized in a mortar to provide the dry powdered cathode-forming material for dispensing by the apparatus in FIGURE 2. When such plastic coated material is employed, the initial adherence is attributable to impaction and/or electrostatic charge attraction as before, but for still further improvements in adherence during intermediate processing steps, the coated cathode substrate may be heated to cause the plastic coating on the individual particles to serve as a temporary binder. The plastic material is of course baked out during exhaust of the tube in the process of activating the carbonate coating and reducing it to the required thermionically emissive oxide.

Thus the present invention provides a new and improved thermionic cathode with greatly improved surface smoothness. This is particularly important in electron tubes such as high transconductance television picture tubes where very close grid-to-cathode spacings are required. Moreover, cathodes formed in accordance with the present invention show good electron emission efficiency and tube life, all attributable to the elimination of carbon residues and occluded gases frequently encountered when a liquid nitro-cellulose binder is employed as in conventional prior processes.

The processes disclosed in conjunction with the present invention are also readily adaptable to automation techniques. For example, the cathode sleeves may be placed on a conveyor which passes successively under a plurality of dispensing nozzles, each of which may have a unique size or shape and be employed to apply particles in a particular size and shape range. These nozzles may be arranged to apply material by direct impaction, electrostatically, or by a combination of the two processes.

While a particular embodiment of the invention has been shown and described, it will be obvious to those skilled in the art that changes and modifications may be made without departing from the invention in its broader aspects, and, therefore, the aim in the appended claims is to cover all such changes and modifications as fall within the true spirit and scope of the invention.

I claim:

1. A process for the preparation of a thermionically emissive coating on an electrically conductive cathode substrate comprising the following steps:

exposing said substrate to electrostatically charged particles of dry cathode-forming pulverulent material comprising an alkaline earth carbonate whereupon said charged particles are bound to said substrate by electrostatic charge attraction to form a coating of said cathode-forming material on said substrate; and thereafter heating said substrate with its coating of cathode-forming material to provide a thermionically emissive coating on said substrate.

2. The process for the preparation of a thermionically emissive coating on a metal substrate comprising the following steps:

applying a high-velocity jet of dry cathode-forming pulverulent material comprising an alkaline earth carbonate to said substrate to cause said material to adhere to said substrate by impaction thereon;

exposing said substrate with said cathode-forming material impacted thereon to electrostatically charged particles of cathode-forming material whereupon said charged particles are bound to said impacted material by electrostatic charge attraction;

and thereafter heating said substrate with its adherent cathode-forming material to provide a thermionically emissive coating on said substrate.

3. A process for the preparation of a thermionically emissive coating on a metal substrate comprising the following steps:

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applying a high-velocity jet of dry cathode-forming pulverulent material comprising an alkaline earth carbonate to said substrate to cause said material to adhere to said substrate by impaction thereon;
 passing a jet of dry particles of cathode-forming material in close proximity to an insulating surface to cause such particles to acquire an electrostatic charge;
 and exposing said substrate with said jet-impacted material thereon to said charged particles, whereupon said charged particles are bound to said impacted material by electrostatic charge attraction.

4. A process for the preparation of a thermionically emissive coating on a metal substrate comprising the following steps:
 suspending dry particles of a pulverulent cathode-forming material comprising an alkaline earth carbonate in a gas jet;

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depositing a first layer of said pulverulent material on said cathode substrate by impinging said jet with said particles suspended therein on said substrate;
 and depositing a layer of electrostatically charged dry particles of pulverulent cathode-forming material on said first layer, whereupon said charged particles are bound to said first layer by electrostatic charge attraction.

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