

May 21, 1968

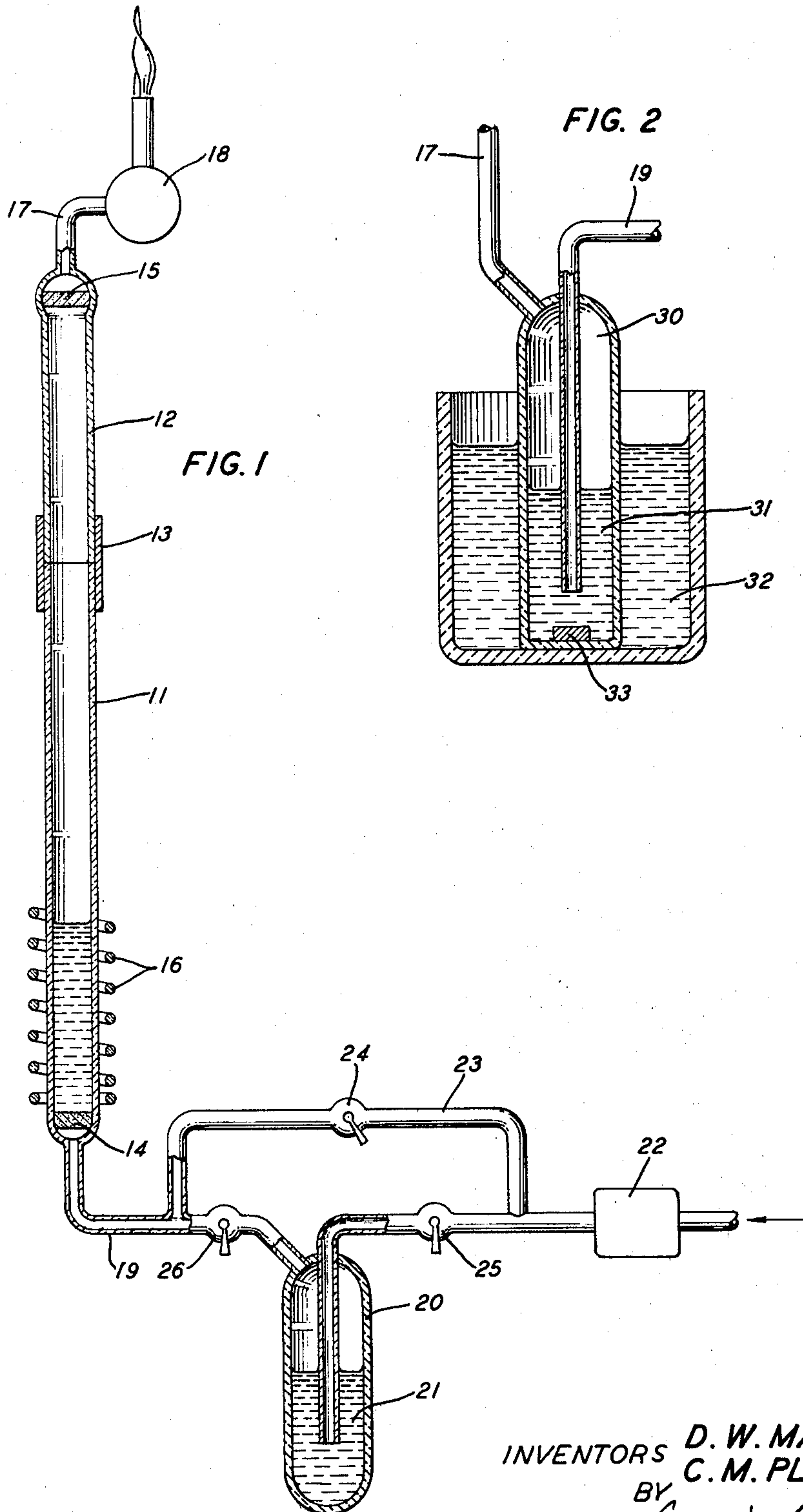
D. W. MAURER ET AL

3,384,511

CATHODE STRUCTURES UTILIZING METAL COATED POWDERS

Filed Jan. 13, 1966

3 Sheets-Sheet 1



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May 21, 1968

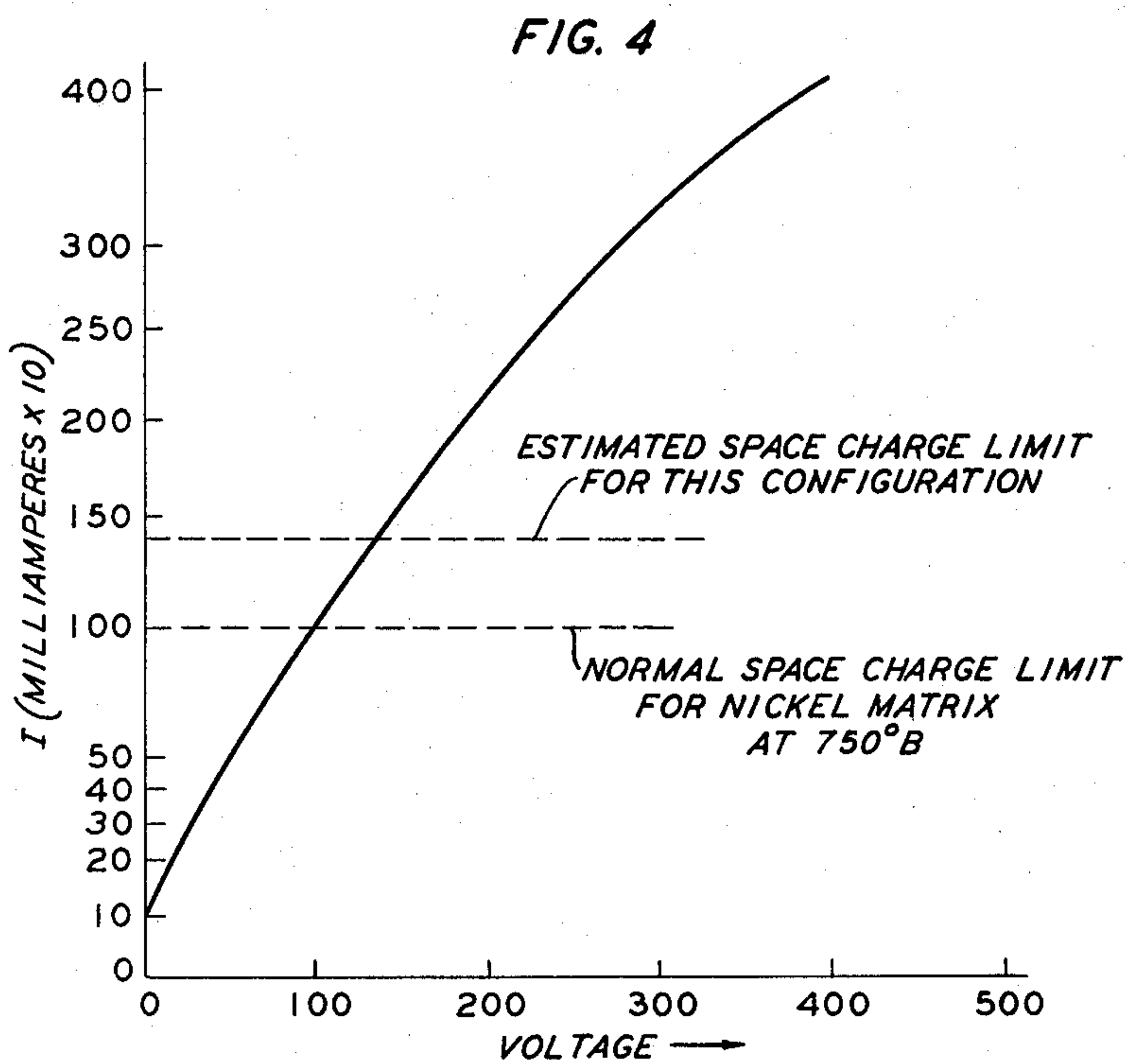
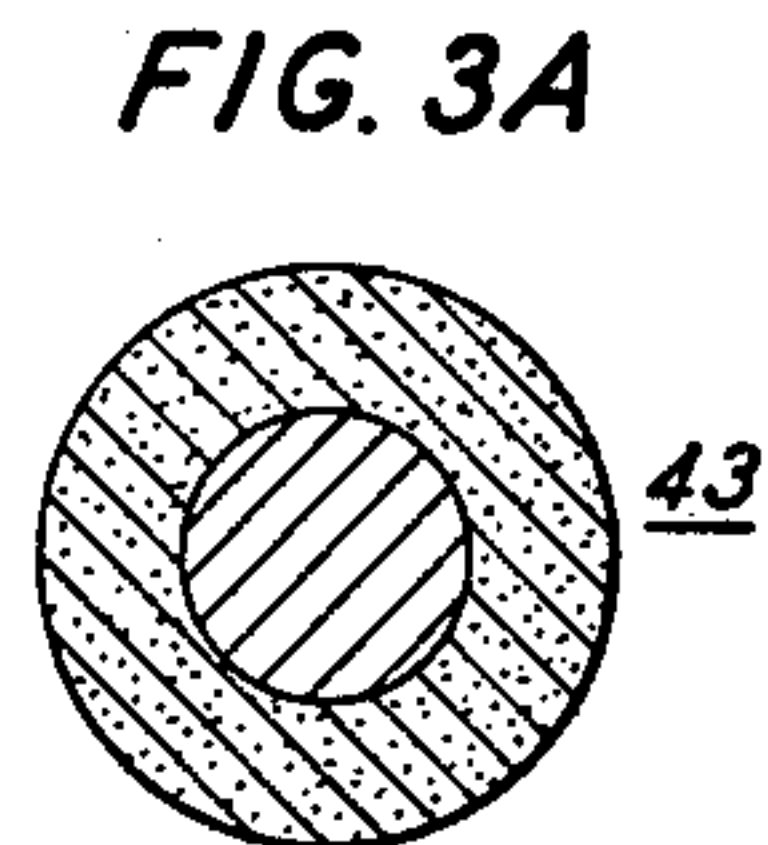
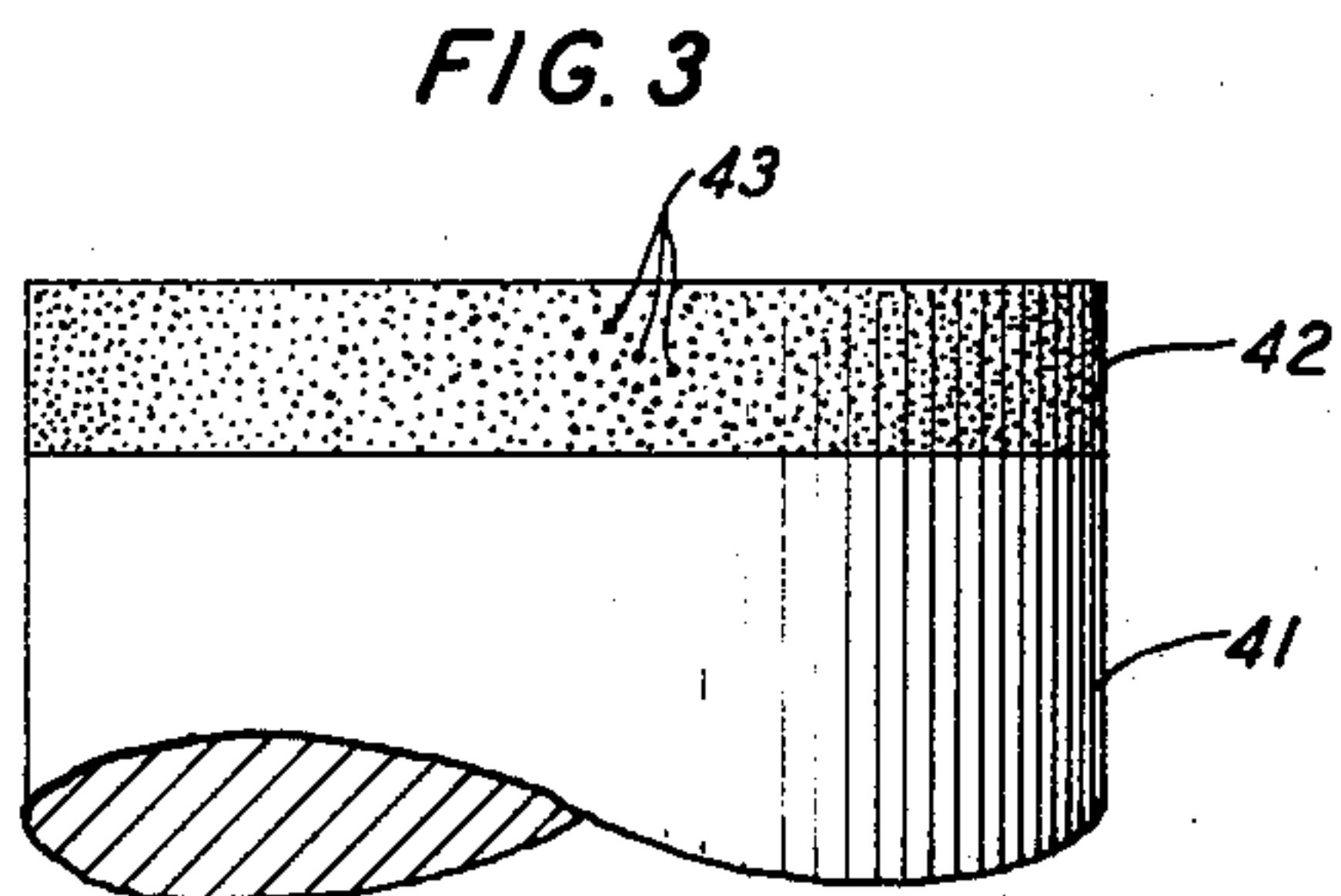
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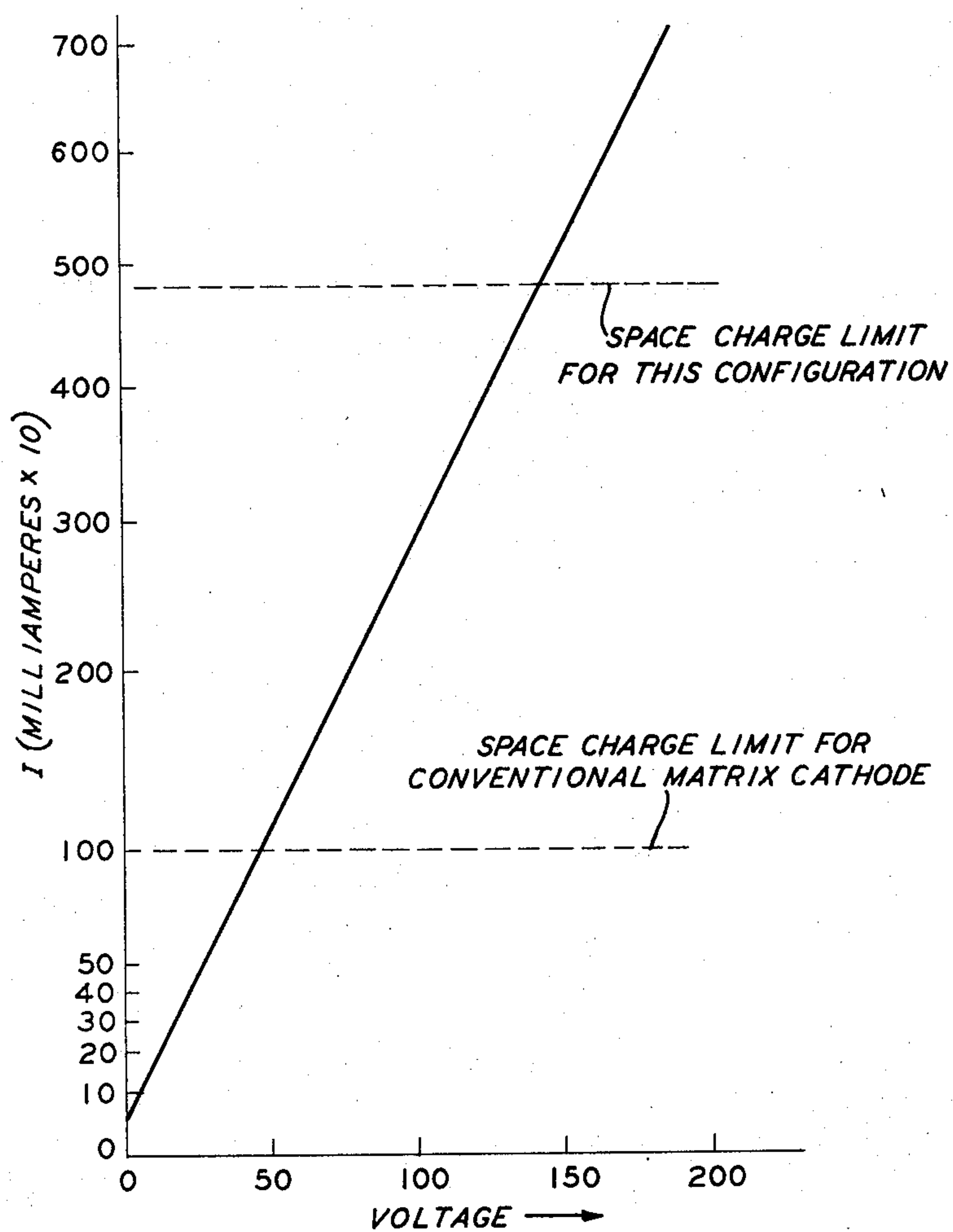
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CATHODE STRUCTURES UTILIZING METAL COATED POWDERS

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FIG. 5



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CATHODE STRUCTURES UTILIZING METAL COATED POWDERS

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Continuation-in-part of application Ser. No. 310,040, Sept. 19, 1963. This application Jan. 13, 1966, Ser. No. 520,488

4 Claims. (Cl. 117—224)

ABSTRACT OF THE DISCLOSURE

Coated and matrix type cathode element destined for use in thermionic tubes include a base member bearing a coating of an emissive material in particulate form, the particles of which have been previously coated with a thin film of a metal.

This application is a continuation-in-part of copending application Ser. No. 310,040, filed Sept. 19, 1963, now abandoned.

This invention relates to a technique for coating discrete particulate material and, more particularly, to a cathode structure including metal coated thermionically active powders which may be coated thereby.

There are three fundamental types of cathode structure in commercial use at this time. The earliest and most conventional type comprises a solid base having a coating of an alkaline earth metal oxide generally including barium oxide. The second type comprises a porous pressure molded tungsten matrix which is impregnated with barium aluminate. The third type of cathode structure in existence today is the nickel matrix cathode which includes a molded element made from a pressed and fired mixture, generally including nickel powder together with an alkaline earth metal oxide.

In general, each of these three types of cathode structures has certain advantages and disadvantages which dictate selection for a particular use. Thus, for a given configuration and operation conditions, the oxide coated cathode is capable of delivering a considerably higher current density than either matrix type structure. On the other hand, the matrix cathodes contain a reservoir of active material which is utilized to continually replenish the active emitting surface layer during life. Accordingly, matrix structures are considered more desirable for use under more adverse conditions, as for example, where there is a high degree of back bombardment, or under other conditions which may cause deterioration of the relatively thin oxide coating of the more conventional structure such as sustained direct-current emission greater than approximately 0.4 ampere per square centimeter.

In accordance with the present invention, a technique is described for the fabrication of both coated and matrix type cathodes including metal coated thermionically active powders. The inventive technique involves coating discrete particles of such powders with a thin film of a metal capable of forming a thermally unstable compound, coating being effected by conventional dry fluidization or plating techniques or by means of a novel wet fluidization technique. Claims in the application are directed to the novel fluidization technique and to the cathode structure and method for the preparation thereof. The particles so coated are then employed as the thermionically active materials in numerous cathode structures, so resulting in a group of devices manifesting higher current densities at lower operating temperatures than

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have heretofore been attained by any prior art cathode structure.

The invention will be more easily understood from the following detailed description taken in conjunction with the accompanying drawing wherein:

FIG. 1 is a schematic diagram of a dry fluidized bed system used in the practice of the present invention;

FIG. 2 is a schematic diagram of a novel, typical, wet fluidized system used in the practice of the present invention;

FIG. 3 is a cross-sectional view of a cathode structure fabricated in accordance with the present invention;

FIG. 3A is a cross-sectional view of metal coated thermionically active particles prepared as described;

FIG. 4 is a graphical representation on coordinates of current in milliamperes to the two-thirds power against voltage in volts showing the space charge break for a plasma sprayed cathode of the present invention at 750° B. after 720 hours of life; and

FIG. 5 is a graphical representation on coordinates of current in milliamperes to the two-thirds power against voltage in volts showing the space charge break for an air sprayed cathode of the present invention at 750° B. after 315 hours of life.

A general outline of the procedure employed in fabricating the novel structures described herein together with the ranges of operating parameters will now be given.

The first step of the inventive technique involves coating discrete particles of a thermionically active material with a thin film of a metal. Typically, the particulate material is an alkaline earth oxide, or carbonate depending upon the particular configuration desired. These materials are conventional emitting materials and commonly employed in the preparation of sprayed oxide and matrix cathodes.

Metals found suitable for coating in accordance with the present invention may be selected from among those metals which are compatible with the functioning of the cathode and are capable of forming thermally unstable compounds over a practical temperature range. Metals found particularly suitable in this use are tungsten, molybdenum, nickel and cobalt.

Coating of the discrete particulate material may be effected by any conventional coating or plating technique, as for example, dry fluidization, barrel plating et cetera. Additionally, coating may be effected by a novel wet fluidization technique. It will be appreciated by those skilled in the art that one objective of the wet fluidization method described herein is to avoid agglomeration of discrete particulate material during the coating operation, such being a major prior art problem. As employed herein, this novel technique is specifically directed to the coating of thermionically active particles, destined for use in cathode elements, with a thin film of tungsten, molybdenum, nickel or cobalt. However, it is evident that this technique is not restricted to the noted metals or even to metals and may be employed in any operation resulting in deposition of a material by means of thermal decomposition.

With further reference now to FIG. 1, there is shown a schematic diagram of a dry fluidized bed system which may be employed in the practice of the invention as one means for coating the active materials. Shown in the figure is stainless steel fluidization column 11 which is connected to glass column 12 by means of polyethylene joint 13. At the lower extremity of column 11 there is shown a porous stainless steel sintered frit 14 which completely obscures the diameter thereof, frit 14 being brazed into column 11. Glass frit 15 of the same porosity as frit 14 is similarly shown fused into column 12 at the upper extremity thereof to prevent the loss of powder in the

stream of fluidizing gas during operation. Column 11 is heated by means of heating coils 16, thereby providing the requisite heat for decomposition of the metal compound during the coating process. Shown connected to column 12 by means of conduit 17 is drying tube 18 through which the gaseous products of the process pass prior to being ignited at the exit end of the system. Shown connected to column 11 by means of conduit 19 is bubbler 20 which contains a metal compound 21 capable of decomposing thermally during the operation of the process. The system is completed by flowmeter 22 positioned at the entrance end of the system through which fluidizing gas enters from a source not shown. Bypass conduit 23 and valves 24, 25 and 26 are employed for controlling the process.

In the operation of the process, a suitable (non-oxidizing) fluidizing gas, for example, hydrogen, nitrogen or argon, depending upon the particles being coated, is admitted to the system at the entrance end, passes through flowmeter 22 and with valves 24 and 25 in the closed position and valve 26 in the open position, passes through bypass conduit 23 and conduit 19 into column 11 which is heated by means of heating coils 16 for a suitable period of time required to effect a bake-out of the system. Next, the thermionically active material which has previously been ball milled to the required particle size, generally within the range of 1-5 microns, is introduced into the system and fluidization initiated, the gas being employed therefor being hydrogen or any of the gases described above. Following, the effluent is ignited at the exit end of the system and burning continued throughout the process. Next, hydrogen is diverted from bypass conduit 23 by closing valve 26 and opening valves 24 and 25, thereby permitting the gas to pass through bubbler 20 and thence to column 11 wherein the metal compound 21 decomposes at elevated temperatures to yield an elemental metal which coats the thermionically active particles. The coated particles are subsequently removed from the system and stored until ready for use in the fabrication of a cathode element.

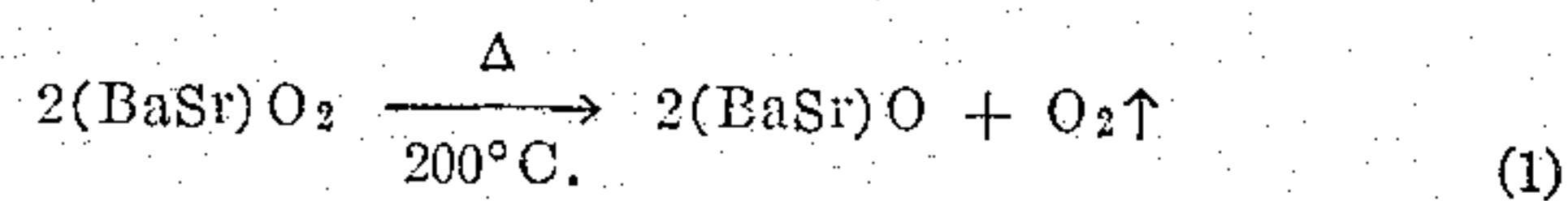
In an alternative inventive technique for coating the discrete particulate material, the apparatus shown in FIG. 2 is employed. This system has conveniently been termed "wet fluidization." In this system, columns 11 and 12 (of FIG. 1) are replaced by fluidization column 30 containing an inert fluid 31 and having a suspension of finely divided thermionically active materials of the type described above. Column 30 is heated by means of a constant temperature bath 32. A suitable stirring device 33, typically a magnetic stirrer, assures the requisite agitation of the particulate material during coating. Once again, bubbler 20 contains a metal compound 21 capable of decomposing thermally during the operation of the process. It will be understood that this compound may be either a liquid or a solid manifesting an appreciable vapor pressure. Thus, as applied herein, liquid nickel carbonyl may be employed as a source material of nickel or a solid carbonyl such as molybdenum carbonyl may be used.

In order that those skilled in the art may more fully understand the inventive concept herein presented, the following examples are given by way of illustration and not limitation.

Example I

This example describes the fabrication of a cathode structure wherein nickel coated alkaline earth oxides (barium-strontium coprecipitated) are plasma sprayed upon a solid active alloy base.

Coprecipitated barium-strontium peroxide was placed in a boat constructed of Driver Harris No. 499 nickel, a high purity passive material. Next, the boat was inserted in a quartz tube furnace maintained under vacuum and heated at 900° C. for a time period of hours, thereby causing decomposition of the peroxides to the corresponding oxides in accordance with Equation 1. The pressure at the conclusion of heating was approximately 10⁻³ torr.



The coarse product was then transferred to a Pyrex mill jar containing aluminum oxide balls and ball milled for 36 hours, thereby forming a fine barium-strontium oxide powder having maximum particle size of 37. The resultant fine powder was then charged to a precleaned and pre-baked fluidization column of the type illustrated in FIG. 1. Fluidization was initiated by admitting a stream of hydrogen saturated with carbonyl derived nickel from bubbler 20 at room temperature and coating attained by heating the fluidization column to a temperature of 100° C. for 20 hours, thereby causing decomposition of the carbonyl and concomitant coating of the barium-strontium oxide particles with a film of nickel. The coated particles contained 14 percent by weight nickel and 86 percent by weight barium-strontium oxide.

Two cathode buttons (machine plugs) of 0.1 percent zirconium-nickel alloy, having a diameter of 0.085 inch were selected and the top surfaces thereof grit blasted with aluminum oxide grit and subjected to a conventional cleaning procedure for oxide cathode bases. The cleaning technique involved racking the caps in a nickel-zirconium boat and subjecting the caps to a conventional vapor degreasing technique. Next, the caps were blown dry with low pressure nitrogen and ultrasonically washed. Following, the washed caps were rinsed in cascading de-ionized water, dried in an air oven at 110° C. for 15 minutes, oxidized in air at 400° C. for 20 minutes and reduced in wet hydrogen at 1050° C. for 30 minutes. Following, the cleansed buttons were mounted in a jig and plasma-spray coated with the nickel coated barium-strontium oxide particles to a thickness of 3 mils in accordance with the following procedure.

The coated particles were deposited by means of a direct-current arc plasma gun wherein hydrogen was ionized by passage through a high power direct-current, arc thereby forming a highly energetic plasma downstream from the arc at which point the recombination energies of the ionic species produced was translated into thermal energy of the gas atoms. The introduction of the discrete particulate material into this high energy area renders them molten. The molten particles were then permitted to impinge upon a substrate, the cathode buttons, where they coalesced to form a dense coating.

One of the buttons so obtained was then fired for 15 minutes at 800° C. in a hydrogen ambient in a conventional furnace and subsequently coined under an applied pressure of 50 tons per square inch. Then, the button was placed in a molybdenum heater sleeve and sintered by firing for 15 minutes at 1000° C. in a hydrogen ambient.

The other cathode button was initially placed in a molybdenum heater sleeve and sintered as described above.

FIG. 3 is a cross-sectional view of a cathode element prepared in accordance with the technique described above. Shown in the figure is a base region 41 including nickel together with an activator and a coating 42 comprising metal coated thermionically active particles 43, the particles 43 being shown in greater detail in FIG. 3A.

When ready for use, the cathode elements so produced were assembled in a tube envelope by conventional techniques and sealed to a vacuum system in which a vacuum of 10⁻⁷ millimeters of mercury could be attained, and in which the structure was baked for 16 hours at 400° C. After bake-out, cathode heater voltage was applied to increase the cathode temperature to 1050° C. at which it was maintained for 5 minutes. Next voltage was applied to the anode until a cathode current of 1 amp./cm.² was attained. The tube was then sealed off the station. The completed diode was then placed on a life test rack and its operating characteristics observed.

The full impact of the present invention can best be seen by reference to FIG. 4. The data reflected therein

was obtained by placing the cathode elements prepared as described in Example I on a life test rack and applying 200 volts to the anodes. After 720 hours of life the direct current of each was measured as a function of the anode voltage at 750° B. The data obtained was then plotted on a graph having current in milliamperes to the two-thirds power as one coordinate and voltage as the other coordinate.

It is noted that the space charge limited emission of the two cathodes fabricated in accordance with the inventive technique is approximately 15 milliamperes at 750° B. (same curve for each) as compared with a maximum space charge limited emission of 10 milliamperes for conventional nickel matrix cathodes, a significant advance from the standpoint of cathode technology.

Example II

This example describes the fabrication of a cathode structure wherein nickel coated alkaline earth carbonates (barium-strontium) are air sprayed upon a solid active alloy base.

80 g. SrCO_3 , 72 g. BaCO_3 , and 200 cc. of amyl acetate were placed in a mill jar containing flint stones and ball milled for 64 hours, so forming a fine suspension of carbonate powder in amyl acetate. The resultant suspension was then charged to a fluidization column (30) of the type illustrated in FIG. 2, the fluidization column being immersed in constant temperature oil bath 33. Fluidization was initiated by admitting a stream of hydrogen containing nickel carbonyl vapor into the fluidization column and coating attained by heating the column by means of oil bath 33 to a temperature within the range of 80–90° C. for 22 hours, thereby causing decomposition of the carbonyl and coating of the carbonates with a thin film of nickel.

The apparatus was next dismantled and the carbonates separated from the amyl acetate by filtration and dried in air at 110° C.

100 g. of the coated carbonates were then mixed with 75 ml. of amyl acetate and 82 cc. of a nitrocellulose binder solution in order to form a carbonate mix.

A cathode button of 0.1 percent zirconium-nickel alloy, having a diameter of 0.085 inch was selected and cleaned in accordance with the procedure described in Example I. The carbonate mix was then sprayed upon the cathode with a conventional artist's air brush, a coating of 0.5 mil in thickness being formed. Following, the sprayed cathode was fired at 250° C. in oxygen to burn off the binder.

When ready for use, the cathode so produced was assembled in a tube envelope by conventional techniques and sealed to a vacuum system in which a vacuum of 10^{-7} millimeters of mercury could be attained and in which the structure was baked overnight at 400° C. After bake-out, cathode heater voltage was applied to increase the temperature to 800° B. for outgassing at which it was maintained for 100 minutes or until the pressure was 4×10^{-7} torr. Next, the temperature was increased to 950° B. and maintained thereat for 5 minutes. Following, the temperature was decreased to 850° B. and voltage

applied to the anode until a cathode current of 0.5 amp./cm.² was attained. The tube was then sealed off the station, placed on a life test rack, and aged.

The data reflected in FIG. 5 was obtained by placing the cathode prepared as described in Example II on a life test rack and applying 150 volts to the anode. After 315 hours of life, the direct current was measured as a function of the anode voltage at 750° B. The data obtained was then plotted on a graph having current in milliamperes to the two-thirds power as one coordinate and voltage as the other coordinate.

It is noted that the space charge limited emission of the cathode fabricated in accordance with the inventive technique is approximately 48 milliamperes at 750° B. as compared with a maximum space charge limited emission of 10 milliamperes for conventional matrix cathodes.

While the invention has been described in detail in the foregoing specification and the drawing similarly illustrates the same, the aforesaid is by way of illustration only and is not restrictive in character. The several modifications which will readily suggest themselves to persons skilled in the art all considered within the scope of this invention, reference being had to the appended claims.

What is claimed is:

1. A cathode element destined for use in a thermionic tube including a base member comprising nickel and a coating deposited upon said base member, said coating comprising a discrete particulate material selected from the group consisting of (a) at least one alkaline earth oxide and (b) at least one alkaline earth carbonate, the particles of said discrete particulate material having been coated with a thin film of at least one metal selected from the group consisting of nickel, tungsten, molybdenum, and cobalt.
2. A cathode element in accordance with claim 1 wherein said base member is an alloy of nickel.
3. A cathode element in accordance with claim 2 wherein said base member is an 0.1 percent zirconium-nickel alloy.
4. A cathode element in accordance with claim 3 wherein said coating comprises nickel coated barium-strontium oxide.

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