United States Patent [19]

Buescher

[11] **3,879,830**

[45] **Apr. 29, 1975**

[54] **CATHODE FOR ELECTRON DISCHARGE DEVICE HAVING HIGHLY ADHERENT EMISSIVE COATING OF NICKEL AND NICKEL COATED CARBONATES**

[75] Inventor: **William E. Buescher,** Emporium, Pa.

[73] Assignee: **GTE Sylvania Corporation,** Stamford, Conn.

[22] Filed: **Dec. 8, 1972**

[21] Appl. No.: **313,571**

Related U.S. Application Data

[62] Division of Ser. No. 158,576, June 30, 1971, Pat. No. 3,772,045.

[52] **U.S. Cl.** ..... **29/182.3;** 29/182.5; 252/513; 252/521; 313/346 DC; 313/346 R; 313/355

[51] **Int. Cl.** **C22c 1/05**

[58] **Field of Search** ..... 29/182.3, 182.5; 313/346 DC, 346 R, 355; 75/213; 252/513, 521

[56] **References Cited**

UNITED STATES PATENTS

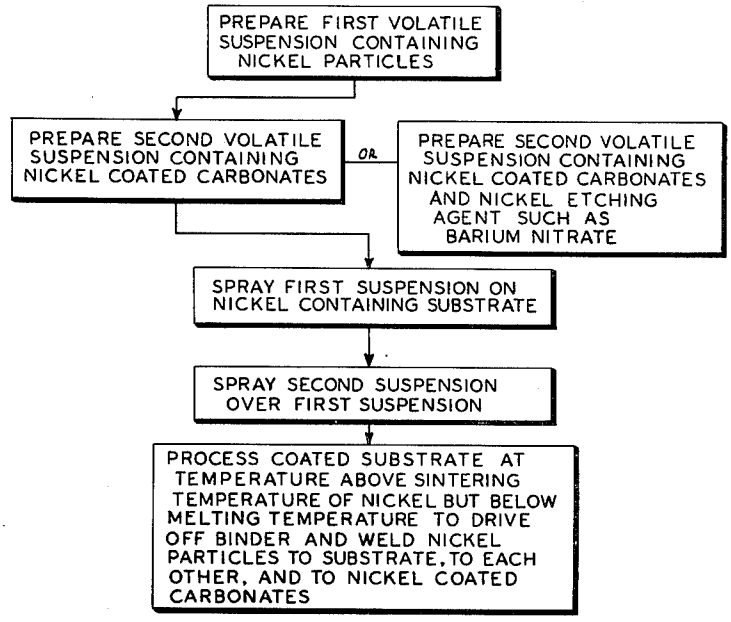
2,543,439	2/1951	Coomes et al.	29/182.3 X
2,681,375	6/1954	Vogt	29/182.3 X
3,031,740	5/1962	Culbertson et al.	29/182.3
3,102,329	9/1963	Horn et al.	29/182.3
3,183,396	5/1965	Becker et al.	29/182.3 X
3,197,847	8/1965	Kerstetter	29/182.3
3,327,158	6/1967	Schwender	29/182.3
3,699,378	10/1972	Buescher et al.	313/346 DC

Primary Examiner—Benjamin R. Padgett
Assistant Examiner—R. E. Schafer
Attorney, Agent, or Firm—Norman J. O'Malley; Cyril A. Krenzer; William H. McNeill

[57] **ABSTRACT**

An application of metal particles comprised substantially of nickel to a nickel containing cathode substrate is followed by the application of potentially emissive materials comprised of nickel coated carbonates of barium and/or strontium and/or calcium. The particles and nickel coated carbonates are diffusion bonded or welded to the substrate and to each other after the cathode is mounted in a tube, simultaneously with activation of the cathode. The coating thus provided is very adherent and reduces arcing during high voltage applications. An alternate embodiment for further increasing adherence of the emissive material comprises adding a nickel etching agent, such as barium nitrate, to the potentially emissive material suspension. During the temperature increase noted above to activate the cathode, the etching material first melts and densifies the carbonates and then decomposes to etch the nickel particles and the substrate. Further heating changes the etching material and stops the reaction.

2 Claims, 2 Drawing Figures



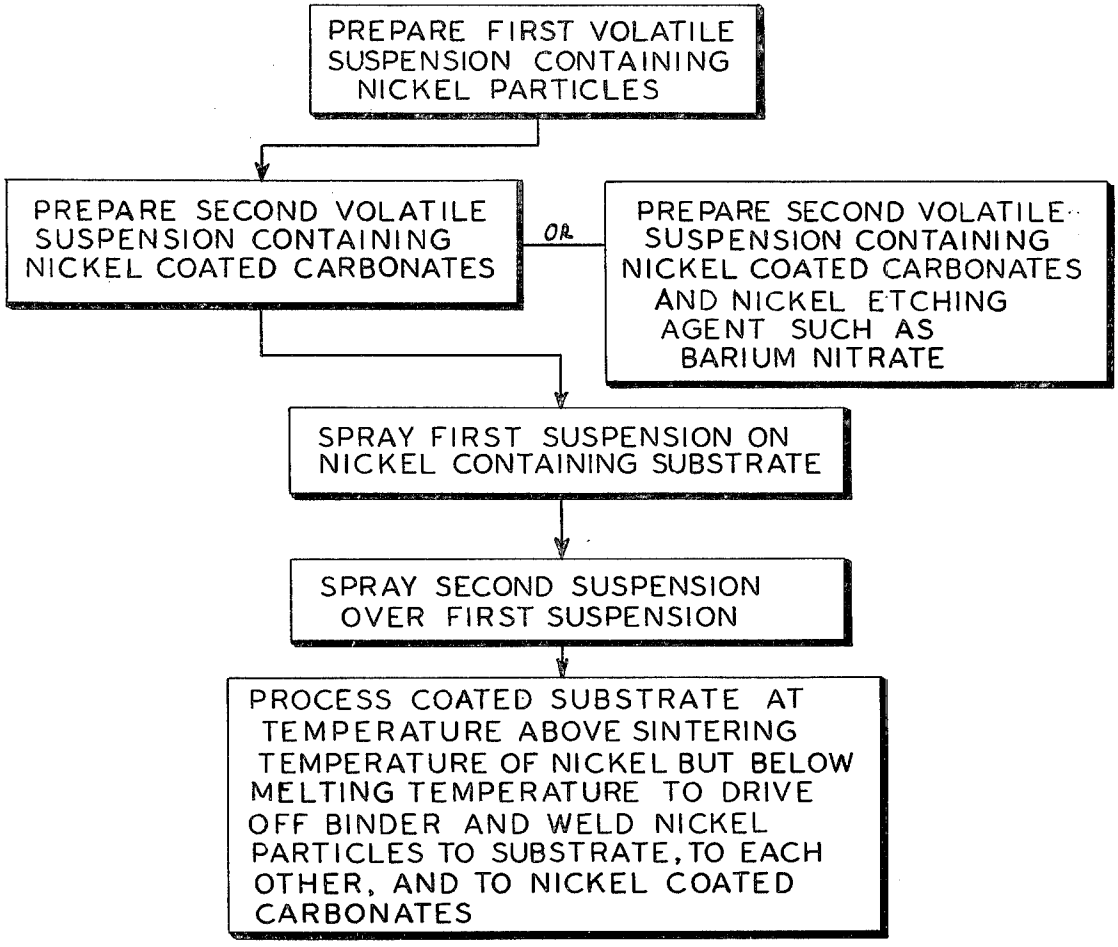

PREPARE FIRST VOLATILE SUSPENSION CONTAINING NICKEL PARTICLES
PREPARE SECOND VOLATILE SUSPENSION CONTAINING NICKEL COATED CARBONATES
OR
PREPARE SECOND VOLATILE SUSPENSION CONTAINING NICKEL COATED CARBONATES AND NICKEL ETCHING AGENT SUCH AS BARIUM NITRATE
SPRAY FIRST SUSPENSION ON NICKEL CONTAINING SUBSTRATE
SPRAY SECOND SUSPENSION OVER FIRST SUSPENSION
PROCESS COATED SUBSTRATE AT TEMPERATURE ABOVE SINTERING TEMPERATURE OF NICKEL BUT BELOW MELTING TEMPERATURE TO DRIVE OFF BINDER AND WELD NICKEL PARTICLES TO SUBSTRATE, TO EACH OTHER, AND TO NICKEL COATED CARBONATES

FIG. 1

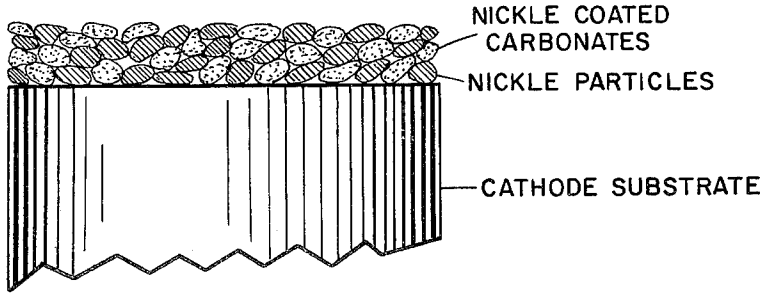

NICKLE COATED CARBONATES
NICKLE PARTICLES
CATHODE SUBSTRATE

FIG. 2

CATHODE FOR ELECTRON DISCHARGE DEVICE HAVING HIGHLY ADHERENT EMISSIVE COATING OF NICKEL AND NICKEL COATED CARBONATES

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a division of Ser. No. 158,576, filed June 30, 1971, now U.S. Pat. No. 3,772,045, and assigned to the assignee of the present invention, recorded June 30, 1971 at Reel 2753, Frame 437.

BACKGROUND OF THE INVENTION

This invention relates to thermionic cathodes and more particularly to a method of increasing adherence of the emissive material to the cathode body or substrate to reduce arcing in high voltage applications and thus improve the performance and life of the cathodes and to cathodes produced thereby. The problem of arcing between the cathode and associated electrodes in high voltage vacuum tubes, with a concomitant peeling of the emissive material, has long been known and many solutions have been proposed to obviate the difficulty. One of the earliest proposals involved roughening the cathode surface to achieve better adherence of the emissive material. The roughening could be accomplished by sandblasting or acid etching the cathode substrate before the application of the potentially emissive material. Another solution, proposed in 1937 by Kolligs et al. (see U.S. Pat. No. 2,172,207) contemplated applying a layer of powdered nickel or other suitable material to the cathode substrate in a paraffin oil carrier and then sintering the powder to the base. This left a roughened surface over which the potentially emissive material was applied. Still another solution was suggested by Toorks in 1945 (see U.S. Pat. No. 2,433,821). This solution involved fixing a wire mesh or screen to the cathode base and filling the holes therein with potentially emissive material. A still further solution was suggested by Hendricks in 1960 (see U.S. Pat. No. 3,110,081). Herein a cathode base had applied thereto a layer of nickel particles or other suitable material which was then sintered. Then potentially emissive material was applied to the sintered layer and the excess removed. Subsequently, sufficient pressure was applied to the emissive material-particle layer to cold-weld the nickel particles to the base and to deform the particles so that the emissive material was retained in re-entrant cavities between the now deformed nickel particles.

While all of these approaches improved the performance of cathodes by increasing adherence of the emissive material, they suffered from disadvantages such as increased cost or the requirement of extra processing steps: viz., extra sintering. Additionally, all prior art attempts formed roughened surfaces or provided pockets in porous material to trap the emissive material without doing anything to the emissive particles per se. In the highly competitive field of vacuum tubes it would be advantageous if a cathode with good emission and a highly adherent coating could be made. Further, since any additional costs can be very detrimental it would be advantageous if a simple, inexpensive method of achieving good emissive material adherence could be developed.

OBJECTS AND SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to obviate the disadvantages of the prior art.

It is another object of the invention to provide a new and novel cathode having a highly adherent emissive layer.

It is a still further object of the invention to provide a method of manufacturing such cathodes.

These objects are accomplished in one aspect of the invention by the provision of a cathode having a substrate or body with a layer of a powdered material, comprising mostly nickel, thereon. The emissive material comprises nickel coated particles which are welded to each other, to the powdered layer and to the substrate.

The cathodes are produced by the provision of a method comprising the steps of applying a layer of powdered material, comprised of mostly nickel, in a volatile binder to a cathode substrate. A first spraying source is used for depositing the material. Directly over this layer is applied a layer of nickel coated emissive particles in a similar volatile binder. In an alternate embodiment this second binder contains a nickel etching agent that is non-reactive at room temperature. A suitable material is barium nitrate [$Ba(NO_3)_2$]. After both the nickel layer and the nickel coated potentially emissive particles are applied, the cathode is completely processed within its associated tube. The processing involves raising the cathode temperature to about 1100°C which simultaneously volatilizes the binders, activates and then changes the nickel etching agent (when it is used), welds the nickel coated emissive particles to each other, to the powdered material and to the substrate, and activates the emissive material. The processing temperature used is greater than the normal sintering temperature usually associated with nickel and less than the melting temperature thereof. This method eliminates the separate sintering step taught by the prior art and provides a thermionic cathode with a strongly adherent emissive coating. The nickel coated emissive material and the etching agent further serve to create an excellent cathode coating.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a flow diagram of the process;

FIG. 2 is a diagrammatic view of a cathode of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For a better understanding of the present invention, together with other and further objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims.

Referring now to the invention with greater particularity, a thermionic cathode comprises a substrate of nickel or a nickel alloy containing substantially nickel together with small percentages of one or more reducing agents such as magnesium, silicon and manganese. The total of all the reducing agents is generally less than 6% by weight of the alloy. One such material is K3 alloy which is available from GTE Sylvania Incorporated, Chemical and Metallurgical Division, Towanda, Pennsylvania. The substrate, for an indirectly heated cathode, is a hollow sleeve which can be of any desired cross-sectional configuration such as circular or rectan-

gular. Applied to the substrate is a layer of nickel particles which is porous, or a nickel alloy such as K3, having thereover and therein an emissive material comprising nickel coated particles. The particles, when applied, are generally in the form of carbonates or combinations of the carbonates of barium, strontium or calcium. During cathode activation, which occurs during the processing of the tube, the carbonates are decomposed to the oxides. The oxides are made highly emissive when a reducing agent in the cathode nickel substrate reacts with the oxides to produce an excess of barium in the barium, strontium-calcium-oxygen matrix. The nickel particles and the nickel coated emissive materials are diffusion bonded or welded to each other and to the cathode substrate, the welding also taking place during the aforesaid activation of the cathode. This cathode has excellent adherence of the emissive coating by virtue of the nickel particle layer and the nickel coated emissive material.

The above-described cathode lends itself to a simple and economical fabrication process. A cathode substrate is suitably cleaned by known techniques in preparation for spraying and is placed in a suitable spraying jig, also known in the art.

A suitable nickel particle suspension can be made in the following non-limiting manner.

In a 1 gallon glass ball mill place

2,000 gms of nickel powder (or K3 or other alloy)

2,300 ml of nitrocellulose lacquer as a binder

470 ml of methyl amyl acetate as a solvent

mill the above for 15 hours with 2,560 gms of borundum cylinders and then decant. Rinse the mill with 1,200 ml methyl amyl acetate and add the rinse to the suspension. The suspension is rolled again for one hour, without the borundum cylinders, before spraying. The nickel particles can be of conventional configuration or they can be dendritic, as discussed in Ser. No. 158,578, filed June 30, 1971.

The potentially emissive materials, which can be mixtures of nickel coated barium and/or strontium and/or calcium carbonates are prepared in a suspension as follows:

In a 1 gallon glass ball mill place

1,300 gms of nickel coated carbonates (2% nickel by weight)

650 ml of nitrocellulose lacquer as a binder

790 ml of diethyl oxylate as a slow drying solvent

700 ml of diethyl carbonate as a solvent.

In the alternate embodiment 556 ml of barium nitrate suspension as a nickel etching agent is added. The suspension comprises about 160 gms of barium nitrate to 1,600 ml of methyl amyl acetate.

Mill these ingredients for 8 hours.

With both suspensions prepared, each is positioned as a supply source to a separate spraying gun and the process is begun. The previously positioned cathode substrate is now sprayed with a desired thickness of nickel powder. This thickness will vary depending upon the type of cathode being manufactured but generally will not be less than 0.001 inch nor more than 0.005 inch. After spraying with the nickel powder the cathode is sprayed with the carbonate suspension. The nickel particles provide a porous layer on the cathode substrate and the solvents in the cathode suspension carry the carbonates throughout the nickel layer.

If the carbonate suspension is sprayed directly after the nickel suspension, so that the nickel suspension is still wet, then methyl amyl acetate can be used as the solvent in the carbonate suspension. Where, however, there is a possibility that the sprayed nickel layer will have dried, it is preferred to utilize the diethyl oxylate as solvent since it is slower drying than the acetate and thus allows more time for the carbonates to penetrate the nickel layer. After the spraying has been completed, the cathode can be stored until it is ready to be used in a tube. After assembly into a tube the cathode is activated, the nickel particles etched by the action of the nickel etching agent, which is not reactive at room temperature, the solvents and binder volatilized and the nickel particles and the nickel coated emissive materials welded to the cathode substrate and to each other during the final tube processing. During the final processing the cathode temperature is raised from room temperature (22°C) to 1,100°C. At about approximately the midpoint of this range (592°C) the barium nitrate (when used in the alternate embodiment) melts and acts to densify the emissive material by carrying it into the nickel layer. As the temperature continues to rise (at some point over 600°C) the [$Ba(NO_3)_2$] decomposes according to the equation $2Ba(NO_3) \gtrless 600°C + 2Ba + 4NO_2 + 2O_2$. It is believed that the NO_2 then reacts with water vapor to form HNO_3. The HNO_3 etches the sleeve, the powder nickel layer and the nickel coated emissive materials, probably by forming NiO. The roughened surfaces thus formed increase the bonding capabilities of the various particles and forms a very adherent, dense layer of emissive material. As the processing continues, the NiO is reduced by CO, which is one of the by-products of the carbonate decomposition, to Ni with the CO being oxidized to CO_2. This is then pumped from the tube at exhaust.

The binding phenomenum is called welding since the 1,100°C temperature which is reached in final processing is in excess of the normal sintering temperature of nickel particles, 975°C, but is below the melting temperature which is approximately 1,460°C.

The emissive layer produced by this method is extremely tenacious and resists even determined scraping with a knife blade. Emission characteristics are excellent as are the life of the cathodes and the resistance to arcing. Excellent heat and electrical conduction is maintained through the nickel particles and the nickel coated emissive materials.

While there have been shown and described what are at present considered the preferred embodiments of the invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention as defined by the appended claims.

What is claimed is:

1. A cathode for an electron discharge device comprising: a substantially nickel substrate having thereon a porous layer of sintered powdered material, said powdered material being substantially nickel; and a quantity of emissive material overlying and permeating said porous layer, each particle of said emissive material being nickel coated, the powdered material and said nickel coated particles of emissive material being welded to each other and to the substrate to form a highly adherent coating.

2. The cathode of claim **1** wherein said nickel coating on said particles of emissive materials comprises from about 2 to 7% by weight of said particles.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,879,830
DATED : April 29, 1975
INVENTOR(S) : William E. Buescher

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 9: "3,772,045" should read --- 3,722,045 ---.

Signed and sealed this 15th day of July 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,879,830
DATED : April 29, 1975
INVENTOR(S) : William E. Buescher

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 9: "3,772,045" should read --- 3,722,045 ---.

Signed and sealed this 15th day of July 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks