

[54] **METHOD OF IMPROVING ADHERENCE OF EMISSIVE MATERIAL IN THERMIONIC CATHODES**

3,048,146	8/1962	Coppola	117/223 X
3,110,081	11/1963	Hendriks	313/346 X
3,393,090	7/1968	Barraco	117/217
3,400,294	9/1968	Kling	29/25.17

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[57] **ABSTRACT**

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An application of dendritic nickel particles to a nickel containing cathode substrate to form a porous nickel is filled with potentially emissive material in one or more alternate spray passes. The nickel particles are welded to the substrate and to each other at the time the cathode is activated at a temperature in excess of the sintering temperature but below the melting temperature of the nickel particles. The procedure eliminates a separate sintering step and provides excellent adherence of the emissive material, thus reducing many arcing problems in high voltage applications.

[52] U.S. Cl. **29/25.17, 29/25.11, 117/217, 117/219**

[51] Int. Cl. **H01j 9/00**

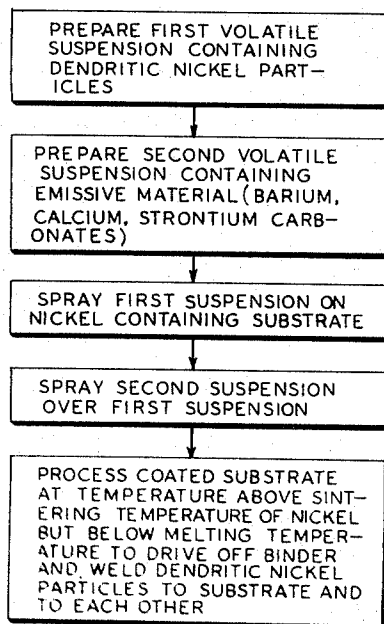
[58] Field of Search.....29/25.1, 25.11, 25.14, 25.15, 29/25.17; 117/215, 217, 219, 223

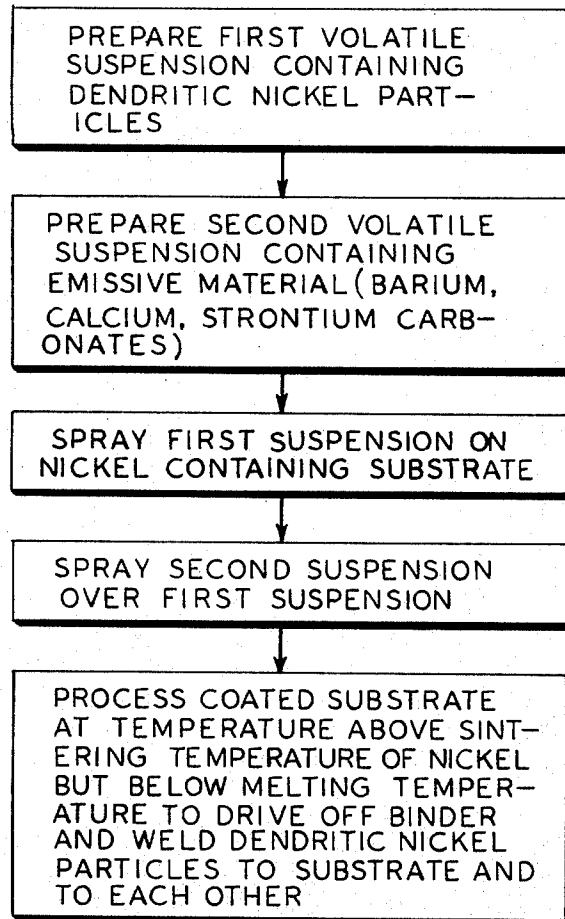
[56] **References Cited**

UNITED STATES PATENTS

2,172,207	9/1939	Kolligs et al.	313/345 X
2,943,957	7/1960	Grattidge et al.	117/223

6 Claims, 1 Drawing Figure





METHOD OF IMPROVING ADHERENCE OF EMISSIVE MATERIAL IN THERMIONIC CATHODES

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 to reduce arcing in high voltage applications and thus improve the performance and life of the cathodes. 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. The roughening could be accomplished by sandblasting or acid etching. 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 powdered nickel 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 all suffered from one or more disadvantages: namely, they were too expensive or they required additional steps such as multiple firings of the cathode base. In the highly competitive field of vacuum tubes, any additional costs can be very detrimental, thus, 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 method of manufacturing thermionic cathodes.

It is a still further object of the invention to provide a method of manufacturing cathodes which have highly adherent emissive layers with good heat and electrical conductivity throughout.

These objects are accomplished in one aspect of the invention by the provision of a method of manufacturing thermionic cathodes by the steps of applying to a cathode substrate a layer of dendritic nickel particles in a volatile binder. Directly over this layer is applied the potentially emissive material in a similar binder. After

both the nickel and potentially emissive material are applied, the cathode is completely processed within its associated tube to simultaneously volatilize the binders, weld the nickel particles to the cathode base and each other, and activate the emissive material. The processing temperature used is greater than the minimum sintering temperature usually associated with nickel and less than the melting temperature thereof. This method eliminates completely the separate sintering step taught by the prior art and provides a thermionic cathode with a strongly adherent emissive coating at reduced cost.

BRIEF DESCRIPTION OF THE DRAWING

The single FIGURE is a flow diagram 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 substrate or sleeve of nickel or a nickel alloy containing substantially nickel together with small percentages of one or more reducing agents is suitably cleaned by known techniques in preparation for spraying, and is placed in a suitable spraying jig, also known in the art. The sleeve may be of any desired configuration such as tubular or rectangular and may be fabricated from a melt or by powdered metallurgical techniques.

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

In a one gallon glass ball mill place
2,000 gms dendritic nickel powder
2,300 ml nitrocellulose lacquer as a binder
470 ml methyl amyl acetate as a solvent

Ball mill these ingredients for 15 hours and then decant. The glass mill is then rinsed with 1,200 ml methyl amyl acetate and the rinse is added to the decanted suspension. The entire suspension is rolled again for one hour before spraying. The dendritic nickel particles are irregular in shape, being elongated and branched, and a suitable type is available from the International Nickel Co. under the designation No. 287 (Grade B) nickel powder.

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

In a one gallon glass ball mill place
1,300 gms of suitable carbonates
650 ml nitrocellulose lacquer as a binder
790 ml diethyl oxylate as a slow drying solvent
700 ml diethyl carbonate as a solvent
Ball mill these ingredients for 15 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 dendritic 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 very irregular shape of the dendritic nickel particles provides a porous nickel layer on the cathode substrate and the solvent in the cathode suspension carries 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 assembled in a tube. After assembly into a tube the cathode is activated, the solvents and binder volatilized and the dendritic nickel particles welded to the cathode substrate and each other during the final tube processing. This occurs at a temperature of about 1,100°C, which is the normal temperature utilized to activate most cathodes. The binding phenomenon is called welding since the 1,100°C temperature is in excess of the normal sintering temperature of nickel particles but is below the melting temperature, 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. The branched and irregularly shaped nickel particles extend throughout the emissive material and provide excellent heat and electrical conduction therethrough. This increase in electrical conductivity reduces the voltage drop through the coating and thus further improves the cathode.

The method of this invention lends itself also to the fabrication of cathodes having relatively thick emissive coatings. To make coatings of this nature multiple, alternate spray coatings can be utilized; i.e., first a layer of nickel particles, then a layer of emissive material, then a layer of nickel particles, then a layer of emissive material, etc. Coatings produced by this method have excellent emission characteristics and heat conduction throughout the coating because of the interconnected nickel particles. Thick coatings applied by this method are much more efficient than would be similar thickness of coating applied by prior art techniques; i.e., first sintering a nickel layer and then applying emissive material. This is because of the more even distribution of the emissive material and nickel.

In addition to a pure nickel powder, further enhancement in emission can be obtained when a blend of activators is used in the nickel powder. One such powder metal composition is K3 alloy. This alloy is substantially nickel and contains minor amounts of magnesium, silicon and manganese as reducing agents. Such material is well known in the art and is often used as the material for the cathode substrate. It is available from GTE Sylvania Incorporated, Chemical and Metallurgical Division, Towanda, Pennsylvania.

It will be seen from the above that there is herein taught a new and novel method of cathode construction that provides a true advance in the art. The elimination of the separate sintering step provides cost savings and the cathode produced has unexpected resistance to arcing and emissive material peel.

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 method of making thermionic cathodes which comprises the steps of first forming on a nickel containing substrate a first layer of dendritic nickel particles by spraying said particles in a first volatile suspension from a first spraying source; then spraying thereover a potentially emissive material in a second volatile suspension from a second spraying source; and subsequently processing said cathode at a temperature in excess of the minimum sintering temperature of said nickel particles but below the melting temperature thereof to simultaneously volatilize said binders, weld said nickel particles to said substrate and each other, and activate said emissive material.

2. The invention of claim 1 wherein said spraying of said nickel particles and said potentially emissive material is alternately repeated at least once.

3. The invention of claim 1 wherein said processing temperature is about 1,100°C.

4. The invention of claim 1 wherein said first suspension comprises a nitrocellulose lacquer as a binder and a solvent therefor having a given drying time and said second suspension comprises a nitrocellulose lacquer as a binder and a different solvent therefor, said different solvent having a drying time greater than said given drying time of the solvent of said first suspension.

5. The invention of claim 4 wherein said solvent of said first suspension is methyl amyl acetate.

6. The invention of claim 5 wherein said different solvent is diethyl oxylate.

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