March 8, 1955 M. L. ANDERSON 2,703,790

# ELECTRON EMISSIVE MATERIALS

Filed Aug. 28, 1952 2 Sheets-Sheet 1

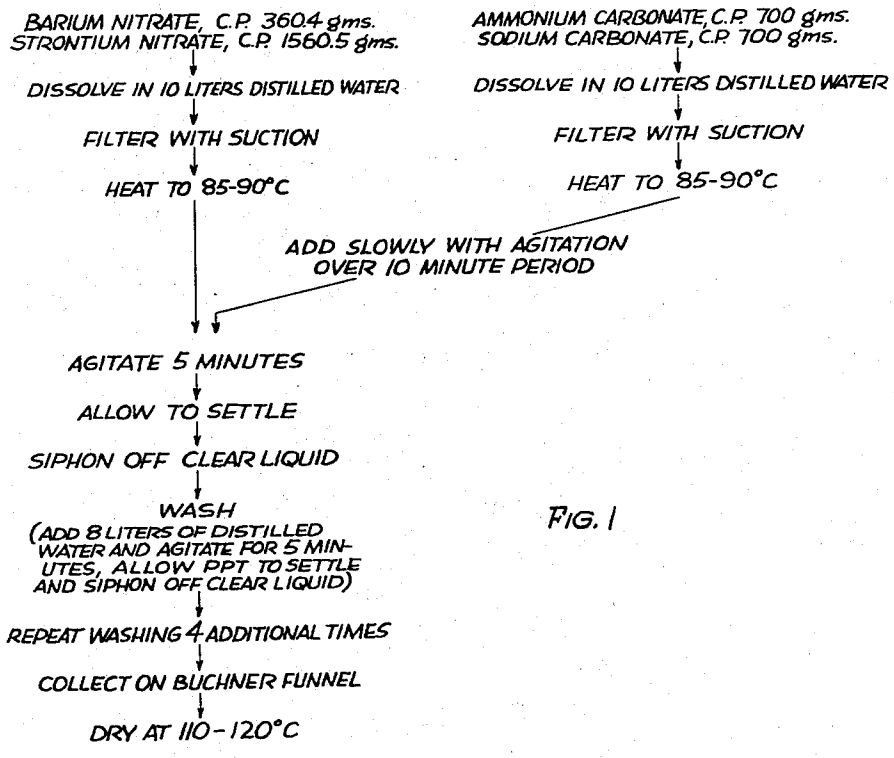



FIG. 1

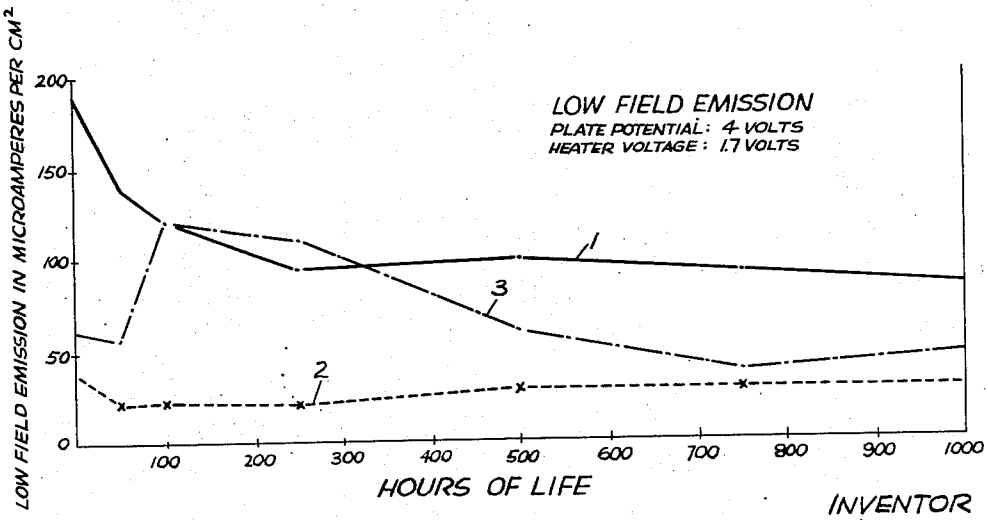



FIG. 2

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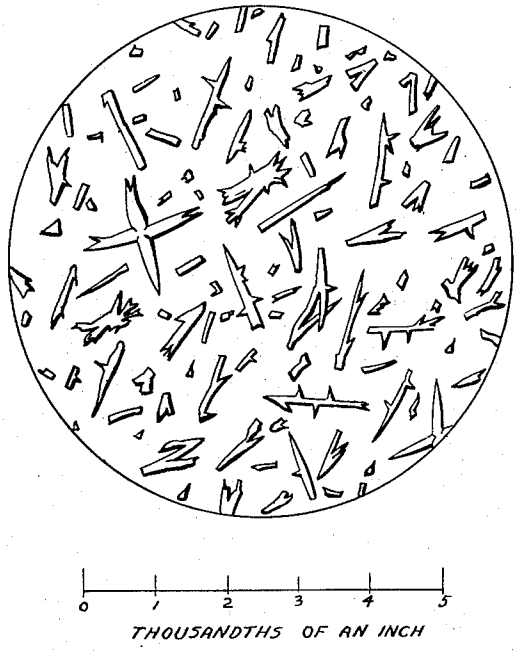



FIG. 3

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# ELECTRON EMISSIVE MATERIALS

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2 Claims. (Cl. 252—521)

This invention relates to an improved emissive cathode coating material for use in thermionic electron discharge devices.

Thermionic electron discharge devices operate by the emission of electrons from a heated cathode. It has long been the practice in the manufacture of such devices to coat the surface of the cathode with materials exhibiting the property of high electronic emissivity, such as the oxides of the alkaline earth metals, either singly or mixed in various proportions. It is customary to apply these materials to the cathode in the form of a suspension of the metallic carbonates in some solvent in which is dissolved a suitable organic binding material, such as nitrocellulose. When the cathode is subsequently heated in vacuo during the exhaust procedure in the manufacture of the electron discharge device, the solvent and binder decompose and evaporate, and the carbonates break down, leaving a coating of the pure oxides deposited on the surface of the cathode.

It has been found that the emissive characteristics of oxide coated cathodes are dependent on the physical as well as the chemical constitution of the coating material. The composition, particle size, degree of dispersion and intimacy of mixing all have a pronounced effect on the life, stability, and efficiency of the finished cathode and of the device of which it constitutes an important part.

A great deal of experimentation and study has been carried out in an effort to determine the underlying factors controlling electron emission from heated cathodes and to develop better and more uniform coating materials, but, up to the present time, no definitive theory has been evolved, and the development of emissive materials has been largely empirical. However, pursuant to this invention, it has been discovered that a cathode coating prepared from branched needle-like crystals consisting substantially of eighty per cent. strontium carbonate and twenty per cent. barium carbonate possesses a higher and more stable emissivity than any product now available.

It is, therefore, one of the objects of this invention to provide a cathode coating composed of barium and strontium carbonates in the proper crystalline form, whose electron emissive powers are superior to those of materials heretofore in use.

The foregoing and other objects of this invention will become clear from the following discussion in connection with the drawing wherein:

Fig. 1 is a flow sheet graphically showing the manufacturing steps required in an embodiment of this invention;

Fig. 2 shows the electron-emissive characteristics of the disclosed material in comparison with materials in prior use; and

Fig. 3 is a drawing of a photomicrograph showing the crystalline form of the disclosed product.

Referring to Fig. 1, the material is prepared by the simultaneous precipitation of barium and strontium carbonates from a hot (approximately 85°–90° C.) solution of the corresponding nitrates by the slow addition of a solution of an equal mixture of sodium and ammonium carbonates, according to the following equation:

$$Ba(NO_3)_2+Sr(NO_3)_2+(NH_4)_2CO_3+Na_2CO_3\rightarrow BaCO_3+SrCO_3+2NH_4NO_3+2NaNO_3$$

For example, to prepare a small batch, 360.4 grams of C. P. barium nitrate and 1560.5 grams of C. P. strontium nitrate are weighed out and dissolved in approximately ten liters of distilled water and filtered The clear



solution is placed in a suitable reaction vessel, such as a glass-lined steam-jacketed kettle equipped with a motor driven agitator.

A separate solution is prepared by dissolving 700 grams of C. P. anhydrous sodium carbonate and 700 grams of C. P. ammonium carbonate in approximately ten liters of distilled water, using gentle agitation, and filtering. The clear solution is placed in a suitable vessel located at a level higher than that of the reaction vessel.

Both solutions are then heated to a temperature preferably between 85° and 90° C. by any suitable means, such as a steam coil or jacket The carbonate solution in the upper vessel is then allowed to flow slowly into the reaction vessel—the latter being agitated continuously—at such a rate that the entire carbonate solution has been added in about ten minutes.

The heat is then shut off and the mixture agitated for five minutes and then allowed to settle. When all the precipitate has settled, the clear supernatent liquid is siphoned off and discarded. The pH of this clear liquid should not be less than 8.0 to indicate complete precipitation of the barium and strontium as carbonates.

The precipitated carbonates are then washed free of sodium and ammonium salts by adding about eight liters of distilled water, agitating for five minutes, after which the precipitate is allowed to settle and the liquid is discarded. This washing is repeated at least four times as described.

The precipitated carbonates are then washed out of the reaction vessel, and recovered on a filter. The bulk of the adhering water is removed by suction, and drying is completed in an oven held at a suitable drying temperature, such as 110°–120° C. The dried material can then be prepared for use as a cathode coating material by the usual methods.

It will be found, when the precipitated carbonates are prepared according to the above-described procedure, that the material has assumed the form of branched needle-like mixed crystals, substantially as shown in Fig. 3.

It has been found that cathode coatings made from these crystals have a higher and more consistent electron emissivity than other materials heretofore used.

Referring to Fig. 2, curve **1** shows the low field (potential drop of four volts from anode to cathode) electron emission in microamperes per square centimeter during a one thousand hour test of a cathode coated with material prepared according to this invention. It can be seen that the emissivity approaches a constant value of about 100 microamperes per square centimeter after about 200 hours and remains substantially constant for the remainder of the test. This uniformity of emission over a long period of time is a highly desirable property, as it extends the useful life of the discharge device of which the coated cathode forms a part.

Referring again to Fig. 2, the emissive characteristics of two other coating compositions are given for purposes of comparison. Curve **2** represents a twenty-five per cent. barium carbonate—seventy-five per cent. strontium carbonate mixture. It will be noted that, although stable operating results are obtained, the level of emission is low. In contrast to this, curve **3** shows the erratic behavior of a standard commercial sixty per cent. barium carbonate—forty per cent. strontium carbonate product. The superiority of the material disclosed by this invention over these other materials is apparent on inspection of the curves.

While this process has been described with reference to the precipitation of mixed crystals from a solution of the alkaline earth nitrates under certain conditions, it is not intended that the process be so sharply restricted. Obviously, other soluble salts of barium and calcium will react, and, with a suitable change in the physical constants, could bring about the formation of the desired branched needle-like crystals. Since the presence of barium and strontium ions in the proper ratio in the solution is the important requirement, any soluble compound of these metals, such as the hydroxide or the acetate, may be used.

In addition, it is to be understod that this invention is not limited to the particular details of apparatus and manufacture as described above, as many equivalents

will suggest themselves to those skilled in the art. It is accordingly desired that the appended claims be given a broad interpretation commensurate with the scope of the invention within the art.

What is claimed is:

1. A method of producing an emissive cathode coating material for thermionic electron discharge devices comprising the simultaneous precipitation of a mixture consisting substantially of eighty per cent. of strontium carbonate and twenty per cent. of barium carbonate from a solution of soluble barium and strontium salts in the proper proportion by the addition of a solution of sodium and ammonium carbonates, said precipitation being carried out at a temperature of approximately 85°–90° C.

2. A method of producing an emissive cathode coating material for thermionic electron discharge devices



comprising the simultaneous precipitation of a mixture consisting substantially of eighty per cent. of strontium carbonate and twenty per cent. of barium carbonate from a water solution of the corresponding nitrates by the slow addition of a slight excess of a water solution of a substantially equal sodium carbonate-ammonium carbonate mixture, said addition being over a period of approximately ten minutes, and said precipitation being carried out at a temperature of approximately 85°–90° C.

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