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INTRODUCING ACTIVE METALS INTO ENVELOPES

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My invention relates to the manufacture of electron discharge devices, particularly to the introduction of active metal or their alloys or compounds into the envelopes of such devices.

Usually active metal alloys or compounds are introduced into the envelope of an electron discharge device by mixing a stable alloy or compound of the powdered metals with a liquid binder such as nitrocellulose and spraying on a metal core which may be heated to dry and solidify the coating. While the usual coating mixtures may be deposited on the core metal, the coating when dried at elevated temperatures usually peels and chips off, and it is particularly difficult to make the coating adhere to final metal wires or ribbons which may be bent or twisted.

An object of my invention is to improve the manufacture of electron discharge devices, particularly the introduction of active metal alloys or compounds into the envelopes of such devices.

A further object of my invention is an improved coating mixture containing active metal alloys or compounds which is easily applied to metal surfaces and which when dried will not easily peel or chip off.

I prepare according to my invention a coating solution containing a stable alloy or compound of the active metal to be introduced into an electron discharge device and binder of nitrocellulose dissolved in glycol ether, such as diethylene glycol monobutyl ether commercially known and sold as "butyl carbitol" with a plasticizer such as camphor. The mixture prepared according to my invention readily wets smooth refractory metals leaving, when dried, an adherent flexible coating which will not readily peel or chip off, even when the coating does not extend entirely around the core. I have found by extensive experimentation that many of the lacquers and binders of commercial paints such as nitrocellulose plasticized with camphor and dissolved in the cotton solvents, including amyl acetate and dimethyl phthalate, were not suitable binders for powders of many of the common active metal alloys and compounds used in the manufacture of radio tubes. Contrary to expected results, these commercial binders when mixed with the powdered material and coated on certain metal cores and dried would draw away from the core metal and fall off in flakes. I discovered, however, that the coating material prepared with the particular nitrocellulose binder of my invention adheres well to the core metal at temperatures below as well as above the temperature at which the nitrocellulose and its solvent vaporize. It is my belief that the reason my improved coating mixture adheres well is that the particles of the compound are floated into the minute crevices and interstices on the surface of the core, and so increases the adherence between the core and the particles, without increasing the adherence between the individual particles, that the coating becomes flexible and will not peel or chip off when the core is twisted or bent.

My improved coating material readily sprays, does not evaporate appreciably at room temperature, yet dries readily at slightly elevated temperatures, and the particles of the compound are held more firmly than with binders heretofore used in intimate contact with the core not only before the binder is evaporated but until the core is heated to a temperature at which the particles may be sintered or fused to the core.

A better understanding of my invention may be had by referring to the specific embodiments described in the following specification.

For purposes of illustration, a specific getter is described comprising a coating of stable compounds of active metals on a metal core. It has been found that a stable oxygen compound of barium and beryllium or barium-strontium carbonate may be mixed in a spraying solution and coated upon a tantalum or nickel strip for mounting in a radio tube where it may be heated to reduce the compound and liberate the active metals. I prepare according to my invention a smooth adherent coating which dries at low temperatures and has sufficient flexibility to withstand rough handling during the manufacture of the electron discharge device in which it is mounted.

I prefer to use nitrocellulose as the binding agent for the particles of the active metal compounds on the refractory core. For a smooth flowing coating solution I have found that "butyl carbitol" may be used as the solvent for the nitrocellulose and, when mixed with the powdered compound, has a relatively steep temperature-vapor pressure curve that prevents rapid evaporation at room temperature and yet permits rapid drying at a temperature below 100° C. To prevent chipping of the coating during handling I lend flexibility to the coating with a plasticizer such as camphor. Nitrocellulose dissolved in "butyl carbitol" and mixed with the powdered material is easy to apply to the core, does not appreciably change in viscosity due to evaporation, and may be quickly dried at slightly elevated temperatures.

Good results have been obtained with a getter comprising 765 grams of powdered barium carbonate ball-milled for two hours with 235 grams of beryllium oxide and heated to a temperature of 1065° in hydrogen for 60 minutes in nickel boats, then heated to 1200 to 1250° in air for 4 hours in clay crucibles, ball-milled, and screened through 60–80 mesh sieve. My improved binding solution comprises 1000 cubic centimeters of commercial butyl carbitol, about 39 grams of

nitrocellulose and 10 grams of natural or synthetic camphor. One hundred grams of the powder is mixed with about 150 cubic centimeters of the binder and a layer of the mixture .005 inch thick coated on a tantalum strip .036 inch wide and .001 inch thick may be dried sufficiently for handling in one minute at 90° C. The ribbon may, if desired, be formed longitudinally with a grove and the groove filled with the mixture. The strip with its smooth adherent coating is welded at its ends to lead-in conductors in the mount of an electron discharge device. After the pressure in the envelope of the device has been reduced to a reasonably low vacuum, a current of 3.6 amperes is passed through the strip to evaporate the nitrocellulose, decompose the compound, reduce the oxides, and liberate the active metals.

Good results also have been obtained in coating molybdenum, iron or nickel with a powdered barium-aluminum alloy mixed with my improved binder and coated on the core, dried and mounted in an envelope. Free metallic barium may be readily evaporated from this coating without the evolution of considerable gaseous by-products. A barium-beryllium compound mixed with powdered aluminum may also be effectively coated on molybdenum, iron or nickel when mixed with my improved binder. Further, barium-strontium carbonates when powdered and mixed with my binder adhere well to tantalum or nickel. Aluminum powder found to adhere well to molybdenum when applied with my improved binder may be evolved directly and advantageously used as a getter when heated to a temperature of 1000 to 1200° C. These powdered materials when coated upon the core materials mentioned may be readily dried in about one minute at 90° C., although at room temperature there is no appreciable evaporation of the binder or its solvent. My improved coating material readily wets the smooth surfaces of the refractory metals and when dried produces an adherent flexible coating which will not readily peel or chip off. Since other powdered metal compounds and alloys may be coated upon metal cores' other than those mentioned above, it is desired that my invention be limited only by the prior art and by the scope of the appended claims.

What I claim as new is:

1. The method of introducing materials, which will adhere at high temperatures to a metal core, into an electron discharge device comprising powdering said material and suspending the material in a binder of nitrocellulose dissolved in diethylene glycol monobutyl ether, plasticizing the suspension with camphor, coating a self-sustaining metal core with said suspension, heating the coating in air to evaporate said ether, mounting the coated core in the envelope of said device, and then heating the coated core in vacuum to evaporate said binder and adhere said material to said core.

2. The method of coating a refractory metal core with an alloy which will vaporize below the melting temperature of said core comprising powdering said alloy and mixing the powdered alloy with a nitrocellulose binder and camphor dissolved in diethylene glycol monobutyl ether, coating said refractory metal core with the mixture, evaporating said ether in air, and heating the coated core in an atmosphere of reduced pressure to evaporate said binder and adhere the powdered alloy to said core.

3. The method of introducing active metal in an electron discharge device comprising mixing a powdered material of the group consisting of an alloy, a stable compound or a free metal of said active metal with a nitrocellulose binder and camphor dissolved in sufficient diethylene glycol monobutyl ether to make a good coating mixture, coating a refractory metal core with the mixture, heating the coating to evaporate said ether, mounting the coated core in the envelope of said device, and heating the coated core to evaporate said binder, adhere said material to said core and liberate said active metal.

4. The method of introducing an active metal in an electron discharge device comprising mixing a powdered stable compound of said active metal with a nitrocellulose binder dissolved in diethylene glycol monobutyl ether, coating a refractory metal core with the mixture, evaporating said ether, mounting the coated core in the envelope of said device, heating the coated core to evaporate said binder and then heating the coated core in vacuum to decompose the compound and liberate said active metal.

5. The method of introducing barium into an electron discharge device comprising mixing a powdered oxygen compound of barium and beryllium with a nitrocellulose binder dissolved in diethylene glycol monobutyl ether, coating a refractory metal core with the mixture, mounting the coated core in the envelope of said device, heating the coated core to evaporate said binder and said ether, and then heating the coated core in a rarified atmosphere to decompose and liberate said barium.

6. The method of introducing an alloy of an active metal and aluminum in an electron discharge device comprising mixing 100 grams of powdered alloy with about 150 cubic centimeters of binder comprising about 39 grams of nitrocellulose and about 10 grams of camphor dissolved in about 1,000 cubic centimeters of commercial diethylene glycol monobutyl ether, coating a core of the metal included in the group consisting of molybdenum, nickel and iron, evaporating said ether, mounting the coated core in the envelope of said device, heating the coated core to evaporate said binder, and then heating the coated core to liberate said active metal.

7. The method of introducing an active metal in an electron discharge device comprising mixing a powdered stable compound of said active metal with powdered aluminum in a binder solution comprising 10 grams of camphor and about 39 grams of nitrocellulose dissolved in 1,000 cubic centimeters of diethylene glycol monobutyl ether, coating a refractory core comprising a metal of the group consisting of molybdenum, nickel and iron, heating the coating to evaporate said ether, mounting the coated core in the envelope of said device, heating the coated core to evaporate said binder, and then heating the coated core in vacuum to decompose the compound and liberate the active metal.

8. The method of introducing an active metal in an electron discharge device comprising mixing a powdered barium strontium carbonate compound with nitrocellulose and camphor dissolved in diethylene glycol monobutyl ether, coating a refractory metal core with the mixture, heating the coating in air to evaporate said ether, mounting the coated core in the envelope of said device, heating the coated core to evaporate said binder and then heating the coated core to decompose the compound and liberate the barium.

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