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INTRODUCING ACTIVE METALS INTO
ENVELOPESDelos H. Wamsley, Caldwell, N. J., assignor to
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of DelawareNo Drawing. Application July 29, 1939,
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6 Claims. (Cl. 250—27.5)

My invention relates to the introduction of active metals or their alloys or compounds into the envelopes of electron discharge devices, particularly to mixtures of powdered alloys or compounds of the metals with liquid binders.

Active metal alloys or compounds are often 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. Factory practice requires exposure of the coating material to the atmosphere with the result that the active metal compounds or alloys mixed with the binders are contaminated and undesired gases and products of decomposition are introduced into the radio tube. Further, because of evaporation of the usual coating materials in the dipping and spray coating containers changes occur in consistency and make uniform coatings difficult. Few coating binders are known which will not peel and chip off when dried at elevated temperatures.

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 which contains active metal alloys or compounds and is not easily contaminated, does not readily evaporate at room temperature, adheres well to core metals, and is easy to apply.

I prepare according to my invention a coating solution containing a powdered stable alloy or compound of the active metal to be introduced into an electron discharge device and a binder of plasticized nitrocellulose dissolved in acetate of diethylene glycol monbutyl ether, commercially known and sold as butyl "carbitol" acetate. 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. I have found 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, are not suitable binders for powders of many of the common active metal alloys and compounds used in the manufacture of radio tubes. Besides the tendency to peel, the commercial binders with the necessary vapor pressure when mixed with the powdered material will absorb water from the atmosphere which attacks

and deteriorates the compounds. Barium beryllate for example readily combines with water to form barium hydroxide from which water vapor is liberated at high temperatures. H_2O in the coating puffs and decrepitates the coating when barium beryllate powder is used. These gases and vapors in a radio tube poison the cathode and destroy electron emission. The butyl carbitol acetate is immiscible with water and has been found to be effective in protecting the compounds. Further, the volatility of the usual plasticizers such as camphor is so high that thin coatings dry out after standing in the factory for a few days so that the coating chips off. I have found that triethylene glycol di-2-ethylbutyrate, commercially known as "3GH," is an ester ideally suited for plasticizing nitrocellulose dissolved in butyl carbitol acetate. 3GH with the butyl carbitol acetate solvent keeps the coating flexible during exhaust and prevents the absorption of moisture from the atmosphere.

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 refractory metal strip such as tantalum or nickel 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 of active metal compounds or alloys which remains flexible for long periods at room temperatures, has sufficient flexibility to withstand rough handling during manufacture, and which will not chemically deteriorate.

Good getters have been made with powdered barium beryllate, $BaOBeO$, mixed with nitrocellulose in a butyl carbitol acetate solvent, plasticized with "3GH." I prefer to prepare the barium beryllate compound by ball-milling grams of powdered barium carbonate for two hours with 235 grams of beryllium oxide and heating to a temperature of 1065° in hydrogen for 60 minutes in nickel boats, then heating to 1200° to 1250° in air for 4 hours in clay crucibles. When ball-milled and screened through a 60-80 mesh sieve, the compound is ready for mixing with the binder and applying to a carrier or core. My improved binding solution is prepared by mixing 1000 cubic centimeters of commercial butyl

carbitol acetate with about 39 grams of nitrocellulose and 10 grams of "3GH." One hundred grams of the powder is mixed with about 30 cubic centimeters of the binder and a layer of the mixture .005 inch thick coated on a tantalum strip .040 inch wide and .001 inch thick may be dried sufficiently for handling in one minute at 90° C. to 130° C. The ribbon may, if desired, be formed longitudinally with a groove and the groove filled with the mixture. The strip with its smooth adherent coating is welded at its ends to conductors and 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, reduce the oxides, and liberate the active metals. During heating in the tube and before actual flashing, the getter coating appears to slightly soften and flow on the core.

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.

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, and which will not chemically deteriorate in the atmosphere. 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.

I claim:

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 the acetate of diethylene glycol monobutyl ether, plasticizing the suspension with triethylene glycol di-2-ethylbutyrate, 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 introducing an active metal into an envelope, comprising powdering a stable compound of said metal and mixing the powder

with triethylene glycol di-2-ethylbutyrate and a nitrocellulose binder dissolved in a liquid solvent, coating a carrier with the mixture, evaporating said solvent in air, and heating the coated carrier in an atmosphere of reduced pressure in said envelope to evaporate said binder and decompose the compound.

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 triethylene glycol di-2-ethylbutyrate dissolved in sufficient acetate of 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 alloy of an active metal and aluminum in an electron discharge device comprising mixing the powdered alloy with sufficient liquid binder to make a good coating mixture, said binder consisting of about 39 grams of nitrocellulose and about 10 grams of triethylene glycol di-2-ethylbutyrate dissolved in about 1000 cubic centimeters of commercial acetate of 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.

5. 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 the proportions 10 grams of triethylene glycol di-2-ethylbutyrate and about 39 grams of nitrocellulose dissolved in 1000 cubic centimeters of acetate 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.

6. The method of introducing an active metal in an electron discharge device comprising mixing a powdered compound of the active metal with nitrocellulose dissolved in a solvent immiscible with water, plasticizing the mixture with triethylene glycol di-2-ethylbutyrate, coating a refractory metal core with the mixture, heating the coating in air to evaporate said solvent, mounting the coated core in the envelope of said device, heating the coated core to evaporate the triethylene glycol di-2-ethylbutyrate and further heating the coated core to decompose the compound and liberate the active metal.

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