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3,598,646

### METHOD FOR PREPARING OXIDE-COATED CATHODES

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5 Claims

#### ABSTRACT OF THE DISCLOSURE

An oxide-coated cathode for an electron tube is prepared with particles of a composition containing at least one alkaline earth metal compound, the compound being heat decomposable to an oxide. The particles are coated with metallic cobalt, preferably produced by the decomposition of dicobalt octacarbonyl in a solution in which the particles are suspended. Subsequently, a layer of the coated particles is coated on a cathode substrate. The cathode is then assembled into an electron tube. During the subsequent tube fabrication, the layer is heated so as to drive off the volatile matter therein and to consolidate the coated particles into a sintered electron-emissive coating on the substrate.

#### BACKGROUND OF THE INVENTION

This invention relates to a method for preparing cathodes for electron tubes, particularly cathodes of the type in which a metal substrate carries an electron-emissive alkaline earth metal oxide coating. Such cathodes are referred to in the art as oxide-coated cathodes.

Oxide-coated cathodes are described in the literature, for example, in U.S. Pats. Nos. 2,209,704 to S. Umbreit and 2,744,838 to R. W. Newman. These cathodes are comprised of a metal substrate usually of cathode nickel coated with an electron-emissive coating of sintered alkaline earth metal oxides. In preparing such cathodes, the surface of the metal substrate is cleaned and then coated with particles of a composition containing one or more alkaline earth metal compounds. Usually, this structure is assembled into the electron tube and subsequently, as during or after the exhaust and sealing steps for making the tube, the substrate and coating are heated to produce the desired electron-emissive coating.

The problem of lifting, peeling, or flaking of the electron-emissive coating from the cathode substrate is commonly encountered during the use of electron tubes resulting, on the average, in a shorter operational life for the cathode. This problem limits the electron-emissive capabilities of the cathode and, in severe cases, results in complete emission failure. This invention provides a novel method for fabricating an efficient electron-emissive cathode for electron tubes, such as oscilloscopes, television picture tubes, and power tubes, which is substantially free from peeling of the electron-emissive coating from the cathode substrate. The cathodes produced by the novel process have, on the average, a longer operational life.

#### SUMMARY OF THE INVENTION

According to the invention, the particles ordinarily used for preparing the cathode coating are first coated with metallic cobalt. This is preferably achieved by suspending the particles in a solution of dicobalt octacarbonyl, heating the suspension at about 100 to 150° C., and then removing the cobalt-coated particles from the suspension. Then, a layer of the cobalt-coated particles is produced upon a surface of the metal substrate. The substrate and

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layer thereon are then assembled into an electron tube. During or after evacuation and sealing of the tube, the substrate and the particle layer thereon are heated so as to produce an electron-emissive coating of sintered cobalt-coated oxide particles.

For reasons which are not yet understood, and quite surprisingly, the life of the cathode and of the electron tube is extended substantially on the average through the use of the novel process. This appears to be the result of reduced peeling and more efficient functioning of the electron-emissive coating from the metal substrate during the life of the electron tube. The preferred method for coating the particles with metallic cobalt is simple, easily controlled and does not involve the use of highly toxic materials.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

##### Example 1

20 Particles of a conventional triple carbonate composition containing carbonates of barium, strontium and magnesium are first coated with metallic cobalt. To this end, 100 grams of particles of the mixed carbonates are suspended in amyl acetate containing 3 grams of dissolved dicobalt octacarbonyl. The suspension containing the mixed carbonates is placed in a reflux condenser and heated for about 2 hours at about 110° C., whereby the particles become coated with metallic cobalt. After heating, the suspension is filtered and the particles are washed in amyl acetate and then dried. The particles have a coating of metallic cobalt thereon which is about 1.0 weight percent of the particle weight.

##### Example 2

35 A cathode substrate is prepared in the usual manner using a cathode nickel alloy composition consisting essentially of nickel and containing about 4.0 weight percent tungsten, about 0.025 percent magnesium and 0.035 weight percent silicon. The substrate in this example is in the shape of a cylindrical cup about 0.08 inch outside diameter and about 0.110 inch high. The substrate is degreased, washed in water and then dried. The substrate is then heated at about 1000 to 1100° C. for about 7 minutes in an atmosphere of water vapor and hydrogen gas. After cooling to room temperature, the substrate is coated, as by spraying, with a suspension of the cobalt-coated particles in a solution containing a binder and a solvent for the binder. A typical coating composition consists of about 40 weight percent cobalt-coated particles (of the type prepared in either Example 1 or Example 3), about 0.5 weight percent nitrocellulose binder and about 59.5 weight percent solvents for the binder. The external end portion of the substrate is coated with this suspension to a coating thickness of about 3.5 mils and a coating weight of about 0.35 milligram. Upon drying in air, the coated substrate is ready for assembly with other parts into an electron tube.

##### Example 3

60 Follow the procedure of Example 1 except substitute 0.9 gram dicobalt octacarbonyl. The product has about 0.3 weight percent cobalt as a coating on the particles.

##### Example 4

65 Follow the procedure of Example 2 except substitute a cathode substrate of a cathode nickel composition containing about 99 weight percent nickel, 0.06 weight percent magnesium, and 0.025 weight percent silicon.

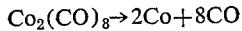
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Example 5

Follow the procedure of Example 2 except substitute a cathode substrate of a cathode nickel composition containing about 99.8 weight percent nickel, about 0.005 weight percent magnesium, about 0.02 weight percent manganese and about 0.01 weight percent silicon.

The foregoing examples are illustrative of features of the invention. There are many variations possible within the scope of the invention. The cathode substrate may be of any size and geometry and still obtain improvements in longer tube life through reduced peeling and more efficient operation of the cathode coating. The magnitude of the improvement will, of course, differ with differences in size, geometry and other factors mentioned below.

The particles to be coated with metallic cobalt may be any composition usable for preparing oxide-coated cathodes. A description of some such compositions appears in a publication entitled, "Cathode Coatings for Oxide-Coated Cathodes," Booklet No. TPM-1503-B, Electron Tube Division, Radio Corporation of America, Harrison, N.J., 1960. Generally, the particles may be comprised of one or more alkaline earth metal compounds which are heat-decomposable to an oxide. These compounds may be bicarbonates, acetates, formates, for example. Preferably, the particles are composed of the triple carbonate mentioned in Example 1.

The particles may be coated with metallic cobalt by any convenient process. It is preferred to heat the particles while they are suspended in a solution of dicobalt octacarbonyl  $\text{Co}_2(\text{CO})_8$  in an organic solvent such as amy1 acetate. During the heating, the dicobalt octacarbonyl decomposes to produce metallic cobalt which deposits on the surfaces of the particles. The reaction is believed to be



The amount of cobalt metal deposited is preferably in the range of 0.3 to 1.0 weight percent of the particles.

The cathode nickel alloy composition for the metal substrate may consist essentially of nickel, 0.0 to 10.5 weight percent tungsten, 0.005 to 0.3 weight percent magnesium, and 0.005 to 0.3 weight percent silicon. The magnesium and silicon are known to be reducing agents for the oxide coating. In addition the alloy may contain (in weight percent) up to about 0.1% Al, 0.04% C, 1.0% Co, 0.2% Cu, 0.1% Fe, 0.20 Mn, and 0.008 S, as nonessential ingredients. Titanium may be substituted for magnesium. The preferred composition is given in Example 1 wherein the maximum content of nonessential ingredients is preferably (in weight percent): 0.008% Al, 0.02% C, 0.06 Co, 0.10 Cu, 0.10 Fe, 0.05 Mn, and 0.008% S. The steps of degreasing and washing the substrate may be by any of the techniques known in the art.

The atmosphere for heating the washed substrate consists essentially of water vapor and hydrogen. It is preferred that the dew point for the water vapor in the atmosphere is in the range of  $-40^\circ\text{C}$ . to  $+20^\circ\text{C}$ . Part of the hydrogen may be replaced with one or more neutral gases such as argon, neon, and nitrogen. The heating step may be conducted in a periodic furnace or a continuous furnace as in the examples. It is preferred that the atmosphere is continuously flowing through the furnace, as by continuously introducing fresh atmosphere into the furnace and removing a corresponding amount of gas from the furnace chamber. The cooled substrate may be coated by any convenient coating technique to provide a coating of the desired thickness, weight, and texture. In some techniques, as with some spraying methods, the substrate is warmed prior to spraying to aid in producing the desired coating.

Subsequent to coating, the coated substrate is assembled with other parts into a complete electron tube structure including means for heating the cathode substrate during the operation of the tube. This complete structure is baked at elevated temperatures (typically about  $440^\circ\text{C}$ ), evacu-

ated and sealed in a single processing step. During the evacuation, the heating means is energized to heat the substrate to about  $1100^\circ\text{C}$ . During this step, the constituents of the coating composition are decomposed, the volatile components removed and the remaining oxides are sintered into a firmly adherent electron-emissive coating on the substrate. Also, during this same step, the metal structures of the tube including the cathode substrate are outgassed. The tube is then completed and tested.

During the decomposition of the coating composition, it is believed that the gases which evolve from the carbonate particles cause eruptions in the cobalt coating and that this action results in exposing the thermionically active oxide particles. At the same time, the heating operation causes at least a partial sintering of the cobalt coatings to themselves, to the thermionically active oxide particles and to the cathode substrate. This process results in an efficient electron-emissive cathode wherein the emissive oxide coating has superior adhesion characteristics to the substrate as compared with cathodes prepared with similar particles which are not coated with cobalt.

It has previously been suggested in Bell System Technical Journal 46, 2374 (1967), that the particles be individually coated with nickel metal prior to their application to the metal substrate by heating the particles in a solution of nickel tetracarbonyl,  $\text{Ni}(\text{Co})_4$ . The nickel coated particles are then coated on a cathode substrate and converted to an electron-emissive coating according to previous methods.

The use of dicobalt octacarbonyl in preference to nickel tetracarbonyl for applying a thin metallic coating to particles of alkaline earth compounds is a significant advance in the manufacture of electron-emissive cathodes. First, dicobalt octacarbonyl is a stable solid at room temperature and therefore easier to handle and control than nickel tetracarbonyl, which is a volatile gas. Second, dicobalt octacarbonyl is soluble in common organic solvents and its decomposition rate in solutions of such solvents may be carefully controlled at low temperatures, whereas nickel tetracarbonyl although soluble, requires a higher decomposition temperature, and the decomposition rate is much more difficult to control. A control of the solution decomposition rate is essential for obtaining a consistently uniform metallic coating on the particles. Third, dicobalt octacarbonyl has a low vapor pressure and is essentially nontoxic and therefore few precautions are required during its storage and use, whereas nickel tetracarbonyl is a very toxic gas which requires many expensive safety precautions for its storage and handling in factory operations. As a result of the foregoing advantages the use of dicobalt octacarbonyl is cheaper and easier to install and cheaper and easier to use. Currently available data indicates that cathodes prepared using particles coated with cobalt metal have, on the average, a longer life and a greater freedom from peeling of the cathode coatings than corresponding cathodes prepared with particles coated with nickel metal. Also, the metallic cobalt in the novel cathode coating does not evaporate as quickly as metallic nickel in cathode coating made with nickel coated particles during the operational life of the tube.

I claim:

1. In a method for preparing a cathode, the steps comprising:
  - (a) suspending particles of a composition containing at least one alkaline earth metal compound in a non-aqueous solution of dicobalt octacarbonyl, said compound being heat-decomposable to an oxide,
  - (b) heating said solution until metallic cobalt coats said particles,
  - (c) removing said cobalt-coated particles from said solution,
  - (d) coating said cobalt-coated particles upon a metal substrate.

2. The method defined in claim 1 wherein the metal substrate is composed principally of nickel.

3. The method defined in claim 1 wherein said particles are composed principally of carbonates of barium, strontium and magnesium.

4. The method defined in claim 1 wherein said metallic coating is about 0.1 to 2.0 weight percent of said particles.

5. The method defined in claim 1 including the step:

(c) heating said coated metal substrate to convert said coating of metal coated particles to a sintered electron-emissive coating.

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