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[54] PROCESS FOR MAKING OXIDE CATHODES HAVING IMPROVED THERMAL EMISSIVITY

15 Claims, 2 Drawing Figs.

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[50] **Field of Search** ..... 117/223, 224, 100 B; 252/518, 519, 520, 521; 75/212; 313/346

[56] **References Cited**

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ABSTRACT: A process for making an oxide cathode having metallic powders finely and evenly interspersed with alkaline earth oxides. An alkaline earth carbonate is dispersed in an aqueous solution having a soluble metal salt dissolved therein. The water is evaporated leaving carbonate crystals coated with the metal salt. The coated crystals are then dispersed in a lacquer which in turn is coated onto a cathode base.

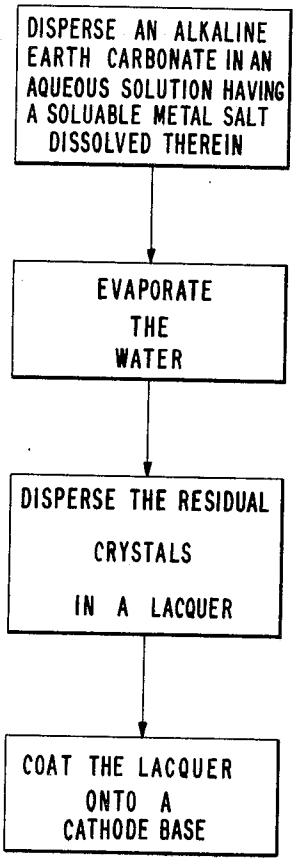


FIG.1

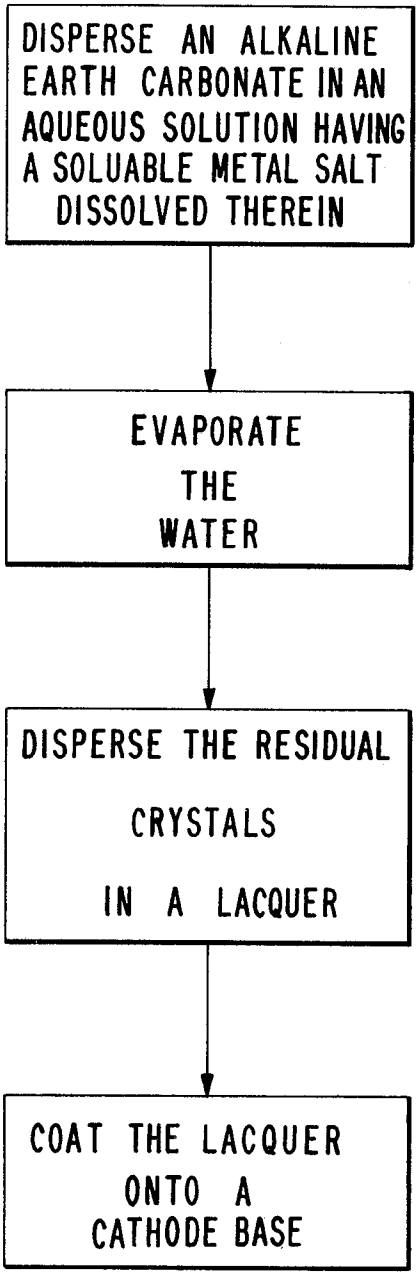
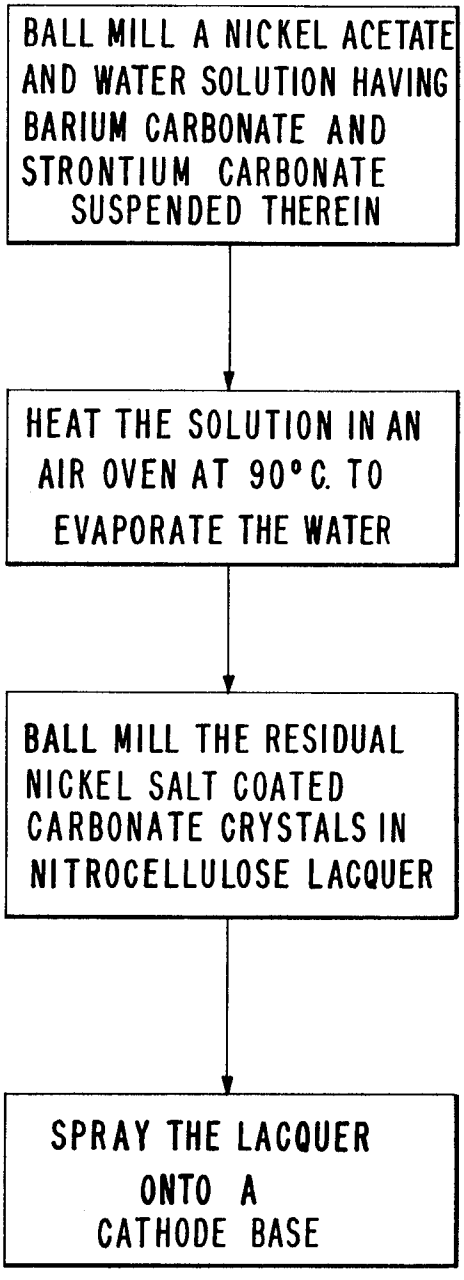


FIG.2



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PROCESS FOR MAKING OXIDE CATHODES HAVING IMPROVED THERMAL EMISSIVITY

The present application is a continuation-in-part of copending original application U.S. Ser. No. 627,689, filed Apr. 3, 1967 now abandoned, and assigned to the same assignee as the present invention. BACKGROUND OF THE INVENTION

This invention relates to a process for making an oxide cathode for use in an electron tube, and particularly to an improved process of making an electron-emissive material having thermal-emissive stability.

Where the thermal emissivity of oxide cathodes increases with tube life, the cathode operates cooler resulting in a decrease in electron emission. Where thermal emissivity decreases with life, the cathode runs hotter causing vaporization of the emissive oxides which in turn likewise results in a decrease in electron emission. Thus in the electron tube art the thermal emissivity of oxide emitters should be stable.

The approach generally taken in stabilizing the thermal emission of electron emitters has been that of developing emissive oxide materials which, by design, have initially as high a combined thermal and electron emissivity as is possible. As metals slowly vaporize within the tube during tube operation, some will arrive at and settle upon the emitter. Metals generally have higher thermal emissivity than electron-emissive oxides. Accordingly, such metals will increase the thermal emissivity of the oxide emitter in those areas in which they settle. By making the thermal emissivity of the initial oxide greater, however, the difference in the thermal emissivity of the oxide and foreign metals is lessened. Such lessening results in increased thermal stability of the cathode since the oxide material contaminated by the foreign metal has a thermal emissivity property closer to that of the metal.

Oxide cathodes of the present day are typically made by spraying or dipping a nickel cathode base with an alkaline earth carbonate and then reducing the carbonate to an oxide. Barium, calcium and strontium carbonates, and combinations thereof, are those alkaline earth carbonates which are most commonly used. The most prevalent method heretofore employed in increasing the thermal emissivity of these emitters has been that of impregnating the oxide material with a finely dispersed metallic powder. Nickel is usually used for this purpose since its introduction onto the emissive oxide-clad nickel base introduces no extraneous element into the chemical makeup of the cathode. The elemental nickel also serves to reduce the bulk electrical resistance of the coating. Fineness is desired in order to maximize surface area, and for the advantages offered by black body radiation in increasing thermal emissivity.

Specifically, this has previously been done by suspending the alkaline earth carbonates and nickel powder in a lacquer, and then spraying the lacquer onto the cathode base. A problem inherent with this method, however, is that there is a difference in densities between the suspended carbonates and nickel powders. Once placed in the lacquer the nickel powder commences to settle out onto the bottom of the bath or spray jar while the carbonate powders are still held in suspension. A cathode base sprayed or dipped into such a nonhomogeneous lacquer becomes irregularly coated, resulting in its surface having areas of nickel powder and carbonate concentrations which result in varying thermal emissivity.

An alternative process which avoids the foregoing problem has been that of pressing the intermixed dry nickel and carbonate powders onto a cathode base in a mold. This, however, is inefficient and uneconomical since each cathode must be individually molded, whether or not the cathode configuration is planar or cylindrical. Then too, with both of the foregoing methods, one is limited in the degree of fineness of nickel powders which are commercially available. Also, the powdering of nickel is expensive and difficult to do without introducing undesirable contaminates.

Yet another general method heretofore employed in achieving an increase in oxide thermal emissivity has been that of passing nickel carbonyl gas through a liquid suspension of alkaline earth carbonates. The residual material is found to be crystals of the alkaline earth carbonates which have a nickel coating. The nickel-coated crystals can then be dispersed evenly in a lacquer and then coated onto a nickel base with the nickel and carbonate evenly distributed on the cathode. Unfortunately this process is quite hazardous to health if nickel carbonyl is inhaled, thus posing a production problem.

Accordingly, it is an object of the present invention to provide a process for making oxide cathodes having thermal-emissive stability.

A more particular object of the present invention is to provide an improved process for impregnating oxide material with finely and evenly dispersed metallic powder of molecular sizes without a significant increase in cost above that of current processes.

SUMMARY OF THE INVENTION

Briefly described, the present invention is a process for making an oxide cathode for use in an electron tube comprising the steps of dispersing an alkaline earth carbonate in a solution having a soluble metal salt dissolved therein, the metal of said soluble metal salt having a vapor pressure not exceeding that of iron, evaporating the solvent solution leaving residual alkaline earth carbonate crystals coated with the metal salt, dispersing the coated crystals in a vehicle to obtain a paint, and coating the paint onto the surface of a cathode base. Where a water soluble lacquer is used as the vehicle for the paint, the first solution having the soluble metal salt dissolved therein may, after the alkaline earth carbonate has been dispersed therein, be mixed directly with the water-soluble lacquer vehicle thereby omitting the evaporation step.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a flow diagram of a series of general steps taken in practicing the invention using an organic vehicle.

FIG. 2 is also a flow diagram which illustrates the specific steps of the preferred embodiment of the process containing the general steps illustrated in FIG. 1.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring now in more detail to the drawing, there is illustrated in FIG. 1 four steps to be taken in practicing the present invention. An alkaline earth carbonate is first evenly dispersed in a solution, such as an aqueous or organic solvent, having a soluble metal salt dissolved therein. The metal of the metal salt should have a vapor pressure not exceeding that of iron in order that it not vaporize at the operating temperatures of oxide cathodes which typically range between 750° and 850° CBT. The melting point of the metal should be above any temperatures achieved during processing to prevent "balling" of the metal in discrete particles separate from the alkaline earth carbonate. The metal should not form a stable oxide at processing temperatures of approximately 1,000° C. or operating temperatures of 700° to 900° C. and at pressures of $10^{116\ 8}$ Torr. Nickel, tungsten, cobalt, platinum, rhodium, ruthenium, osmium, rhenium, iridium, molybdenum and iron satisfy this requirement. And, of course, the salt must not contain elements which are widely known as detrimental to electron tubes such as sulfur or the halides. The solvent is next removed from the solution by vaporization leaving residual alkaline earth carbonate crystals coated with the metal salt. These dry, coated crystals are then evenly dispersed in a volatile vehicle to obtain a paint. A cathode base is then coated with the paint by either spraying or dipping techniques. Suitable volatile vehicles for the paint include lacquer mediums or water-soluble lacquer substitutes. Such lacquer mediums include, nitrocellulose dissolved in amyl acetate, any other organic solvent which is liquid at room temperature, or one or more of the methacrylate resins dissolved in such solvents as butyl acetate or butyl alcohol. The water-soluble lacquer substitutes include water or aqueous solutions of, ethyl and methyl cellulose, caseins, or dextrins. These lacquer

substitutes would require longer drying periods to permit the complete loss of the water, leaving the metal compound and alkaline earth carbonate adhered to the cathode base. Heating during subsequent cathode processing will decompose or volatilize the solids contained in the residue of the vaporized lacquer substitute.

The flow diagram of FIG. 2 details a specific embodiment of the more generalized steps shown in FIG. 1. First a nickel acetate and water solution having approximately equal parts by weight of barium carbonate and strontium carbonate suspended therein is ball milled for approximately 4 hours to effect an intimate intermixing. A nickel salt is preferred because the cathode base itself is made of nickel. Thus the introduction of nickel into the cathode adds no additional metal thereto, and consequently does not effect the cathode's chemistry. If desired, the mixing action may be dispersion-milled or blended rather than ball-milled. A nickel-to-carbonate proportion by weight of 2-½ percent nickel to 97-½ percent carbonate is preferred although any proportion within the proportional range by weight of ¼to 10 percent nickel and 99-¾ to 90 percent carbonate is possible. The preferred proportion may be achieved by mixing 1 part by weight of dry nickel acetate to approximately 10 parts by weight of the dry barium and strontium earth carbonate mixture.

Next the ball-milled solution is heated in an air atmosphere oven at 90° C. between 8 and 12 hours, depending on the quantity of the solution being prepared and the ambient humidity, in order to evaporate the water. A temperature less than 100° C. is used to prevent thermal disassociation of the nickel acetate. A temperature below 90° C. could, of course, be used with an increase in evaporation time. Examination of the dried, greenish residual material reveals the presence of the carbonate crystals coated with a nickel salt.

Next the dry nickel salt-coated carbonate crystals are mixed with a nitrocellulose lacquer which acts as the vehicle for coating the cathode base with the alkaline earth-emissive material. Alternatively a normal butyl methacrylate lacquer could be used. The lacquer is then ball-milled to break up the dried glomerate crystals which are now held in suspension in the lacquer. The ball-milling action also has served to evenly disperse the suspended coated crystals.

Finally the lacquer is sprayed onto the surface of a nickel cathode base which is then incorporated into an electron tube. Upon subsequent heating of the cathode during tube evacuation procedures, the nickel acetate disassociates, and the calcium and strontium carbonate crystals decompose to the oxide. The organic lacquer decomposes, vaporizes and is removed. Only the alkaline earth oxides with finely divided nickel of molecular dimensions dispersed evenly therein remain, which is an oxide material of high thermal stability.

It is also possible to coat cathode bases with an alkaline earth oxide using a water-soluble lacquer substitute, as above-described, as the vehicle with some loss in adhesion over that offered by organic lacquers. In practicing this invention with a water-soluble lacquer substitute, the evaporation step may be omitted in which case the aqueous solution, having a soluble metal salt dissolved therein and an alkaline earth carbonate homogeneously suspended therein, is mixed directly with the water-soluble lacquer substitute and then coated onto the cathode base. Though this process is more simple to practice than that utilizing the organic vehicle, the latter is nevertheless preferred because, as above stated, of its better adhesion to the cathode base.

Although nickel acetate has been described, thus far, as an exemplary metal salt to be employed in practicing the method of the present invention, many other metal salts may be employed. For example, any of the nickel salts listed in the table below may be employed.

TABLE

Nickel Salt	Soluble In
Nickel Nitrate	Water and alcohol
Nickel Acetate	Water
Nickel Acetate Tetrohydrate	Water
Nickel Formate	Water
Nickel Stearate	Hot Water and Acetone
Diaquotetrammine Nickel Nitrate	Water
Hexamminenickel Nitrate	Water
Dicyclopentadienylnickel	Alcohol
Dicyclopentadienenickel	Alcohol

Also other suitable salts of metals such as iron, rhodium, ruthenium, molybdenum, tungsten, cobalt, platinum, iridium, osmium and rhenium may be used. For example, the following iron salts are suitable: iron nitrate, iron acetate, iron formate and iron stearate. The following considerations apply to selection and use of the metal salts:

The metal salts should not contain halides or sulfides; they should be soluble in either aqueous or organic solvents which do not dissolve the alkaline earth carbonates; after dissolving the metal salt in a suitable solvent and mixing with the insoluble alkaline earth carbonate, the metal salt should not sublime from the carbonate in subsequent processing of the cathode; and the metal salt should remain equally suspended with the alkaline earth carbonate in the volatile vehicle of the paint prior to and during application to the cathode. This insures that the ratio of available metal to alkaline earth carbonate will remain constant throughout storage and application.

The metal salt may be soluble in the volatile vehicle of the paint and go out of solution to deposit on the alkaline earth carbonate particles when the vehicle solvent evaporates after application to the cathode. The ratio of available metal to alkaline earth carbonates can also be maintained within close limits by this procedure.

Obviously, many modifications may be made in the specific details described in the preferred embodiments of the present invention without departing from its spirit and scope as set forth in the appended claims. For example, there are several alkaline earth carbonates and combinations thereof, as well as a number of soluble metal salts which may be used. And, of course, there are many ways available of evaporating water, dispersing carbonates and coated crystals in aqueous solutions and lacquers, and of coating cathode bases with fluids.

What is claimed is:

1. The process for making an oxide cathode for use in an electron tube comprising the following steps:
   A. Dispersing an alkaline earth carbonate in an aqueous solution having a soluble metal salt dissolved therein, said salt being substantially free of sulfur and halides, the metal of said soluble metal salt having a vapor pressure not exceeding that of iron said soluble metal salt comprising less than 10 percent of the total weight of salt and carbonate,
   B. Evaporating the water from the aqueous solution leaving residual alkaline earth carbonate crystals coated with the metal salt,
   C. Dispersing the coated crystals in a vehicle comprising a binder dissolved in a liquid solvent, said binder being selected from the class comprising nitrocellulose, the methacrylate resin, ethyl cellulose, methyl cellulose, caseins and dextrins, said solvent being selected from the class comprising amyl acetate, butyl acetate, butyl alcohol and water, said binder and solvent being so selected as together to readily form a solution, and
   D. Coating the dispersion of step C onto the surface of a cathode base.

2. The process of claim 1 wherein said soluble metal salt is selected from the group consisting of nickel salt, tungsten salt, cobalt salt, platinum salt, iron salt and rhodium salt.

3. The process of claim 1 wherein step A said alkaline earth carbonate is selected from the group consisting of calcium carbonate, barium carbonate and strontium carbonate.

4. The process of claim 1 wherein step A said alkaline earth carbonate is dispersed in said aqueous solution by ball-milling action.

5. The process of claim 1 wherein step C the coated crystals are dispersed in the organic lacquer by ball-milling action.

6. The process of claim 1 wherein step B is accomplished by heating the aqueous solution in an air atmosphere oven at approximately 90° C.

7. The process of claim 1 wherein step C is accomplished by mixing the crystals with a nitrocellulose lacquer.

8. The process of claim 1 wherein step C is accomplished by ball-milling a butyl methacrylate lacquer having said coated crystals suspended therein.

9. The process of claim 1 wherein step A said aqueous solution has barium carbonate and strontium carbonate suspended therein.

10. The process of claim 9 wherein said barium carbonate and said strontium carbonate are present in substantially equal proportions by weight.

11. The process of claim 1 wherein said soluble metal salt is a nickel salt.

12. The process of claim 11 wherein the nickel of said nickel salt and said alkaline earth carbonate are present in the respective proportional ranges by weight of 174 to 10 percent nickel and 99-¾ to 90 percent carbonate.

13. The process of claim 11 wherein the nickel of said nickel salt and said alkaline earth carbonate are present in the approximate proportions by weight of 25 to 975 respectively.

14. The process of claim 11 wherein step A said nickel salt is dissolved in said aqueous solution by mixing nickel acetate with water.

15. The process of claim 14 wherein said nickel acetate and said alkaline earth carbonate are present in the approximate proportions by weight of 1 to 10 respectively.

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