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PROCESS AND COMPOSITION FOR COATING ELECTRODES

Eugene A. Giard, Shorewood, Wis., assignor to Cutler-Hammer, Inc., Milwaukee, Wis., a corporation of Delaware

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8 Claims. (Cl. 250—27.5)

Electron discharge tubes are frequently equipped with cathodes which are coated with emission increasing materials such as barium oxide and strontium. The methods of coating such electrodes employed heretofore are very cumbersome and result frequently in failures due to the difficulty of causing the oxides to adhere to the surface of the electrodes.

With the methods heretofore used it is customary to start with a desired mixture of barium carbonate and strontium carbonate to which are frequently added barium nitrate and/or strontium nitrate and sometimes small quantities of various organic substances. These materials are put into a ball mill together with a sufficient amount of water to form a slurry of proper consistency, the slurry being processed in the mill for a prolonged period of from 12 to 20 hours. The cathodes are then given several coats of the slurry and baked after each coating at an elevated temperature in an atmosphere of carbon dioxide. The coating mixture wets the electrode surface only with difficulty due to its large surface tension and has a tendency to collect into "beads" on the surface of the electrode especially if the electrode is in filamentary form. Great care is therefore necessary to insure even wetting of the metal surface and to prevent small bubbles. The ball-milling operation usually results in the formation of a foam on the surface of the slurry which is very difficult to break down; and the small bubbles thereof, if allowed to reach the surface of the electrode, result in bare spots and areas of unequal coating density. As a result the final coating is uneven and flakes off during subsequent handling of the cathode particularly if the latter is of filamentary form and has to be bent after processing. The baking temperature must also be carefully controlled as too low a temperature produces insufficient adherence of the coating, while too high a temperature causes it to sinter on the surface of the electrode and to crack when the electrode is bent.

The present invention has for its object to provide a method of and means for coating electrodes which will be free from the aforementioned disadvantages.

Another object of the invention is to provide a method of coating electrodes which produces a tenaciously adhering coating.

Another object is to provide a coating which is easily and expeditiously applied.

Another object is to provide a coating which evenly covers the electrode.

Another object is to provide a coating which will not crack off the electrode upon the moderate bending of the latter.

Other objects and advantages will hereinafter appear.

With my present method approximately equal quantities of barium oxide and strontium oxide are dissolved in ethylene glycol. It is known at the present time whether this forms a true solution or whether the glycol forms compounds with the barium and strontium. This property of the glycols and related compounds may be analogous to the well known property of sugar solutions which take hydrates of these elements into solution. Indeed, as is the case with sugar solutions, it is impossible to precipitate all the barium and strontium with carbon dioxide. Further, it was found that a small quantity of the solvent or the compound remains in the completed coating, as will be described later, and acts as a decomposition accelerator, thus eliminating the necessity of adding a separate agent for this purpose as is the case with other methods.

The solution containing the barium oxide and strontium oxide is next heated to boiling temperature (197° C.) while carbon dioxide gas is passed through it. This causes precipitation of substantially all of the barium and strontium in the form of their carbonates. The latter are in a very finely divided condition and are thus well suited for the coating operation. By regulating the temperature of the solution and the rate of the addition of the carbon dioxide gas, it is possible to regulate the particle size within wide limits. The ball milling for securng small particle sizes used with other methods as aforedescribed is thus obviated.

I have found that barium nitrite and strontium nitrite are easily soluble in glycols. In the present process I preferably dissolve a small quantity of barium nitrite in ethylene glycol and mix the resulting solution with the aforedescribed solution of barium carbonate and strontium carbonate at the boiling temperature of the glycol and stir until all evolution of gas ceases. While the exact function of the barium nitrite is not known, it presumably acts as a binder and it has been found to be very beneficial for the production of a good coating.

The resulting composition or slurry of barium nitrite in solution and barium carbonate and strontium carbonate in suspension in ethylene glycol is next applied to the cathode while hot. The slurry flows freely and wets the metal surface very readily having a tendency to spread thereon. Thereafter the ethylene glycol is

evaporated in an atmosphere of carbon dioxide at a temperature of approximately 200° C., such temperature not being critical. By suitably adjusting the ratio of solids to liquids, it is possible to apply in a single coating a strongly adhering deposit of emission increasing material which is of equal efficiency to a coating applied in accordance with another frequently used method, but which to obtain equal adherence requires that the coating be applied by about nine successive applications.

The coating produced by the present method is far superior to the coating obtained by the older methods in that it adheres better to the cathode and is more readily decomposed at elevated temperatures. Thus, for instance, a thin ribbon coated by the new method was wound in the form of a spiral on a one-eighth inch mandrel thereafter removed and straightened and then wound on the same mandrel in the opposite direction without losing an appreciable quantity of the coating. With the methods used heretofore such a treatment would have resulted in the removing all of the coating from the ribbon.

It should also be pointed out that the temperature to which the material has to be heated for conversion from the carbonates to the oxides is considerably lower than that which has to be employed with the older processes. This lower temperature requirement is probably due to the extremely small size of the barium carbonate and strontium carbonate, and the presence of a small amount of carbon which remains from the decomposition of the organic material, and which is known to be beneficial for this purpose.

This invention is not limited to the use of ethylene glycol. Several other glycols with both primary and secondary alcohol radicals have been found satisfactory as have also certain polyhydric alcohols. For instance, a mixture of ethylene glycol and glycerine has been found an excellent means of introducing additional carbon into the coating to promote the decomposition of the carbonates to the oxides. The glycerine, a tri-hydric alcohol, can be used alone and functions in a manner similar to the glycols. It obviously becomes possible to produce coating mixtures with widely varying physical and chemical properties by a suitable choice and blending of the various members of the glycol and polyhydric alcohol families. Thus wherever I use the term glycol in the appended claims, it is to be understood to cover any or all of the aforementioned substances.

It is also possible to use barium compounds or strontium compounds alone or use them in any suitable mixture. Wherever the term barium is used in the claims, it is to be understood that it is also to cover the corresponding strontium compound or a mixture of both compounds.

What I claim as new and desire to secure by Letters Patent is:

1. An electron emission increasing coating consisting of a glycol base containing soluble salts of barium, colloidal barium carbonates, and barium compounds with the glycol.

2. An electron emission increasing coating containing the mixtures of barium carbonate with a glycol.

3. An electron emission increasing coating which consists of a mixture of barium carbonate with a glycol and other barium and strontium salts.

4. The method of producing an emission increasing coating mixture which consists in precipitating barium carbonate from a solution of barium oxide in a glycol by carbon dioxide and adding a solution of barium nitrite in a glycol.

5. The method of producing an emission increasing coating mixture which consists in precipitating barium carbonate from a solution of barium oxide in a glycol by carbon dioxide under application of heat and adding a solution of barium nitrite in a glycol.

6. The method of producing an emission increasing coating mixture which consists in precipitating barium carbonate from a solution of barium oxide in a glycol by carbon dioxide and adding a solution of barium nitrite in a glycol, applying the mixture to the surface in an atmosphere of carbon dioxide and evaporating the volatile constituents.

7. The method of producing an emission increasing coating mixture from a solution of barium oxide in a glycol which consists in precipitating barium carbonates by carbon dioxide and adding a solution of barium nitrite in a glycol, applying the mixture to the surface in an atmosphere of carbon dioxide and evaporating the volatile constituents at an elevated temperature.

8. The method of producing an emission increasing coating mixture from a solution of barium oxide in a glycol which consists in precipitating barium carbonates by carbon dioxide, adding a solution of barium salts in a glycol and applying the mixture to the surface while maintaining the latter at an elevated temperature to rapidly evaporate the volatile constituents.

EUGENE A. GIARD.

CERTIFICATE OF CORRECTION.

Patent No. 1,974,608. September 25, 1934.

EUGENE A. GIARD.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 62, before "known" insert the word not; and line 89, for "securng" read securing; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of February, A. D. 1935.

Leslie Frazer

Acting Commissioner of Patents.

(Seal)