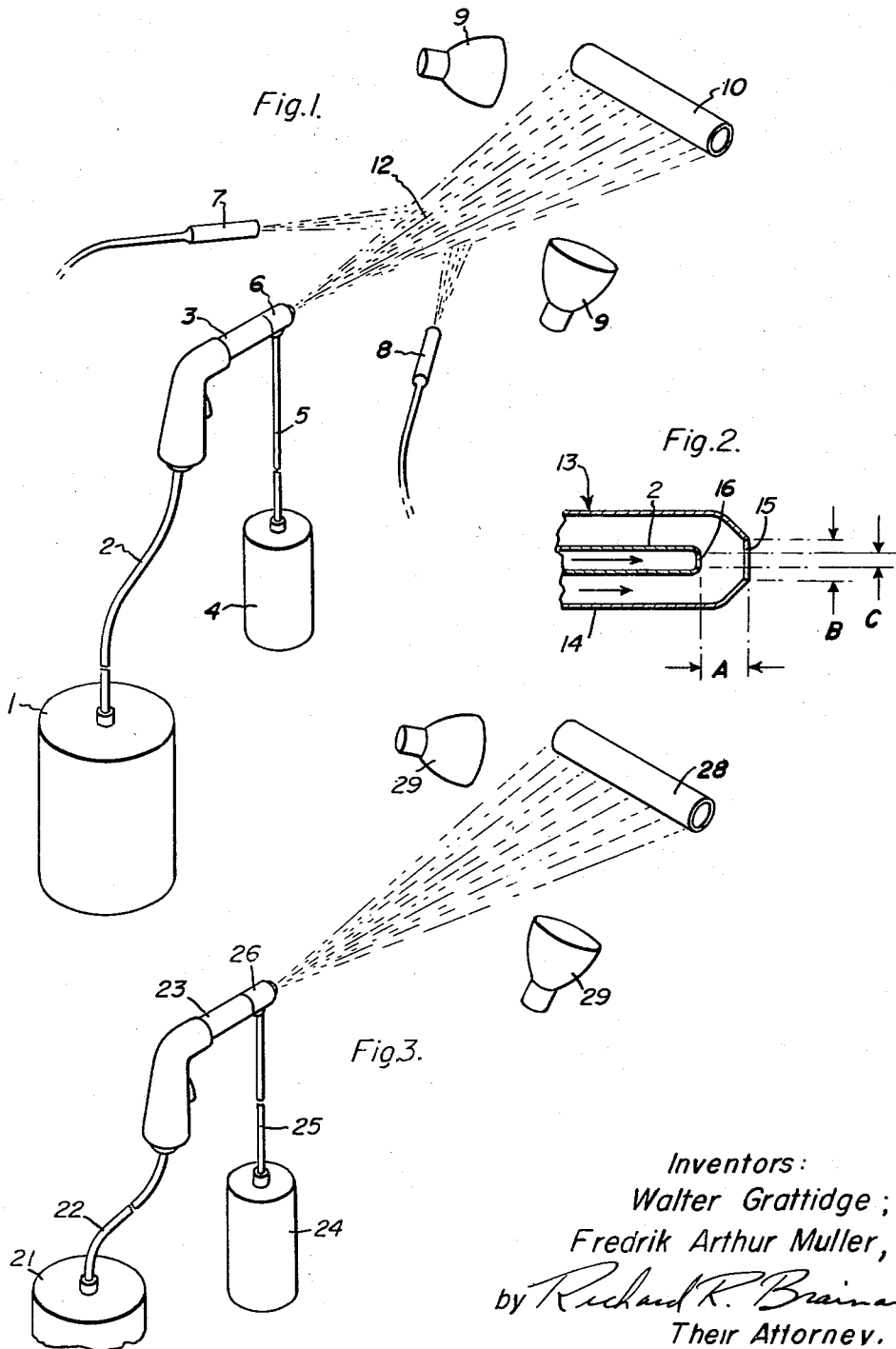


July 5, 1960

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Filed Oct. 21, 1958

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1

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METHOD FOR THE SPRAYING OF ELECTRON EMITTING THERMIONIC CATHODES

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Filed Oct. 21, 1958, Ser. No. 768,654

11 Claims. (Cl. 117—223)

Our invention relates to electron emissive coatings and more particularly to an improved method for producing such a coating on an electron emissive cathode base.

Many present day electron tubes depend for their source of electrons upon the heating of a coated metal cathode made of nickel with specific additives such as aluminum, magnesium, titanium, and silicon. The coatings applied to this cathode metal usually consist of compounds of the alkaline earth elements such as barium, strontium, and calcium, or mixtures of such compounds in appropriate proportions. The usual method of preparation of such coatings involves the spraying onto the cathode of a single carbonate or mixtures of precipitated carbonates from a solution of these materials in some suitable binder. This spraying operation is performed prior to assembly of the various tube electrodes and the carbonate coatings are converted to oxides by heating the electrode during the evacuation process for the tube.

This previous method and others similar to it have certain inherent disadvantages which result primarily from the formation of large irregularly shaped crystals of the carbonate. These disadvantages include lack of adherence of the carbonate to the surface, high relative porosity, high surface roughness, and poor hardness and mechanical strength qualities. The lack of adherence may result in the flaking of the coating or the lifting of the coating away from the metal base before or during conversion of the carbonate coating to the oxide. The high surface roughness is detrimental to good operation of the cathode in high voltage rectifiers and prevents or limits the necessarily close grid-to-cathode spacing in low noise high frequency triodes. The poor strength qualities require that the handling of the cathode after coating must be kept to a minimum.

Accordingly, it is an object of our invention to provide an improved method of making an electron emissive coating which exhibits improved surface texture, density, adherence, and mechanical strength qualities.

It is a further object of our invention to provide an improved method of spraying a cathode coating on the cathode supporting surface.

In accordance with one form of our invention, these enumerated difficulties and disadvantages are avoided by spraying very finely divided droplets of a chemical compound towards the surface to be coated and simultaneously propelling a second gaseous or vaporized compound to converse with the first in the region preceding the work surface to facilitate contact and interaction between these compounds to take place prior to contact with the work surface but after formation of the spray. This reaction produces the final compound which is to be deposited on the surface to be coated and during transit the vehicle carrying the reaction product is partially evaporated. Such a method produces a large number of small particles of coating material to produce a coating

2

which exhibits the improved characteristics of strong adherence to the underlying base, mechanical strength, high density, small particle size and also, a smooth surface.

Other and further objects and advantages will appear from a perusal of the following detailed description considered with the accompanying drawings in which:

Fig. 1 illustrates one arrangement of apparatus which may be utilized in one embodiment of our improved method,

Fig. 2 illustrates one form of nozzle construction which can be utilized to spray the coating according to our improved method, and

Fig. 3 illustrates a second embodiment of our improved method.

Referring to the embodiment of our invention illustrated in Fig. 1, a gaseous compound such as compressed air, from a source free of carbon dioxide, is supplied to the spray gun 3 through the communicating conduit 2.

By aspirator action, the compressed air acts as a vehicle and the solution in container 4 is drawn through the communicating passage 5 into the spray gun where it is "atomized" or converted into small droplets, preferably of approximately 1 mil in diameter, by the nozzle apparatus shown generally at 6. The droplets are propelled towards the object 10 which is preferably a cathode base to be coated. The apparatus designated by the numerals 7 and 8 represent nozzles for supplying a second gaseous or "atomized" compound which is directed to converge with the mist or spray from the spray gun approximately at the region 12 which is somewhat removed from the surface to be coated. The compound from nozzle 6 and the second compound from the nozzles 7 and 8 react in region 12 so as to produce the third compound which is to be deposited on the surface 10. A pair of heat lamps are directed at the cathode base 10 to heat the surface of the cathode exposed to the spray and being coated and to heat the droplets in the latter portion of their distance of travel, supply the necessary energy to evaporate the solvent for the first solution which is used to form the vapor droplets.

In accordance with a specific form of our invention, air which is made substantially inert by the removal of carbon dioxide therefrom, is supplied to the spray gun 3 through the communicating conduit 2 to be used as the propelling medium. By aspirator action, a saturated water solution of barium hydroxide, which is contained at 4, is drawn through the communicating conduit 5 into the spray gun where it is converted into a fine spray that is carried towards the surface 10 by the propelling air medium. Two streams of carbon dioxide are directed towards the intersection region 12 from the nozzle apparatus shown at 7 and 8. The carbon dioxide reacts with the barium hydroxide contained in the droplets so as to form very small insoluble crystals of compounds of barium, such as barium carbonate or barium bicarbonate. These crystals are carried directly to the surface of thermionic cathode element 10 which may be from two to three feet away from the region 12, and are deposited thereon. The minute size of the droplets facilitates a quick and complete reaction between the barium hydroxide solution thereof and the carbon dioxide gas in a fraction of the distance between region 12 and surface 10 whereby the water in the droplets is partially evaporated and the barium carbonate precipitate is added to the cathode surface in minute increments. The radiations from the heat sources 9 serve to evaporate the remainder of the water solvent for the barium hydroxide which dries the surface and also insures surface uniformity by preventing "running" of the deposited coating. The minute amount of precipitate in the different droplets enables a fine and even deposit to produce a smooth and even coating.

In performing the method of our invention, various compounds may be utilized in the manner described. Solutions of compounds of alkaline earth elements or any combinations of these may be utilized in nozzle 6 while carbon dioxide, solutions of ammonium carbonate or any of the substituted ammonium carbonates such as monoethanolamine or any combinations of these solutions are utilizable in the nozzles 7 or 8. The reaction product is a carbonate precipitate depositable on the cathode surface. Although various alkaline earth compounds are conceived as useful in performing our method, compounds considered particularly useful are acetates, chlorides, formates, hydrates and nitrates of barium and strontium.

As shown in Fig. 2, a nozzle, designated generally at 13, is effective in accomplishing the improved spraying method of our invention and may include propellant carrying conduit member 14 coaxially surrounding one end of communicating conduit 2 and extending beyond the end of conduit 2 by a distance designated A in the drawings. The open end of conduit 13 converges to an opening 15 of dimension designated B and conduit 2 converges to an opening 16 of dimension designated C. It has been experimentally determined that the opening 16, if it is in the range of 4 to 10 mils in diameter, will supply droplets of the alkaline earth hydroxide approximately 1 mil in diameter which has been found to be a satisfactory particle size in accordance with our improved method. The dimensions A and B become particularly important if the second reagent is to be used as the propelling medium as is set forth in the second embodiment of this invention. The distance A is selected so as to limit the reaction time within the spray gun and the dimension B is selected so as to be sufficiently large as not to clog with particles formed during the reaction time determined by the distance A. According to one embodiment of our invention the dimension B has been determined experimentally to be within the range 10 to 40 mils and the dimension A has been found to vary within the range of 20 to 40 mils. A nozzle, which has been successfully used with either of the illustrated embodiments of this improved method, has the dimensions of 4 mils for opening 16, 20 mils for opening 15, and 25 mils for distance A. Using a nozzle with opening B of substantially 10 mils, a coating of .6 mil at a density of 1.8 gr./cc. may be applied in 10 to 15 minutes of spraying time.

It is implicit in our invention that the smallest droplet possible be utilized in accordance with the reasonable spray speed which may be desired; that is, the larger the droplet is, the less chance there is of full reaction with the second reagent before contact with the surface. It is seen, therefore, that the distance from the gun to the work surface is also determined by the degree of completeness desired in the chemical reaction. Thus, a wide range of dimensions of nozzle components and spacings between the spray nozzle and the surface to be coated can be utilized without departing from the spirit of this invention. It is an essential feature of this invention, however, that no carbon-dioxide be drawn into the storage vessel for the barium hydroxide. That is, there should be no reaction between the two reagents in any storage vessel.

Referring to Fig. 3, a modified apparatus is shown wherein the propelling gas for the alkaline earth hydroxide is also one of the reacting compounds in the improved method. This propelling gas is supplied from the container 21 through the communicating conduit 22 to the aspirator spray gun 23 which draws a portion of the second liquified compound in the container 24, through the communicating conduit 25 to the spray gun 23 where a fine spray is created from the two compounds by the nozzle apparatus shown generally at 26. These two compounds react during the course of travel from first contact within the spray gun to the surface to be coated 28. The relative nozzle dimensions, as previously described

with respect to Fig. 2, are maintained in this embodiment so that the particles formed by the reaction, when deposited on a surface 28, will be of optimum size for proper coating. The heat source 29 can be used to accelerate the drying process of a deposited coating and to further insure the uniformity of the cathode coating by preventing undesirable effects from "running" by a fluent deposit.

A specific example embodying the principles disclosed by the apparatus of Fig. 3 would involve the use of carbon dioxide from the container 21 as the propelling medium and being supplied to the spray gun 23 through the communicating conduit 22. The aspirator action of the spray gun draws the barium hydroxide, which is contained in a saturated solution at 24, through the communicating conduit 25 to the spray gun 26 where the carbon dioxide and barium hydroxide mixture is converted to a fine mist which is directed toward the surface 28 to be coated. The barium hydroxide and carbon dioxide react along the path of travel to produce barium carbonate which is deposited on the surface 28. The radiant heat energy source 29 serves to evaporate the solvent from the barium hydroxide.

The mechanical strength of the type of coating produced by our method allows for filing or other mechanical abrasion to produce coatings of any requisite thickness. For example, coatings of substantially .6 mil have been sprayed on nickel cathodes and then filed to a coating thickness of .3 mil. Such a filed coating has been used in a triode with resultant improved noise figures.

Having thus described this invention in such full, clear, concise and exact terms as to enable any person skilled in the art to which it pertains, to make and use the same and having set forth the best mode contemplated of carrying out this invention, we state that the subject matter which we regard as being our invention is particularly pointed out and distinctly claimed in what is claimed, it being understood that equivalents or modifications of or substitutions for parts of the above specifically described embodiment of this invention may be made without departing from the scope of the invention as set forth in what is claimed.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The method of coating a cathode base with an electron emissive material comprising the formation of small droplets of a hydroxide solution of alkaline earth elements, propelling said droplets towards the cathode base to be coated, directing a flow of carbon dioxide toward said droplets for producing an intermixture therebetween during transit, the reaction of the hydroxide contained in said droplets with carbon dioxide forming a carbonate of the alkaline earth metal prior to contact with the cathode base to be coated, evaporating the liquid in said droplets, and deposition of said carbonate on the cathode base.

2. The method of coating a cathode base with an electron emissive material comprising the formation of small droplets of an hydroxide solution of alkaline earth elements, propelling said droplets towards the cathode base to be coated, enveloping said droplets in transit in a cloud of carbon dioxide to effect a reaction forming carbonate of the alkaline earth metal in each of said droplets, said reaction taking place after formation of the droplets but before contact with the cathode base to be coated and depositing said carbonate on the cathode base.

3. The method of coating a cathode base with an electron emissive material comprising the formation of small droplets of an hydroxide solution of alkaline earth elements substantially one mil in diameter, propelling said droplets towards the cathode base to be coated, enveloping said droplets in a cloud of carbon dioxide to effect a reaction forming a carbonate of the alkaline earth metal, said reaction taking place after formation of the droplets but before contact with the cathode base to be coated,

and heating the droplets of formed carbonate prior to and after contact with said cathode base.

4. The method of coating a cathode base with an electron emissive material comprising the formation of small droplets of an hydroxide solution of alkaline earth elements substantially one mil in diameter, propelling said droplets towards the cathode base to be coated, reacting the alkaline earth element hydroxide contained in said droplets with carbon dioxide to form a carbonate of the alkaline earth metal prior to contact with the surface to be coated, and depositing said carbonate of the alkaline earth metal on the cathode base to be coated.

5. The method of coating a cathode base with an electron emissive material comprising the steps of forming a spray of droplets of barium hydroxide solution, propelling said droplets toward a cathode base to be coated, enveloping said droplets in a cloud of carbon dioxide during transit toward said cathode base, said droplets and carbon dioxide reacting to form a precipitate of barium carbonate deposited on said surface, evaporating a portion of the liquid in said droplets during transit and drying said surface after deposition.

6. The method of coating a cathode base with an electron emissive material comprising the steps of forming a spray of droplets of a solution of barium and strontium hydroxides, propelling said droplets toward the cathode base to be coated, enveloping said droplets in a cloud of carbon dioxide during transit toward said surface, said droplets and carbon dioxide reacting to form a precipitate of barium and strontium carbonates deposited on said cathode base and drying said cathode base during transition and after deposition on said cathode base.

7. The method of coating a cathode base with an electron emissive material comprising the steps of forming a spray of droplets of a solution of barium hydroxide, propelling said droplets toward the cathode base to be coated, forming a spray of droplets of a solution of ammonium carbonate and propelling the same to converge with the droplets of said first solution at a region adjacent to the cathode base, the droplets of different solutions reacting to form a precipitate of barium carbonate and depositing said precipitate on the cathode base to be coated.

8. The method of coating a cathode base with an electron emissive material comprising the steps of forming a spray of droplets of a solution of ammonium carbonate, propelling said droplets toward the cathode base to be coated, forming a spray of droplets of a solution of

barium acetate and propelling the same to converge with the droplets of ammonium carbonate solution at a region adjacent to the cathode base, the droplets of different solutions reacting to form a precipitate of barium carbonate and depositing said precipitate on the cathode base to be coated.

9. The method of coating a cathode base with an electron emissive material comprising the steps of producing a spray of small droplets of a solution of a compound selected from one of the group consisting of acetates, formates, hydrates, chlorides and nitrates of alkaline earth elements, propelling said droplets toward the cathode base to be coated, mixing the solution in said droplets during transit with a carbonate compound at a region removed from said cathode base, and thereby producing as a precipitate a carbonate derivative of said one compound of said group and depositing and drying said precipitate on said cathode base.

10. The method of coating a cathode base with an electron emissive material comprising the steps of producing a first spray of small droplets of a solution of a compound selected from one of the group consisting of acetates, chlorides, formates, hydrates and nitrates of alkaline earth elements, propelling said droplets toward the cathode base to be coated, intermixing with said first spray, a second spray of small droplets of a carbonate compound and thereby producing as a precipitate, a carbonate derivative of said one compound of said group and depositing and drying said precipitate on said cathode base.

11. The method of coating an electron emissive coating comprising the steps of producing a spray of small droplets of a combination of solutions of a compound selected from the group consisting of acetates, chlorides, formates, hydrates and nitrates of an alkaline earth element, propelling said droplets toward the surface to be coated, mixing the solutions in said droplets during transit with a carbonate compound at a region removed from said cathode base, and thereby producing as a precipitate, a carbonate derivative of said compound of said group and depositing and drying said precipitate on said cathode base.

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