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COATING SUSPENSION AND METHOD OF PREPARATION

Joshua R. C. Brown, Jr., Chatham, N. J., assignor to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

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This invention relates to coating suspensions and methods of preparation and more particularly to colloidally dispersed particles in suspensions for coating electrodes of electron discharge devices.

In the manufacture of oxide coated emitters for electron discharge devices and more especially low current emitters of the filamentary type for miniature devices employed in easily portable and inconspicuous apparatus, such as hearing aids or audiphones and personal radio sets of the hand-bag type, considerable difficulty has been experienced in obtaining emission efficiency and operating life comparable with conventional types of emitters in larger devices. In the miniature devices, the filament is of small diameter, of the order of .001 inch to .0004 inch, and due to such small size, the usual coating procedure is unsatisfactory for many reasons since loss of adherence, low emissivity, non-uniformity of coating and short operating life are some of the effects resulting from simulating prior technique.

It has been found that the physical character of the coating or emitting surface has an important bearing on emission, uniformity of surface, freedom from bombardment at high anode potential, arc-overs and sputtering and that control of the physical character of the coating permits closer grid-cathode spacing to be attained. Furthermore, the purity of the suspending medium, and the particle size and stability of the colloidal suspension have been found to be important factors in the successful deposition of the coating by machine methods in manufacturing processes.

The principal object of this invention is to achieve uniformity in the particle size of active material contained in a colloidal suspension for coating purposes.

Another object of the invention is to insure the stability of the suspension so that the particle size of the active material is constant.

A further object of the invention is to germinate colloidal monodisperse suspensions by chemical decomposition methods.

In accordance with a broad aspect of the invention, the coating mixture or suspension is produced by chemical reaction in which a nuclear sol of alkaline earth compounds is mixed with a solution of alkaline earth salts and then converted by chemical reaction to the insoluble compound desired in the coating mixture. The presence of the nuclei results in a final suspension containing particles of smaller particle size than would be obtained were the reaction carried out

without the addition of the nuclei, the degree of particle size reduction depending on the ratio of the amount of compounds formed to the number of nuclei added. The number of nuclei will probably not be known but if the average particle size in the nuclear sol is maintained the same in two similar test specimens, the number of nuclei is proportional to the weight of the compounds in the nuclear sol.

If the course of the chemical reaction is so controlled that no new nuclei are formed and coagulation does not occur uniform growth of the nuclei, as the reaction proceeds, results in a suspension of particles of essentially uniform size. The particle size obtained with a given nuclear sol being controlled by the ratio of weight of material in the nuclear sol to the weight of alkaline earth salt in the solution mixed therewith.

In a specific aspect of the invention a nuclear sol is prepared by dissolving barium and strontium hydroxides in methyl alcohol and bubbling dry carbon dioxide through the solution for a short period to form the soluble barium-strontium salt of methyl carbonic acid. The solution is added to a relatively large amount of boiling ethyl alcohol and after partial evaporation under continued heating, the soluble salt decomposes with the evolution of carbon dioxide to give nuclei of the insoluble carbonate of colloidal particle size.

The nuclear sol is cooled and then mixed with similarly cooled methyl carbonate salt solution, and dry air, free from carbon dioxide, is passed through the mixture while heating the mixture to the boiling point. The solution gradually becomes cloudy and finally milky white which signifies that the reaction is autocatalytic and proceeds largely on the surface of the added nuclei. As the particles grow the surface of each particle increases as the square of its diameter. Centrifuging a suspension prepared according to the above procedure shows that the suspension is essentially monodisperse, i. e., of a single particle size. Furthermore, subsequent centrifuging at monthly intervals shows that particle size growth does not occur so that the uniformity of the particle size once established is constant over long periods. By proper control of the ratio of nuclear sol to carbonate solution monodisperse suspensions of controlled particle size may be obtained for the deposition of uniform highly active coatings on emitters.

In the development of the coating suspensions of this invention, one particular procedure which may be followed comprises a mixture of 500 mil-

ligrams of barium hydroxide and 350 milligrams of strontium hydroxide, in powdered form, suspended in 50 cubic centimeters of methyl alcohol. Partial solution occurs and is accelerated by bubbling dry carbon dioxide through the suspension for five to ten minutes to form barium-strontium salt of methyl carbonic acid. If persistent cloudiness occurs, this is probably due to the presence of carbonate in the original hydroxides as an impurity which may be removed by centrifuging the suspension.

A portion of the alcohol solution, for example, 10 cubic centimeters, is then added to 100 cubic centimeters of boiling ethyl alcohol and by continual heating until approximately half of the alcohol is evaporated, decomposition occurs in which the soluble salt is converted to insoluble carbonate with the evolution of carbon dioxide. Continued heating and sweeping with air, free from carbon dioxide, facilitates the conversion to form the carbonate nuclei having a particle size of less than 0.1 micron diameter.

The nuclear sol prepared as above described is cooled in an ice container, to avoid rapid reaction, due to the high temperature of the sol, when mixed with the similarly chilled methyl carbonate salt solution. The cooled nuclear sol is then added to the remainder of the barium-strontium methyl carbonate solution and heated slowly to the boiling point while passing dry air, free from carbon dioxide, through the mixture.

The mixed solution slowly becomes cloudy and finally milky white, indicating by visual observation that an autocatalytic reaction occurs on the surface of the added nuclei. As the nuclei particles grow, the surface of each particle increases as the square of its diameter.

A suspension prepared as above described on being tested for particle size shows that the suspension is essentially monodisperse or of a single particle size. This was proved by centrifuging, at 1000 revolutions per minute for 900 seconds, a two-centimeter column of the suspension in a cylindrical tube. After centrifuging, the column of suspension appears sharply separated into approximately one centimeter of clear liquid floating on one centimeter of suspension of unchanged concentration, indicating uniform particles of about 0.2 micron diameter. No further growth was evidenced as indicated by subsequent monthly centrifuging.

The invention indicates that any desirable particle size coating material over a considerable range may be attained and controlled simply by varying the weight ratio of nuclear sol to total weight of carbonates in the final suspension and such ratios may be from 10 to 1 to 1000 to 1. Such suspensions will contain only monodisperse aggregates of limits well within the colloidal range, i. e., below 0.5 micron diameter.

While the invention has been disclosed with respect to a specific alkaline earth salt and solvent material, it is, of course, evident that other monodisperse suspensions may be developed in accordance with the teaching of this invention. Furthermore, the nuclear sol of one emissive compound may be mixed with a different salt solution than the nuclear sol compound to result in a coating suspension for the cathode, the suspension having a uniform particle size. Accordingly, the scope of the invention is not intended to be limited thereto, since other compounds of electronic active materials and other solvents may be used to achieve the results of this invention. Therefore, the spirit of the invention is to be

limited only by the scope of the appended claims. What is claimed is:

1. A coating suspension for electrodes of electron discharge devices, comprising colloidal particles of insoluble alkaline earth compounds formed by chemical reaction of a soluble salt of said compounds in a solvent mixed with a nuclear sol of alkaline earth compounds.

2. A colloidal coating suspension for cathodes of electron discharge devices, comprising particles of cathode coating compounds formed by chemical reaction of a soluble salt of said compounds in a solvent mixed with a nuclear sol, the nuclear sol consisting of colloidal particles of cathode coating compounds of a size considerably smaller than that of the particles in the coating suspension.

3. A colloidal coating suspension for cathodes of electron discharge devices, comprising the product of chemical decomposition of alkaline earth salt of methyl carbonic acid in an alcoholic solvent mixed with a nuclear sol of alkaline earth compounds, the sol particle forming the core of the product particle.

4. A colloidal coating suspension for filamentary emitters of electron discharge devices, comprising the product of chemical decomposition of a solution of barium-strontium salt of methyl carbonic acid mixed with a nuclear sol of barium-strontium carbonate.

5. A colloidal coating suspension for emitters of electron discharge devices, comprising the product of chemical decomposition of an alkaline earth salt solution mixed with a nuclear sol of insoluble alkaline earth compound in a solvent in the weight ratio range of 10 to 1 to 1000 to 1.

6. A coating for emitters of electron discharge devices, comprising a monodisperse suspension of barium-strontium insoluble carbonate having uniform particle size in the colloidal range from 0.1 to 0.5 micron diameter, the nuclei of the carbonate particles being predetermined prior to formation of the particles by the introduction of a nuclear sol.

7. A coating composition, comprising colloidal alkaline earth carbonate of uniform particle size resulting from decomposition of alkaline earth salt of methyl carbonic acid in the presence of colloidal nuclei of alkaline earth carbonate.

8. The method of obtaining small particle size in a coating suspension for cathodes which comprises, mixing, as a nuclear sol, a colloidal suspension of cathode coating insoluble compounds with a soluble salt of the cathode coating compounds prior to conversion of the soluble salt to the insoluble cathode coating compounds, and developing the nuclear sol particles by accretion of said insoluble compounds under autocatalytic reaction.

9. The method of preparing fluid suspensions having single particle size aggregates for coating an emissive surface which comprises, preparing a nuclear sol of the aggregate material, mixing the sol in a solution of soluble salt, and converting the aggregate to colloidal insoluble salt in suspension by chemical reaction on the surface of the nuclei.

10. The method of growing uniform particles having diameters in the colloidal range for coating emitters of electron discharge devices which comprises, preparing a nuclear sol of insoluble alkaline earth compound in a solvent, adding the sol to a solution of soluble alkaline earth salt of methyl carbonic acid, and heating until reaction is completed to increase the growth of the

sol particles and convert the soluble salt to insoluble carbonates as evidenced by its milky white character.

11. The method of growing uniform particles having diameters in the colloidal range for coating emitters of electron discharge devices which comprises, preparing a nuclear sol of barium and strontium carbonate by diluting methyl carbonate salt of barium and strontium with ethyl alcohol, heating for a short period, chilling the said nuclear sol, adding the sol to a chilled solution of barium-strontium salt of methyl carbonic acid, heating the mixture to boiling temperature until autocatalytic reaction occurs to form a monodisperse suspension having particles less than 0.5 micron diameter.

12. The method of growing uniform particles having diameters in the colloidal range for coating emitters of electron discharge devices which comprises, preparing a suspension of barium and strontium hydroxides in methyl alcohol, bubbling carbon dioxide through said suspension to accelerate dissolvment of the hydroxides, separating a portion of the methyl carbonic acid salt, boiling said salt in ethyl alcohol to form a nuclear sol, adding the sol to the remainder of the acid salt solution, and heating to boiling temperature to cause reaction between the salt solution and the nuclei to grow particles of colloidal size.

13. The method of forming emissive coatings for cathodes of electron discharge devices which comprises, preparing a suspension of barium and strontium hydroxides in methyl alcohol, convert-

ing the hydroxides to soluble semicarbonates, diluting a portion of the carbonate solution in alcohol, heating to the boiling point to form a nuclear sol of insoluble carbonate with the evolution of carbon dioxide, flushing with dry air free from carbon dioxide, cooling the resultant sol in an ice bath, adding the sol to chilled barium-strontium salt of methyl carbonic acid, and heating to a temperature whereby accretion by autocatalytic reaction occurs on the nuclei to form monodisperse particles in suspension having a diameter less than 0.5 micron.

14. The method of forming an emissive coating for cathodes of electron discharge devices which comprises, preparing a suspension of barium and strontium hydroxides in 50 cubic centimeters of methyl alcohol, passing carbon dioxide through the suspension to form methyl carbonic acid carbonate, diluting 10 cubic centimeters of the carbonate solution with 100 cubic centimeters of ethyl alcohol, heating to the boiling point to evaporate a portion of the alcohol while introducing dry air to the boiling solution to form a nuclear sol of insoluble carbonate in suspension, cooling the sol to low temperature, adding the sol to the remainder of the chilled methyl carbonic acid suspension, and slowly heating the combined solution to reaction temperature to increase the growth of the nuclei to particles of monodisperse dimension within the colloidal range.

JOSHUA R. C. BROWN, JR.