United States Patent Office

2,966,449

Patented Dec. 27, 1960

2,966,449

ELECTROPHORETIC COATING AND PROCESS

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No Drawing. Filed May 22, 1958, Ser. No. 736,994

3 Claims. (Cl. 204—181)

This invention relates in general to electrophoretic coating and in particular to a cataphoretic method and formula for coating objects.

Cataphoretic methods for coating objects have largely displaced such methods as dipping, spraying, or plating in many areas, particularly in the electronics industry. In the case of electron tube manufacture especially cataphoretic methods have been widely used because of their numerous advantages. Nevertheless, there have been limitations to the extent of use of cataphoresis which are imposed by the nature of the materials used for coating, the preparation of the material, the type and configuration of the articles to be coated, and the difficulties and hazards involved in carrying out the cataphoretic processes. In the specific case of coating wire with insulating material such as aluminum oxide, it has been necessary to add to a suspension of the oxide some cataphoretic activator which will not be harmful in the finished electron tube, but which will aid in the deposition process. Apart from the judicious selection of materials that is required, the preparation of the coating material has been a long and involved process. In some instances it has been necessary to roll or ball-mill the mixtures for hours, and even days. The mixtures used are often most sensitive to temperature and humidity changes, and the storage problems are accordingly aggravated.

Moreover, in the case of coating such articles as coils for electron tube heaters or other applications, the coating is often inferior on the inside coil surfaces rather than being uniform and smooth as is desired. Because high voltages are commonly used in the coating process, the voltage gradient along an article being coated is so steep that a tapered coating, heavy at one end and light at the other end of the article, often results.

Numerous efforts have been made to solve the various problems of cataphoretic coating, not only in the case of insulating coatings, but in the case of electron-emitting coatings for cathodic tube elements as well as electron emission-inhibiting coatings for grids or other tube elements. The problems outlined are common to other applications also; for example, in the cataphoretic deposition of films for inhibiting corrosion or wear, or for insulating surfaces. It is with a general solution to these problems that the present invention is concerned, although it will be described for purposes of clear understanding in connection with the specific operation of coating wire coils for electron tubes with a refractory insulating material such as aluminum oxide.

It is, therefore, a primary object of the present invention to provide an easily prepared cataphoretic formula which is relatively insensitive to atmospheric changes.

A further object of the invention is to provide a cataphoretic process operable at low voltage levels to produce a uniform and smooth coating on objects of any reasonable configuration.

A still further object is the provision of a cataphoretic

process and formula in which deposition efficiency is high and which is capable of substantially automatic and unattended use.

In general, the invention consists of a formula which is prepared quickly and by simple methods, which is easily and efficiently applied by low voltage cataphoretic methods, and which provides a smooth and uniform coating. An outstanding feature of the invention is the dual purpose served by the binder of the formula. Not only does the binder perform the usual function of binding the coating material to the article being coated, but it also aids in the quantitative deposition of the coating. Other features such as the rapid coating of all types and configurations of coils at low voltages; quick and simple preparation of the coating material; and relative insensitivity of the coating material to atmospheric changes are derived from the process and formula of the present invention. The formula contains elements which combine to form a complex ion, highly suitable for cataphoretic deposition as well as elements which serve as plasticizers and binders. The formula is a water-based suspension with which cataphoretic deposition of a highly efficient kind is possible at low voltages. The formula may be prepared from raw materials to a state where it is ready for use in approximately 1 hour. Its operating potentials for coils of reasonable size run from 20 to 60 volts D.C. with a current ranging from 4 to 50 ma. Coating cycles for representative samples run about 2 seconds. The deposition takes place at the negative electrode of a coating bath, and this electrode may be formed of a clamp or tweezers which hold the unit being coated. After the coating operation, units are briefly rinsed and dried and following coating operation, the coated coils are sintered to drive off unwanted materials and to cause tenacious adherence of the coating to the coil. For a better understanding of the present invention together with other objects, features, and advantages, reference should be made to the following detailed description:

The process of preparing the coating material is begun by washing aluminum oxide powder of a particle size from 5 to 10 microns with one of the following acids; hydrofluoric, hydrochloric, or sulphuric. Following the acid wash, a deionized water rinse is employed until the particles have no further tendency to settle. The powder is then baked briefly at a temperature which is not critical, but which may be about 350° F. for at least several hours. The material may then be stored until it is needed for preparing a quantity of coating.

Independently of the treatment of the aluminum oxide powder in a typical preparation, 12 ml. of distilled water are added to 590 ml. of anhydrous methanol, and to this solution 25 grams of urea are added, this solution being mixed until the materials are completely dissolved. Following the mixture of the solution, 5.5 ml. of Carbo-wax 350 and 5.5 ml. of Carbo-wax 550 are stirred into the solution. Carbo-wax 350 and Carbo-wax 550 are trade names of polyethelene glycols of different molecular weights, hence the numbers 350 and 550. Next, 10 drops of 20 percent normal solution of aluminum acetate are mixed into the solution and 10 drops of 13 percent aluminum nitrate solution are then added and mixed. Finally, 400 grams of the aluminum oxide powder treated as outlined above are added to the solution with vigorous stirring. The mixing is continued for about 5 minutes following which the solution is filtered through a 325 mesh wire screen. It is then ready for use.

In a typical coating process cathode heater coils are suspended from clamping members and connected electrically to a power supply to act as the negative terminal or cathode. The power supply is preferably of about 30 volts D.C., and its anode is immersed in cataphoretic solution. The coils to be coated are placed in the solution for about 2 seconds each. Following this operation, the coated coils are immediately rinsed in a 50 percent methanol—50 percent acetone solution and rinsed again in a 90 percent acetone—10 percent petroleum ether solution. Finally, a third rinse in 100 percent petroleum ether is given to the coils. After the three rinses the coated coils are dried and then fired at 1675° C. in wet hydrogen. An alternative set of rinses would be 2 nitropropane followed by a rinse in petroleum ether or nitroethene followed by a rinse in petroleum ether or in general a rinse in any of this series of nitro paraffin solvents followed by a rinse in petroleum ether. This set of rinses is superior to the normal methanol-acetone, acetone-petroleum ether, petroleum ether series of rinses when automatic equipment is used in the coating process.

The coating obtained on coils processed as described is smooth in texture and uniform in thickness and quality. An important factor contributing to the general excellence of the results obtained is believed to be the use of the diamide of carbonic acid, urea, with the other electrolytes, aluminum nitrate and normal aluminum acetate in the coating suspension. Upon ionization, these form a relatively complex ion which enhances the general efficiency of deposition. A further point of interest lies in the use of the polyethylene glycols of which the Carbowaxes are typical. These act as plasticizers which contribute to the smoothness, toughness and general quality of the deposit.

In an actual operating set-up, 150 ml. of the coating suspension were placed in a round container. A circular anode such as a stainless steel plate was then immersed in the suspension. Heater coils to be coated were attached to conducting clamps which were connected to the cathodic end of the power supply and dipped in the suspension. A period of from 1 to 3 seconds with a potential across the solution of 20 to 50 volts D.C. provided an excellent coating. It is desirable that the suspension be agitated at least slightly between actual coating periods. In other words, the suspension is at rest during the actual 2 second coating cycle and agitated at the completion of the cycle until coating resumes. Superior results are forthcoming from a quiescent suspension. In automatic coating the procedure is somewhat different in that the suspension is always agitated, but the coating electrodes are so positioned as to keep the suspension substantially equiescent in the area where the actual coating takes place.

The particular composition of the suspension may be varied to some extent, depending upon the results desired and the nature of the objects being coated. By way of example, the water-alcohol ratio cited above is about 98 percent and 2 percent water. This can be made as little as 70 percent alcohol and 30 percent water. Moreover, the ratio of aluminum oxide powder to liquid components in the suspension may be varied from 50 percent to 70 percent by weight if desired.

The various rinses described may also be varied in the manner noted or otherwise, but the first rinse should break any "bridging" of coating between turns of coils, if such are being processed, remove the water and smooth the coated surface. Succeeding rinses should further smooth the surface of the coating and dry it to permit the coated coil to be laid on a surface without injury or disruption. Alternatively, a forced air drying process may be used as a substitute for, or supplement to, the processes described. Pre-sintering may also be used, either by radio frequency heating or passing a current through the coated object in an inert atmosphere. Such heating would heat the object and preset the aluminum oxide.

The firing previously mentioned may be done in any one of several ways. However, a firing at about 1700° C. in an atmosphere of wet hydrogen has proven quite satisfactory to sinter the aluminum oxide to the underlying object.

The nature of the solvent medium in the preferred suspension is such that large quantities of water may be tolerated without deleteriously affecting the quality of the coating, and this, of course, permits storage and handling with relative freedom of concern for humidity problems.

The invention is applicable to a variety of problems in the coating art. The objects being coated and the coating material itself may be selected from a wide range of alternatives. So, too, may specific steps and quantities of components in the formulation be varied over reasonable limits without departure from the scope of the invention. The invention should, therefore, be limited only as required by the appended claims.

What is claimed is:

1. A cataphoretic coating formulation consisting essentially of a mixture of 12 to 180 ml. of distilled water, approximately 25 gms. of urea, 588 to 420 ml. of methanol, about 5.5 ml. of polyethylene glycol of a first molecular weight and soluble in said formulation, about 5.5 ml. of polyethylene glycol of a second molecular weight and soluble in said formulation, about 10 drops of 20% normal solution of aluminum acetate, approximately 10 drops of 13% aluminum nitrate solution, and about 400 gms. of aluminum oxide particles of 5 to 10 microns in size.

2. In a method of coating objects which includes immersing one of said objects in a bath consisting essentially of distilled water, aluminum oxide particles, urea, methanol, polyethylene glycol soluble in said bath, aluminum acetate, and aluminum nitrate, the steps which comprise placing an electrode in said bath, applying a voltage of 20 to 50 volts D.C. between said one of said objects and said electrode, removing said one of said objects from said bath, rinsing said one of said objects, drying said one of said objects, and sintering to said one of said objects the coating deposited thereon.

3. The method of preparing a catophoretic coating formulation which comprises washing particles of aluminum oxide powder having a particle size of 5 to 10 microns with an acid from the group which includes hydrofluoric, hydrochloric or sulfuric acids, washing said particles with deionized water, baking said particles, forming a solution of 12 to 180 ml. of distilled water with 588 to 420 ml. of anhydrous methanol, and approximately 25 grams of urea, adding 5.5 ml. of polyethylene glycol of a first molecular weight, and dissolving 5.5 ml. of polyethylene glycol of a second molecular weight in said solution, adding 10 drops of 20% normal solution of aluminum acetate and 10 drops of 13% solution of aluminum nitrate to said aqueous solution, adding 400 gms. of said aluminum oxide after baking to said aqueous solution and filtering said mixture through a 325 mesh wire screen.

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