Sept. 18, 1945. E. A. THURBER ET AL 2,385,313

METHOD OF PREPARING A COATING SUSPENSION

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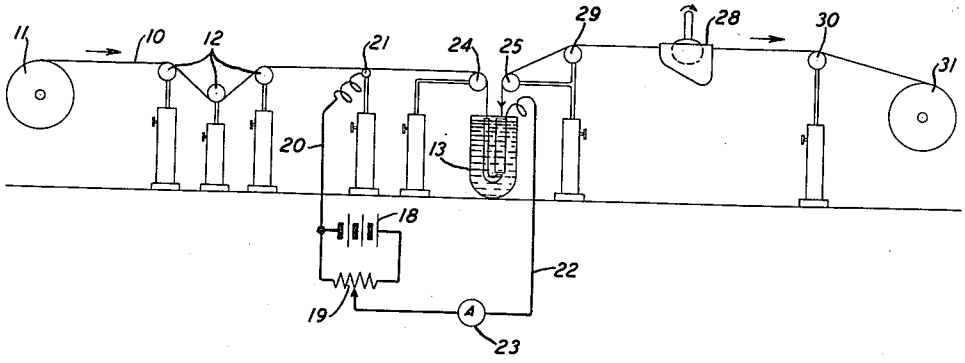
FIG. 1



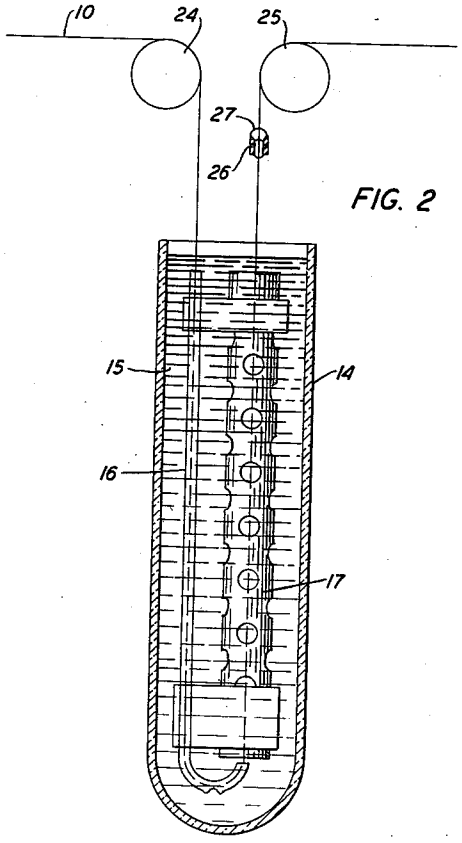


FIG. 2

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METHOD OF PREPARING A COATING SUSPENSION

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1 Claim. (Cl. 204—181)

This invention relates to coating suspensions and methods of preparation and more particularly to colloidal suspensions for coating electrodes of electron discharge devices.

In the manufacture of oxide coated emitters for electron discharge devices and more particularly 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 handbag 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 procedures, such as spraying or dipping are not practical from a commercial standpoint, and a more involved deposition process is required in which the coating is applied or deposited by electrophoresis. In this process colloidal particles of the carbonates are precipitated from a suspension and are deposited on the fine filament after which the coating is decomposed to the active state.

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 higher anode potentials, arc-overs, and sputtering and that control of the physical character of the surface permits closer grid-cathode spacings 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 increase the percentage of small particles in the emission layer applied to filamentary cathodes of electron discharge devices.

Another object is to maintain the purity of the suspension at the highest degree to increase the electrophoretic efficiency thus permitting the coating to be deposited at low voltages and to assure stability of the particles in the coating mixture.

A further object of the invention is to overcome interfacial tension in the coating process in order to effect adherence of the particles to the fine filamentary material.

Still another object of the invention is to increase the intensity of emission of the coated cathode made with suspensions produced in accordance with this invention.

Further objects are to maintain the electrophoretic properties of the suspension particles at a premium value to increase the rate of precipitation in the coating process, to reproduce the optimum result with successive mixtures, and to minimize shrinkage in the coating during the decomposition and activating processes of the emitting surface.

In accordance with a broad aspect of the invention, the suspension or coating mixture is produced by mechanically disintegrating insulating compounds, such as alkaline earth compounds, in a dispersing medium, such as a purified polyhydric alcohol vehicle having a viscosity equal to that of ethylene glycol under conditions which will result in producing suspensions having high electrophoretic activity and in which approximately 50 per cent of the particles will not be greater than 0.5 micron diameter.

As a specific example of the invention, mixed crystals of barium and strontium salts, such as hydroxides or carbonates, are suspended in a viscous liquid, such as a mixture of glycerine and alcohol or vacuum-distilled ethylene glycol alone, in the ratio of 1 part salts to 3 parts liquid and the mixture ground in a ball-mill with flint pebbles, the ratio of mixture to pebbles being 1 to 1 by volume and the agitation speed being approximately 150 revolutions per minute for a period of 100 to 200 hours. After this treatment the stock mixture or concentrate is diluted with anhydrous alcohol to a concentration of approximately 1.5 grams per 100 cubic centimeters although the concentrate may be varied through a range of 1 to 5 grams per 100 cubic centimeters. The dilute colloidal suspension forms an electrolyte which is placed in a cataphoretic cell having an anode through which the filament to be coated is to be passed and a low potential is applied to the filament while passing through the cell for a definite travel time and temperature to accurately control the thickness of coating applied to the filament, the

particles being precipitated from the suspension in the cell to the filament by cataphoresis under conditions which insure the highest deposition efficiency and uniformity of coating. This continuous coating or machine method whereby quantity production of coated filaments is achieved is possible in a great measure to the high ratio of colloidal size particles in the coating mixture and the stability, low conductance, cataphoretic properties of the particles in the suspension.

The method of preparing electrophoretically active suspensions by mechanically dispersing the alkaline earth crystals in the vehicle is to be distinguished from the chemical method in which the compounds are precipitated by a chemical reaction in essentially the medium or vehicle from which the particles are later to be deposited. The mechanical method is more generally applicable and more easily controlled and therefore more readily adapted to mass manufacturing processes.

The invention and its various features and advantages are more explicitly set forth in the following detailed description and will be more clearly understood when considered with the accompanying drawing which shows in Fig. 1 a continuous coating procedure involving the coating suspension of this invention and Fig. 2 is an enlarged detail view of the cataphoretic cell employed in the process of Fig. 1 and shown partly in cross section with the associated components for the progressive movement of the filamentary conductor through the cell.

In the electrophoretic coating processes heretofore practiced, particularly on small diameter filaments, chemical and mechanical colloidal suspensions of alkaline earth salts have been employed with varying success in small batches, but when attempts were made to increase production of filaments to a large magnitude, various physical difficulties ensued such as flocculation, rapid settling of carbonates in suspension and excessive shrinkage on drying. Also the weight-gain of the coating was difficult to control, the conductance was increased by contamination of the mixture with impurities, and discontinuities of deposition of coating occurred which resulted in bare spots or thin spots. Other difficulties encountered in the development of a continuous process were non-uniformity of coating surface, slow rate of deposition, and unreproducible results; in some cases no deposition was obtained probably owing to high interfacial tension between the filament and the suspending medium.

In accordance with this invention, these difficulties and disadvantages are materially reduced or completely eliminated and the colloidal suspensions or coating mixtures are highly stable, have high cataphoretic activity, increased intensity of emission and overcome interfacial tension frictional forces of small dimension filaments passing through the suspension fluid in the cell at fairly high deposition speeds suitable for machine coating technique.

Mechanical disintegration offers the most practical solution to the reduction of particle size in a colloidal suspension fluid but serious difficulties are usually encountered by the introduction of impurities which detract from the efficiency expected or the percentage of colloidal particles in the suspension are not materially increased due to slipping and cushioning effects during disintegration caused by the character of the dispersing fluid and the disintegrating media.

In order to obtain the required efficiency in mechanical disintegration, the dispersing fluid should have a definite viscosity to prevent slipping and cushioning effects. Furthermore, it should have the highest possible purity, particularly with respect to the silica and alkali content being not greater than 0.10 per cent and preferably as low as 0.025 per cent, since a higher impurity content reduces the cataphoretic properties of the suspension and causes objectionable difficulties in emission of the finished coating on the filament. It has been found that the dispersing fluid should have an optimum viscosity to obtain the best results. Examples are the polyhydric alcohols of which glycerine and ethylene glycol are representative members. When glycerine is used it is desirable to prepare a 50–50 per cent solution of glycerine and alcohol by weight to obtain the desired fluidity and when the glycol is employed it is preferable to distill under vacum to remove impurities.

In order to efficiently apply emissive coatings to filamentary cathode cores of small diameter, of the order of 0.0004 inch, the electrophoretic process is ideally suited to this problem in which highly dispersed particles suspended in a fluid acquire a surface charge which causes them to migrate to an oppositely charged electrode when subjected to an electric field. The usual electron emitting coating material, such as barium and strontium carbonates, are lyophobic and therefore difficult to prepare in stable colloidal form. However, mechanical disintegration or ball-milling may be employed with highly satisfactory results to reduce the crystalline particles to a suitable size for colloidal suspension.

This is accomplished in accordance with this invention, by preparing a mixture of 75 grams of mixed barium and strontium carbonate crystals with 225 grams of vacuum-distilled ethylene glycol in a 500 cubic centimeter bottle half filled with clean riddled flint pebbles. The mixture is ground by rotation in the usual bottle roller for a period from 100 to 200 hours at a speed of approximately 150 revolutions per minute. The vacuum distillation of the glycol may be carried out by mixing one-half pound of freshly crushed barium oxide, which serves as a dehydrating agent, with one gallon of glycol. This is agitated for one hour and allowed to settle until only slightly turbid. The mixture is poured into a fractionating still, preferably of Pyrex glass, and the heater and vacuum pump started to distill the glycol. The pressure should be about 1 centimeter or lower so that the boiling point does not exceed 60° C. The purity of the glycol under these conditions is very high as shown by specific conductivity of 4×10^{-7} mhos.

The glycol may be replaced by a solution of 50 per cent glycerine and 50 per cent alcohol to achieve similar results but it is not necessary to resort to vacuum distillation since this material is usually of high purity. Similarly, mixtures of glycol and glycerine may be used as the dispersing medium. However, for cataphoretic coatings of satisfactory adherence it is necessary to remove the glycerine after the ball-milling operation by centrifuging and to resuspend the sedimented carbonates in absolute alcohol. The mixed crystals of barium and strontium carbonates are preferred since they insure uniformity of composition over the entire particle size range as each crystal contains the barium and strontium in constant ratio. These crystals consist of a solid solution of barium and

strontium carbonates formed by coprecipitation. However, other forms of the alkaline earth compounds may be employed to obtain varying proportions of the carbonate.

The percentage of fine particles of barium and strontium carbonates in the concentrated suspension increased considerably under the mechanical disintegration methods according to this invention so that about 50 per cent of the solid aggregate consists of particles of a diameter of less than 0.5 micron, or well within the colloidal range, and 90 to 100 per cent are not greater than 2.0 microns in diameter, a micron being equal to 10^{-3} millimeter.

The following table shows the progressive diminution of the particle size of the aggregate with varying periods of disintegration with different vehicles and various types of pebbles:

Table No. 1

	Mechanical preparations	Weight percent less than—	
		0.5μ	2.0μ
A	6 hrs in glycol	<5	55
B	48 hrs in glycol	<10	75
C	100 hrs in glycol	30	85
D	200 hrs in glycol	35	85
E	100 hrs in glycol	45	100
F	200 hrs in glycerine and alcohol	30	90

The highest per cent of particles with diameters less than 0.5 micron in sample E was attained with odd size riddled flint pebbles whereas in the other examples uniform size oval pebbles were employed. Sample E also shows that no particles in the whole suspension were larger than 2.0 microns.

The relative effectiveness of ball-milling the mixed carbonates in various media for various milling periods is shown in Table 2 in which the weight per cents of the solid aggregate remaining in suspension after centrifuging under standard conditions are shown. The suspensions were centrifuged in an International clinical centrifuge at 500 revolutions per minute for 400 seconds with the cylindrical centrifuge tubes filled to a height of 3 cm. or 7 cm. as indicated by $R-S=3$ and $R-S=7$, respectively.

Table No. 2

Mechanical preparations	Time, hours	Percent in suspension	
		R−S=3	R−S=7
Alcohol	48	7.4	24.0
Glycerine—alcohol	48	27.0	45.5
	100	47.4	68.1
Glycol—glycerine	48	26.5	43.5
Glycerine	100	45.0	63.9
	100	10.5	27.0
Glycol	48	20.0	35.7
	100	44.0	62.8
	200	53.1	74.0
Glycol	100	66.0	

The suspension containing the highest percentage of fine particles, as indicated by 66 per cent of the solid aggregate remaining in suspension after the standard centrifuging procedure with $R-S=3$ cm. is the result of grinding in vacuum distilled ethylene glycol with small riddled flint pebbles.

An analysis of a typical suspension ball-milled for 200 hours in glycol, such as shown in Table No. 2, is represented in Table No. 3 in which 100 $(1-p)$ is the weight per cent of the aggregate remaining in suspension after centrifuging for 400 seconds at 1000 revolutions per minute with the centrifuge tubes filled with suspension to a height indicated by $R-S$.

Table No. 3

$R-S$ in cm.	1	2	3	5	7
$100\,(1-p)$	8.5	17.5	22.0	31.7	38.0
$100\frac{\partial p}{\partial s}$	10.1	6.9	5.0	3.85	2.55
$100\,(R-S)\frac{\partial p}{\partial s}$	10.1	13.8	15.0	19.2	17.9
W in weight, percent	18.5	31.0	37.0	51.0	56.0
D in mm. × 10^{-3}	0.31	0.45	0.56	0.75	0.94

W is the weight per cent of particles with diameters less than D, $\frac{\partial p}{\partial s}$ is the slope of the $1-p$ vs. $R-S$ curve and W is calculated by the following equation:

$$100\,(R-S)\frac{\partial p}{\partial s}+100\,(1-p)=W$$

$$D\text{ (in microns)}=1.82\sqrt{\log_{10}\frac{15.15}{15.15-(R-S)}}$$

This analysis of the experimental data to obtain the particle size distribution is subject to the assumption that the suspension is free from vibrations during centrifuging and that the error caused by the use of cylindrical instead of sector-shaped tubes is negligible.

The particular efficiency of the coating suspensions made in accordance with this invention is realized when machine or continuous coating is practiced for the mass production of filaments. Experience has shown that suspensions having a high proportion of large particles do not have a satisfactory life for use on a continuous coating machine. Such a suspension may be used for a short time until the available supply of particles below a critical maximum size, approximately 0.5 micron, is exhausted. The remaining particles are then too large or heavy to obtain satisfactory adherence at low voltages.

On the other hand the mechanical suspensions as above described contain such a large percentage of the critical size particles, especially for filaments of the order of 0.4 mil, that the adherence to the moving filament is greatly improved and a high speed of deposition is secured. Furthermore, the thickness of the coating is more easily controlled, depending on the time, temperature and voltage conditions during deposition, and it is possible to control the diameter of the coated filament to 0.001 inch ±.00005 inch with ease at a relatively high deposition rate.

A typical coating procedure by machine method is shown in Fig. 1, in which a small diameter filament 10, for example, of tungsten, of the order of 0.4 mil, is unwound from a supply reel 11 and passes between slack adjusting rollers 12 to an electrophoretic cell 13, shown more clearly in Fig. 2. This cell involves a deep glass beaker 14, filled with a mechanical dispersing suspension 15 which is made up of 1.5 grams of the ball-mill stock concentrate in 100 cubic centimeters of anhydrous ethanol or other suitable alcoholic fluid suspension. The filament enters the cell 13 through a glass sleeve 16 immersed in the suspension, the sleeve being curved at the lower end to insure concentricity of the filament which is made the cathode of the cell, with a tubular metallic anode 17 having a perforated wall to facilitate the flow of the suspension in the cell. It may be desirable to

substitute a mesh sleeve for the perforated metal tube to increase deposition.

The colloidal carbonate particles are precipitated from the suspension cataphoretically by the application of a voltage source 18 shunted by a potentiometer 19, the negative side of the source 18 being applied to the moving filament by a conductor 20 connected to a low resistance tungsten contact 21 engaging the filament and the sliding contact on the potentiometer being connected to the anode 17 by a conductor 22 having an ammeter 23 in circuit to register the current flowing in the cell. The filament is guided by rollers 24 and 25 adjacent to the cell to insure proper alignment of the filament passing through the cell. However, on the emergence of the coated filament from the cell, it is desirable to apply a binder coating thereto so that the deposited coating is not rubbed off. This is accomplished by the capillary binder applicator 26 through which the filament passes before reaching the roller 25. This applicator contains a few drops of a binder material 27, such as nitrocellulose in amyl acetate. The adherence is further enhanced by passing the filament through a container 28 positioned intermediate a pair of guide rollers 29 and 30 in which a sufficient binder layer of nitrocellulose in amyl acetate is applied to protect the coating when wound on the take-up reel 31 and during subsequent handling. The schematic arrangement of the machine elements, as shown, simplifies the description and except for the substitution of the cell 13, the coating machine is a modification of the type disclosed in United States Patent 1,986,533, issued January 1, 1935, to V. L. Ronci et al.

The cataphoretic deposition process facilitates the precipitation of the particles of carbonates from the colloidal suspension due to the surface charge of the particles and the applied electromotive force between the anode 17 and the cathode or filament 10 in the cell 13 so that the particles adhere to the surface of the filament. The thickness of the coating applied is easily controlled by regulating the voltage and time since the rate of deposition is directly proportional to the current in the usual range of coating thickness for small diameter filaments, namely, 10 to 15 microns. The average thickness 12 microns is approximately equivalent to 4 milligrams per square centimeter. As a typical example, a fine tungsten filament of 0.00041 inch diameter may be coated with barium and strontium carbonate particles to a uniform thickness of 0.001 inch by applying a low potential of 10 volts between the filament and the anode in the cell for 10 seconds with the filament traveling at the rate of 3.5 centimeters per second. The deposition voltage may vary from 7.5 volts to 15 volts and the rate and duration of coating will be proportional to the voltage, depending on the different diameters of filaments passing through the cell.

The increased rate of coating will be realized from a comparison with prior chemical suspensions in which the maximum coating rate for 0.4 mil filament was 0.5 centimeter per second so that the present suspension increases the coating rate eight-fold. Furthermore, a greater amount of filament may be coated in a given quantity of suspension in the cell due to the high percentage of colloidal particles contained in the suspension. The resulting coating is of greater purity and compactness so that a smooth uniform layer of controllable thickness may be obtained on the filament.

While the invention has been directed specifically to the coating of fine tungsten filaments with a colloidal suspension of barium and strontium carbonates of high colloidal particle content employing high purity viscous carrier materials as the disintegrating and dispersing medium, it is, of course, understood that other electron emissive compounds or materials may be employed in producing the electrophoretic suspensions in accordance with this invention. Furthermore, other normally insulating colloidal suspensions may be produced in accordance with the mechanical disintegration process of this invention for the cataphoretic machine coating of cathode heater wire with alumina or similar insulating materials or the deposition of various films on grid wires, to counteract primary or secondary emission, and coatings on anode parts, such as zirconium, to dissipate heat in the operation of discharge devices. Therefore, the invention is to be construed in accordance with the manner of treatment and mode of procedure in preparing the colloidal suspensions to attain the desired characteristics for the deposition of colloid particles of the coating substances on fine wires by electrophoresis.

What is claimed is:

The method of preparing aggregate suspensions having a high percentage of colloidal particles from carbonates of relatively large size particles for deposition by electrophoresis on filamentary wire of small diameter, which comprises grinding crystalline barium and strontium carbonates for an extended period from 100 to 200 hours in a dispersing medium of vacuum distilled ethylene glycol with riddled flint pebbles in a ball-mill whereby the particles are reduced in diameter to 2.0 microns or less and from 35 to 50 per cent of the aggregate has a particle size of 0.5 micron in diameter, or less.

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