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B. B. BERGER ET AL
ELECTROSTATIC ENCAPSULATION

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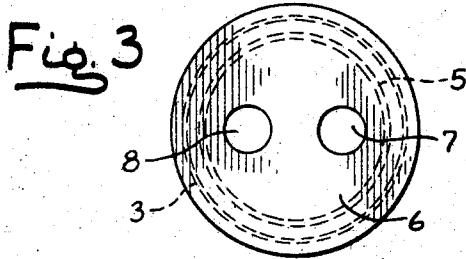


Fig. 1

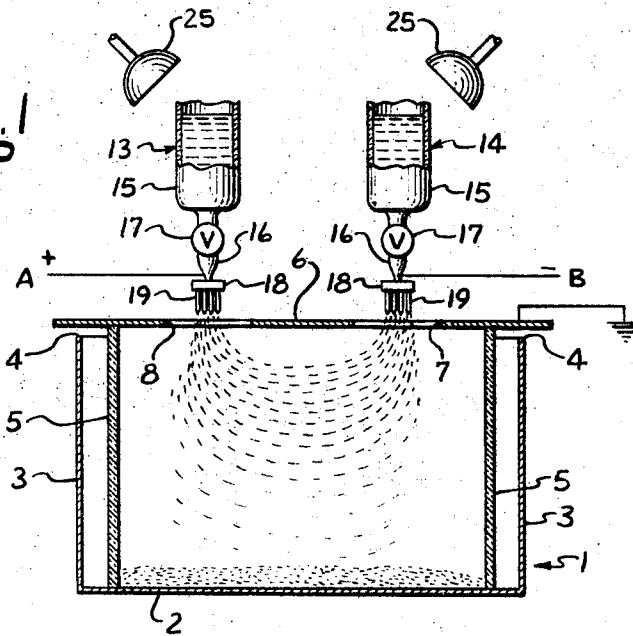


Fig. 2

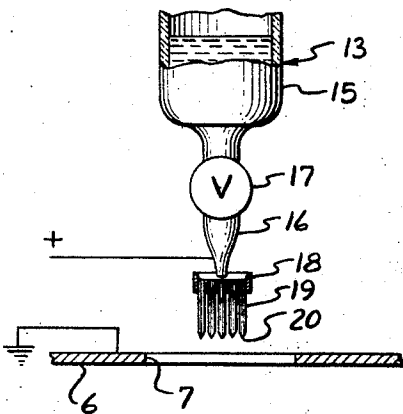
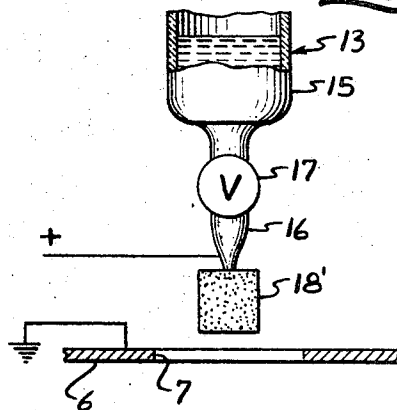


Fig. 4



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ELECTROSTATIC ENCAPSULATION

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This invention relates to electrostatic encapsulation and to the products obtained thereby. More particularly, the invention concerns novel methods for the electrostatic encapsulation of a liquid or solid core particle in the form of an aerosol or fine mist and bearing an electric charge, by envelopment of the core particle with a coating of an encapsulating substance maintained in the form of an aerosol or fine mist and bearing an opposite electric charge.

The electrostatic coating of articles or surfaces made of metal or of nonconducting materials such as plastics, glass, and wood by depositing thereon a coating material, such as paint or lacquer, in finely divided form under the influence of an electrostatic field is a well known process which has been extensively adopted for industrial use. In most of these systems a liquid coating material is discharged into a chamber as a mist using an atomizing device. The mist is given an electric charge either at the time it leaves the atomizing device or shortly thereafter, and is then deposited by electrostatic attraction upon the article or surface to be treated. To create the mist of coating material there may be employed, for example, either a pneumatic or liquid atomizer in which the liquid is forced through a nozzle under compression, or a rotating disc type of atomizer from the annular edge of which the liquid is spread into a thin expanding film and thence into a spray of finely divided liquid particles. The mist of coating liquid may be electrically charged by projecting it into an electrostatic field containing an ion discharge or a corona type discharge, the article or surface to be coated bearing an opposite electrical charge. Alternatively, an electrostatic field is maintained between the atomizing device and the article to be coated by applying a high voltage of the order of several thousand volts to the portion of the atomizing device where the mist is formed, by connecting one terminal of a high voltage source thereto and grounding the other terminal. In the electrostatic field thus created, the finely divided material particles in suspension become charged and move toward and impinge and coalesce upon the oppositely charged surface to be coated, by reason of their opposite polarity. Where nonconducting materials or surfaces are being coated it may be necessary to provide an auxiliary electrode to establish lines of force along which the movement of the charged coating mist particles can be guided. These known methods have been adapted to the coating of flat surfaces and webs with wax and with thermosetting polymers. A method is also known whereby solid pellets of medicinal or nutrient substances ranging in size from 5 to 125 thousandths of an inch or larger are projected into a chamber in which they encounter a spray of a coating material such as a natural resin or gum, the pellets and the spray being charged with opposite electric charges as they enter the chamber, causing the spray to be drawn to the pellets. The respective charges are imparted as the pellets and the coating particles pass through an ionized area in a nitrogen atmosphere under action of a high voltage in the neighborhood of 100,000 volts.

The known electrostatic coating processes have proved to be of limited effectiveness, however, for the enveloping or encapsulating of finely divided liquids or solids which are of colloidal dimensions, that is, where the particle

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sizes are measured in microns, of the order of 100 microns or less, and where the thickness of the coatings is also measured in micron dimensions. There has existed a need for a direct and efficient method whereby liquid or solid particles in the size range of about 1 to 50 microns could be coated with thin, tough, films or encapsulations of waxes, synthetic resins, and analogous materials, so that the final product would still remain at or near the aforementioned size range, but having the form of discrete, minute, free-flowing granules.

In accordance with the present invention there is provided a method whereby particles of liquid or solid in the size range of about 1 to 50 microns can be encapsulated with thin films of solid polymers, waxes, or the like. The resulting products are useful, for example, in photocopying and other processes, where the reactivity of water-sensitive substances can be controlled by encapsulation with suitable polymers.

The invention involves the principle of electrostatic interaction of aerosols or fine mists of bipolar or oppositely charged particles of core and coating materials, to achieve a state of substantial electrical neutrality, the particle sizes of the respective materials in said aerosols or mists being of colloidal dimensions, ranging predominantly between about 1 and about 50 microns. At these particle size ranges, it has been found according to the invention, that core particles, and especially liquid core particles, in finely dispersed aerosols, become encapsulated by electrostatic interaction, to form products which are capable of handling as free-flowing powders.

In accordance with one aspect of the invention, a method is provided whereby a core material and a coating material are separately atomized to a particle size ranging from about 1 to about 50 microns and the respective particles in the form of an aerosol are electrostatically charged so as to be of opposite polarity. For the successful performance of the method, neutralization side-effects arising from the formation of ions or other oppositely charged small particles at the time of aerosol production must be kept at a minimum. This involves application of the principle that upon contact, particles in the form of bipolar aerosols are governed in their attractive or repulsive behavior by two kinds of forces. The general attraction between oppositely charged particles, the so-called Coulomb force varies inversely as the second power of the separating distance. The polarities determine whether the forces are those of attraction or repulsion. At smaller separating distances the so-called "image effect" prevails and varies as the fifth power of the distance, which is attractive, without regard to charge. Calculations of the coagulation process taking place in a bipolar aerosol mixture indicate that, in general, the rate of coagulation is proportional to the product of the average positive and negative charges where the particles are of about equal size. If particles of small size are coagulating with an aerosol of opposite polarity but of larger size, the coagulation will decrease, because enhanced Brownian movement of the small particles will counteract the directional effect of the Coulomb attraction forces. Accordingly, the method of this invention preferably employs bipolar aerosols in which the respective particle sizes are essentially the same. This size has been found advantageously to be between about 1 and 50 microns.

In accordance with another aspect of the invention, a method is provided whereby finely divided liquid particles in the size range of 1 to 50 microns are enveloped or encapsulated by a solid or a liquid layer of coating having a thickness of a few microns, preferably less than about 10 microns. The relative size of core particles and the coating particles should be chosen to produce a coating of the optimum thickness compatible with the end use to

which the product will be put. It is desirable that the negative charge on the coating particles be substantially equal to the positive charge on the core particles and vice versa.

The basic requirement for the core liquid is that it must possess a high surface tension so that the coating material will spread readily over its surface. Examples of suitable core liquids of this type include water, glycerine, and ethylene glycol, which have respective surface tensions of 72, 63 and 49 dynes per centimeter. Viscosity is not a critical factor; thus a viscosity of 10,000 millipoises (glycerine at 20° C.) may be regarded as a general upper limit for efficient atomization.

For good electrostatic atomization, the conductivity of the liquid should be within the range of about 2×10^{-3} to 5.8×10^{-6} ohm-centimeters. Other materials or fine particles can be suspended in the core liquid provided the surface tension is not widely altered.

Coating materials which may be dispersed into aerosols and electrostatically charged for interaction with an aerosol of an oppositely charged core liquid to form an enveloping shell thereon include substances which may be either waxes or resins. Thus, there may be employed for this purpose, for example, phthalate polyesters, solid or liquid paraffin, microcrystalline wax, and the like, or synthetic resins, such as linear polyamides, polyvinyl esters, ethers and formals, polystyrene, polyesters, acrylics, epoxies, and other classes of polymers. The core aerosols may be encapsulated by condensation of a liquid monomeric material on the core particles and initiating a rapid polymerization reaction. Component concentration, temperature, reaction time, bulk properties, and the like, can be varied within wide limits in the production of such encapsulated aerosols, in accordance with the invention, to provide a range of volatilities, stabilities, and water or water vapor permeabilities, as desired.

The temperature of encapsulation is not a critical factor as long as the core and/or coating materials are reasonably fluid.

In general, it has been found that the coating material must possess a low surface tension and good wetting properties, permitting it to spread over the surface of the core particles. The preferred surface tension range is from about 20 to about 30 dynes per centimeter. Furthermore, the conductivity of the coating material should, in general, correspond to that of the core material.

In accordance with another aspect of the invention, it was found that conductivity may be favorably influenced and atomization greatly improved by incorporating in the coating material additives such as an aliphatic diamine, or a hexamethylene diamine. Thus, for example, when hexamethylene diamine was added in small amounts to molten wax, aerosol production increased by one or two magnitudes and smaller particles were generated.

In accordance with still another aspect of the invention, a solid coating of a synthetic resin is formed by electrostatic encapsulation upon liquid core particles by condensation polymerization. This method necessitates the selection of two resin-forming reagents which will react rapidly to form a solid polymeric condensation product. One reagent is dissolved in the core material, and the other in a suitable solvent, both reagents being identifiably stable. Polyamide type resins are particularly suited to this method, and such coatings may be formed, for example, by reaction at the interface of the core and coating aerosols where glycerine containing hexamethylene diamine is the core material, and toluene containing dissolved adipyl chloride is the coating material. The interfacial polymerization reaction results in the formation of hexamethylene diamine adipate, more commonly known as nylon.

Another factor of importance in improving the interaction of oppositely charged aerosols for encapsulation purposes is the control of the rate of collision of the suspended oppositely charged aerosol particles in an elec-

trostatic field. In addition to the force due to the electrostatic field, which tends to move the charged particles toward opposite poles, there is an electrostatic attractive force (Coulomb force) between the charged droplets. Opposing the Coulomb force is the aerodynamic drag force which at the particle size range here in question is a simple function of droplet size and speed. Calculations have indicated that in the case of droplets having a radius of 10 microns, the terminal horizontal velocity at which the electrostatic field force and the aerodynamic drag forces are balanced, is approximately 56.2 cm. per second. At this equilibrium point, the influence of the Coulomb forces will depend upon the relative closeness of the respective sets of droplets. Thus the probability of collision and effectiveness of encapsulation can be influenced by control of the speed with which the oppositely charged particles are impelled toward each other and mixed.

It has been found, in accordance with the invention, that the control of the speed of the particles in the electrostatic field so as to utilize the Coulomb forces, may be effectively achieved by control of field strength and distribution and of the direction of the lines of force. Thus, where oppositely charged aerosols are projected into a chamber using electrostatic atomizers, and at a high velocity, the build-up of a strong field is prevented by employing an intervening metal plate in two portions, each insulated and assuming a potential of the same sign as the atomizing device. This permits the particles to intermingle freely subject essentially only to forces of gravity and convection, promoting gentle mixing and a narrower size range. At the same time, the concentration of the droplets is maintained as high as possible, 10^4 - 10^5 particles per cc., to accelerate their interaction. The space charge created in this manner tends to reduce internal field effects in the cloud. The substantial absence of a field reduces relative particle motion, which, as mentioned previously, should be at a minimum for good interaction.

The charging of the core and coating particles is accomplished by electrostatic atomization. The preferred voltages range from about 5 to about 50 kv., and are preferably direct current. One terminal of a source of high voltage is connected to the atomizing device at the point at or near which the atomization takes place, while the other terminal is connected to a plate of metal, such as aluminum, serving as a ground, as described more fully below, and which is insulated from the mixing chamber.

Any suitable type of atomization feeding system may be employed, but it has been found that for the purpose of the invention, one employing a demand type feed system is preferable. Thus there may be used a type of device which utilizes capillary action to feed discharge material to layers of cloth or paper, such as filter paper, velvet, rayon or cotton, surrounding a discharge nozzle. These cloth layers should be arranged to terminate in fine tips. For large scale operation, there may be employed as atomizing devices any of the conventional means used for this purpose, including pneumatic or hydraulic needle sprays, rotating disc atomizers, and the like. By using the cloth or plastic electrodes we avoid the danger of generating gaseous ions which neutralize the charges on the aerosols and thereby prevent encapsulation.

We have also found that the atomizing device will act very efficiently if formed of a block of porous refractory material. Such a device will cause a discharge of the aerosols through the porous body of the material in substantially all directions.

The detailed method of accomplishing the foregoing will be better understood by reference to the following description of a presently preferred form of apparatus as depicted in the accompanying drawing, in which

FIG. 1 represents a schematic view, partly in cross-section, of a form of apparatus suitable for carrying out the electrostatic encapsulation of a liquid;

FIG. 2 is an enlarged view of the atomizing device shown in FIG. 1 showing in more detail the support for carrying the cloth or paper discharge surface for the material being atomized;

FIG. 3 is a top plan view of the plate member with the openings therein through which the atomized material is discharged; and

FIG. 4 is a view similar to FIG. 2 showing a modified form of discharge surface for the material being atomized.

Referring to FIG. 1, the electrostatic encapsulation apparatus comprises a chamber 1 which may be of any desired shape, having a bottom portion 2, and side walls 3 which terminate at upper edges 4. Supported on pillars 5 of a nonconducting material, such as glass or plastic is a thin metal plate 6 having openings 7 and 8 therein, which plate acts as a ground for the applied high voltage current.

Positioned above the openings 7 and 8 in the plate 6 are a pair of atomizing devices designated generally as 13 and 14, which comprise means for containing and supplying core and coating materials respectively including a vessel 15 having its lower portion terminating in a nozzle 16, through which the flow of material is controlled by a valve or stopcock 17. As shown in more detail in FIG. 2, the exit portion of the nozzle 16 is fitted with member 18 of nonconducting material which serves as a support for several downwardly extending pieces 19 of cloth or paper which terminate in sharp edges 20, which provide a discharge surface for the material being atomized.

In FIG. 4 there is shown another type of atomizing device. Mounted on the discharge end of the nozzle 16 is a block 18' of any desired shape formed of porous refractory material whereby the discharge of the material from the nozzle 16 will be atomized as it passes through the block 18'. By reason of this type of atomizing device the material being atomized will be caused to flow through substantially the entire surface area of the block.

It will be understood that additional pairs of atomizing devices may be similarly provided in the apparatus, and that other types of atomizing devices such as rotary disc atomizers may be employed instead of the types shown in the drawings.

Sources of high voltage designated generally as A and B supply positive and negative high voltages to the atomizers 13 and 14, respectively, via conductors which are attached to the nozzles 16. Where the liquids or other materials such as, for example, wax, require heating in order to maintain fluidity for atomization, heat may be supplied by means of a set of infrared lamps 25, or by other suitable means, such as a heating coil wrapped around the atomizer vessel 15.

In the operation of the apparatus, the core material and the coating material are caused to flow by gravity, or under pressure (by means not shown), from vessels 15 through valves 17 outward through the openings of the nozzles 16, the liquid passing through and wetting the cloth or paper discharge layers 19. Simultaneously a negative and positive high voltage is applied to the respective nozzles and the metal plate 6, whereby the particles of core and coating material issue from the tips 20 of the cloth or paper discharge layers or block 18' of porous refractory material, in the form of oppositely charged aerosols or fine mists. These aerosols pass downward into chamber 1 through openings 7 and 8, under the action of gravity. In the chamber, a gentle mixing of the oppositely charged aerosols occurs, while convection is promoted by electrostatic field lines of force extending downward into the chamber through openings 7 and 8 underneath central plate 6. In this manner a high percentage of single encapsulated drops or particles are produced, said encapsulated particles collecting at the bottom of the chamber as a dry, free flowing, fine powder.

The following examples serve to illustrate the novel method of the invention, but are not to be regarded as limiting.

EXAMPLE 1

Encapsulation of liquid by liquid

Employing the apparatus previously described, aerosols were formed of core material, glycerine (positively charged) and dibutyl phthalate (negatively charged), the particle size of the glycerine aerosols ranging from about 3 to 10 microns, while that of the dibutyl phthalate was slightly coarser, about 5 to 20 microns, indicating that the positive polarity produced the finest spray. A voltage of 10 kv. was applied to each atomizer. The dibutyl phthalate coated the glycerine, with only a small proportion of unreacted particles being present. Under microscopic examination it was found that dibutyl phthalate had formed a thin skin or film around the glycerine, the size of the inner drops being around 10 microns, and that of the film being 1 to 2 microns.

EXAMPLE 2

Encapsulation of liquid by solid shell

Employing the apparatus disclosed herein, aerosols were formed of glycerine as core material, as in Example 1, and of paraffin wax as the coating material, the wax being kept molten by heating means, such as the infrared heater shown in FIG. 1. It was found that greatly improved encapsulation was obtained by the addition of 5% of hexamethylene diamine to the wax in order to improve conductivity. Applied voltages of 10,000 volts were used, the glycerine being negative and the wax positive. The aerosols coagulated readily to form tiny spheres of glycerine encapsulated by the wax. When pressure was applied, as by placing spheres between two cover slips and viewing under a microscope, the spheres cracked open, allowing the glycerine to escape. Considerable force was required to crack open the wax spheres. The product is a free flowing white powder.

EXAMPLE 3

Encapsulation of liquid by condensation polymerization

Employing the apparatus of FIG. 1, aerosols of glycerine containing from 1 to 5 percent by weight of hexamethylene diamine were converted to negatively charged aerosol droplets having an average radius of 10 microns. A solution of from 5 to 10 percent of adipyl chloride by weight in toluene was simultaneously converted to a positively charged aerosol, employing in both instances an applied voltage of 10 kv. The mixing of the aerosol results in the reaction of the hexamethylene diamine and adipyl chloride to form nylon, which coats the glycerine droplets with a shell about 0.4 micron thick. If properly hardened the product is a free-flowing white powder.

It will be understood that while the invention has been described in part by means of specific examples, reference should be had to the appended claims for a definition of the scope of the invention.

What is claimed is:

1. Method for the electrostatic encapsulation of a liquid core material by a liquid coating material which comprises electrostatically atomizing said core material and said coating material from respective sources thereof, said core liquid having a higher surface tension than said coating liquid, to form a negatively charged aerosol of said core liquid and a positively charged aerosol of said coating liquid, the particle size of said aerosols being predominantly between about 1 and about 50 microns, supplying said aerosols to a mixing zone and allowing said aerosols to interact in said zone to achieve a state of substantial electrical neutrality, with formation of core particles encapsulated by a coating layer having a thickness of about 10 microns or less.

2. The method of claim 1 in which the conductivity of the coating liquid is improved by the addition thereto of a small amount of an aliphatic diamine.

3. The method of claim 2 in which the diamine is hexamethylene diamine.

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4. The method of claim 1 in which the core liquid is glycerine and the coating liquid is molten paraffin wax.

5. Method for the electrostatic encapsulation of a liquid core material by a solid synthetic resin which comprises electrostatically atomizing a solution of a first resin-forming component in said core material to form a negatively charged aerosol of said core liquid, and a solution of a second resin-forming component in an organic solvent therefor to form a positively charged aerosol, the particle size of said aerosols being predominantly between about 1 and about 50 microns, supplying said aerosols to a mixing zone and allowing said aerosols to interact to achieve a state of substantial electrical neutrality and to permit formation of said synthetic resin by condensation and polymerization of said components about the surface of said core liquid particles.

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6. The method of claim 5 in which the resin components are adipyl chloride and hexamethylene diamine.

7. The method of claim 5 in which the atomized core liquid is a solution of hexamethylene diamine in glycerine and the atomized second resin-forming component is a solution of adipyl chloride in toluene.

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