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METHOD OF COATING CARRIER BEADS

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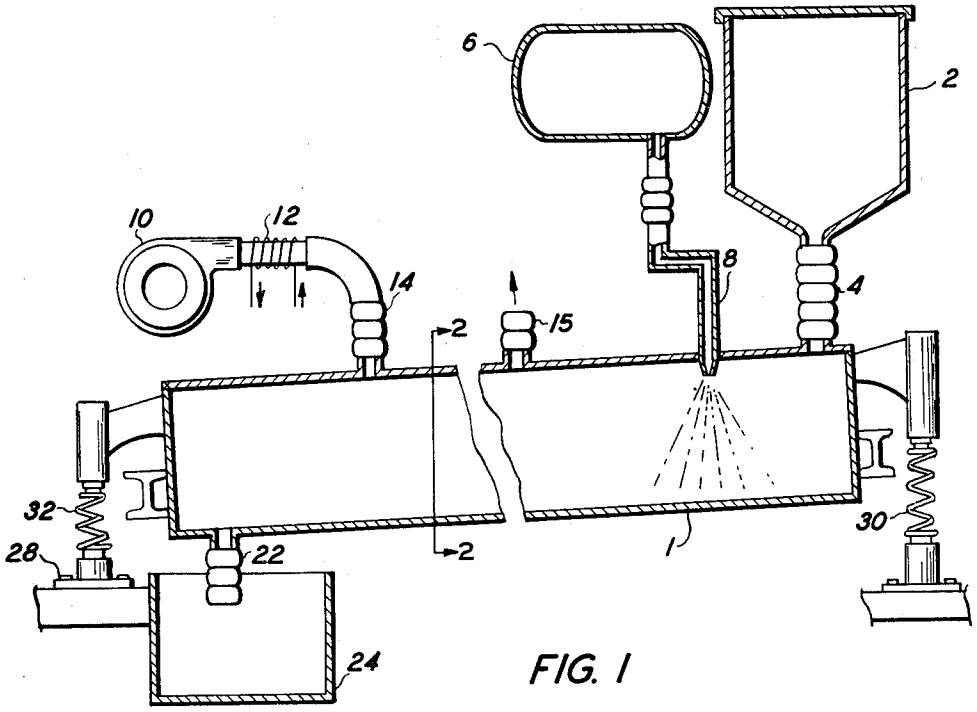


FIG. 1

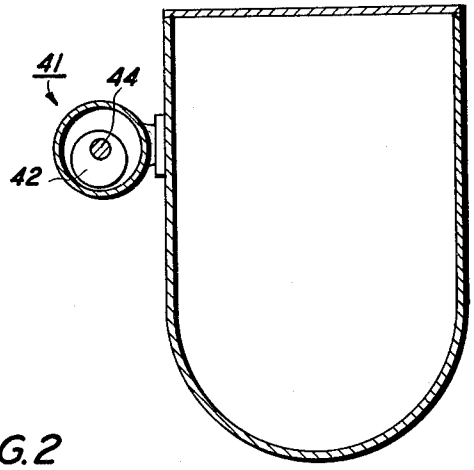


FIG. 2

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METHOD OF COATING CARRIER BEADS

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U.S. Cl. 117—100 9 Claims

ABSTRACT OF THE DISCLOSURE

A method of coating carrier beads comprising contacting the beads with a resin solution and imparting oscillatory energy to the beads and resin solution while evaporating the resin solution solvent.

BACKGROUND OF THE INVENTION

This invention relates in general to imaging materials and, more particularly, to an electrostatographic developing material and a method and apparatus for its production.

Electrostatography is best exemplified by the process of xerography as first described in U.S. Patent 2,297,691 to C. F. Carlson. In this process, the photoconductor is first provided with a uniform electrostatic charge over its surface and is then exposed to imagewise activating electromagnetic radiation which selectively dissipates the charge in illuminated areas of the photoconductor while the charge in the non-illuminated areas is retained thereby forming a latent electrostatic image. This latent electrostatic image is then developed or made visible by the deposition of finely-divided electroscopic marking particles referred to in the art as "toner." The toner will normally be attracted to those areas of the layer which retain a charge, thereby forming a toner image corresponding to the latent electrostatic image. This powder image may then be transferred to a support surface such as paper. The transferred image may subsequently be permanently affixed to the support by heat fusing. Instead of forming a latent image by uniformly charging the photoconductive layer and then exposing the layer to a light and shadow image, a latent image may be formed by charging an insulting or photoconductive insulating member in image configuration. The powder image may be fixed to the imaging member if elimination of the powder image transfer step is desired. Other suitable means, such as solvent or overcoating treatment, may be substituted for the foregoing heat fixing steps.

Several methods are known for applying the electroscopic particles to the latent electrostatic image to be developed. One well-known development method is the "magnetic brush" process disclosed, for example, in U.S. Patent 2,874,063. In this method, a developer material containing toner and magnetic carrier beads is carried by magnets. The magnetic field of the magnet causes alignment of the magnetic carrier particles in a brush-like configuration. This "magnetic brush" is engaged with an electrostatic image bearing surface and the toner particles are drawn from the brush to the electrostatic image by an electrostatic attraction.

Another technique for developing electrostatic latent images is the "cascade" process disclosed by L. E. Walkup in U.S. Patent 2,618,551 and E. N. Wise in U.S. Patent 2,618,552. In this method, a developer material comprising relatively large carrier beads having fine toner particles electrostatically coated thereon is conveyed to and rolled or cascaded across the electrostatic image bearing surface. The composition of the carrier particles is so chosen as to triboelectrically charge the toner particles to the desired polarity. As the mixture cascades or rolls across the image bearing surface, the toner particles are electrostatically deposited and secured to the charged portion of a latent image and are not deposited on the unchanged or background portion of the image. Most of the toner particles accidentally deposited in the background areas are removed by the rolling carrier, due apparently, to the greater electrostatic attraction between the toner and carrier than between the toner and the discharged background. The carrier and excess toner are then recycled. This technique is extremely good for the development of line copy images.

Coated or uncoated carrier beads may be employed in the cascade process. When coated beads are employed, the coating should be characterized by smooth outer surfaces, high tensile strength, stable triboelectric characteristics, strong adhesion to substrates, and good solubility in conventional solvents. Uncoated carrier beads must also possess high tensile strength and stable triboelectric characteristics.

In most commercial processes, the cascade technique is carried out in automatic machines. In these machines, small buckets on an endless belt conveyor scoop the developer mixture comprising relatively large carrier beads and smaller toner particles and convey it to a point above an electrostatic image bearing surface where the developer mixture is allowed to fall and roll by gravity across the image bearing surface. The carrier beads along with any unused toner particles are then returned to the sump for recycling through the developing system. Small quantities of toner material are periodically adding to the developer mixture to compensate for the toner depleted during the development process. This process is repeated for each copy produced in the machine and is ordinarily repeated many thousands of times during the usable life of the developer mixture. It is apparent that in this process, as well as in other development techniques, the developer mixture is subjected to a great deal of mechanical attrition which tends to degrade both the toner and the carrier particles. This degradation, of course, occurs primarily as a result of shear and impact forces due to the tumbling of the developer mixture on the image bearing plate and the movement of the bucket conveyor through the developer material in the sump. Deterioration or degradation of coated carrier beads is characterized by the separation of portions of or the entire carrier coating from the carrier car. The separation may be in the form of chips, flakes, or entire layers and is primarily caused by poorly adhering coating materials which fail upon impact and abrasive contact with machine parts and other carrier particles. Carriers having coatings which tend to chip and otherwise separate from the carrier core must be frequently replaced, thereby increasing expense and consuming time. Print deletion and poor print quality occur when carrier particles having damaged coatings are not replaced. Fines and grit formed from carrier coating disintegration tend to drift and form unwanted deposits on critical machine parts. Many materials having high compressive and tensile strength often do not possess the desired triboelectric characteristics.

High quality uniform coatings on carrier beads have not been readily achieved with the coating processes known in the prior art. For example, production batches of coated carrier cores formed by dipping or spraying a carrier core with a solution or hot melt contain an undesirably high quantity of carrier bead agglomerates, particularly when thick coatings are applied, and individual beads which are not uniformly or completely coated. Generally, the agglomerates formed cannot be economically reclaimed. Further, it is difficult, if not impossible, to remove from a batch any carrier cores

having non-uniform or incomplete coatings. Carrier cores may also be coated by tumbling carrier cores with carrier coating material in rotating barrels. The results obtained with this technique are limited. Control of the coating thickness is extremely difficult. In addition, excessive bead agglomeration, considerable sticking of the wetted beads to the barrel walls and substantial barrel wall cleaning difficulties occur. Also, the barrel coating system is primarily a batch rather than a continuous system.

Another system which has been employed to coat carrier cores is the fluidized bed system. Generally, the fluidized bed system consists of a vertically moving column of air which suspends the carrier cores during the coating process. The coating material is applied to the suspended particles in the form of an atomized spray introduced at the bottom of the vertically moving air column. Although uniform coatings may be achieved with this process, an undesirably long retention time is necessary. Further, the fluidized bed coating process is a batch rather than a continuous process and, therefore, is characterized by limited throughput.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a system for coating carrier beads which overcomes the above noted disadvantages.

It is another object of this invention to provide a system for coating carrier cores which is relatively simple to operate.

It is another object of this invention to provide a system for coating carrier cores which is relatively easy to clean.

It is another object of this invention to provide a system for coating carrier cores which provides relatively uniform coatings.

It is another object of this invention to provide a system for coating carrier cores which provides coatings which adhere comparatively tenaciously to the carrier cores.

It is another object of this invention to provide a system for coating carrier cores which produces relatively few agglomerates.

It is another object of this invention to provide a system for coating carrier cores which is relatively free of beads sticking to the walls of the apparatus.

It is another object of this invention to provide a system for coating carrier cores which is capable of applying a relatively heavy uniform coating.

The foregoing objects and others are accomplished by a system wherein carrier beads are placed in a container and preheated. A solution of resin in a solvent is then poured into the container containing the carrier material. The container is then vibrated as the volatile solvent evaporates off. Preferably, heat application is continued until all of the solvent is removed and the coated carrier material is completely dried and free flowing.

Alternatively, a prepolymer such as an uncured thermosetting compound in a solvent or a mixture of monomers may be used. The drying air will then serve the duel purpose of evaporating off the solvent and curing or polymerizing the coating.

Although suspensions, emulsions, mixtures and solutions of resin and volatile component may be used, it is preferred to use a solution for uniformly coating the carrier material.

In a preferred embodiment the coating is accomplished by individually vibrating the carrier particles as a mass with the solution in a generally cyclical or orbital path. The movement of both the individual beads and the stream mass in this preferred embodiment is effected by a device which imparts regular oscillatory motion to the bead treatment container. Uniform distribution of the coating throughout the mass of beads to be treated is promoted by moving the bead mass and solution as a stream in a cyclical path and simultaneously vibrating each individual bead. The vibratory movement of each bead is not necessarily parallel to the stream path. The combined vibratory movement of each bead effectuates both fluidized suspension and cyclical movement of the total mass of beads. The individual beads appear to vibrate in tiny orbits rather than in a linear path and may be the principal reason for the improved mixing and cyclical bead stream movement achieved in this system. Due to both the constant vibratory motion of the individual beads and the general cyclical movement of the bead mass and solution, a great number of different beads are brought into contact with each incremental surface area of other beads during a given unit of time. The circulating bead mass is contained within a rapidly oscillating chamber or housing having a concave bottom surface. Although the actual cross section of the chamber of the preferred embodiment comprises a roughly arcuate configuration, it should be understood that the outer shell of the treatment chamber may be of any suitable shape which allows the conditions necessary for coating as set forth in the specification to occur. Typical shapes include "bowl" or U-shaped treatment chambers or variations thereof. The treatment chamber may be modified by changing the slope of the sides and/or tilting the chamber axis. Further, baffles may be employed in the chamber to promote uniform flow of the beads and solution from one end of the chamber to the other in a continuous treatment process. The particular modification, of course, may depend upon the direction of the circulating bead stream. The direction of orbital flow of the circulating bead material stream depends upon the direction of oscillatory energy imparted to the treatment chamber. The oscillatory energy imparted to the chamber has an axis of oscillation parallel to the axis of bead stream motion. The direction of bead stream flow may be reversed by reversing the direction of oscillatory energy applied. Oscillatory motion may be imparted to the treatment chamber by any suitable means capable of producing high frequency oscillatory energy. Typical well-known sources of high frequency oscillatory energy include electric motors having fixed or adjustable eccentric weights attached to the motor armature shaft and ball type vibrators such as the Vibrolator vibrators sold by the Martin Engineering Company. The total mass of bead and solution in the treatment housing, the bead material stream velocity desired, the shape of the treatment housing, and the total mass of equipment actually being vibrated all effect the degree of oscillatory amplitude and frequency necessary to achieve the desired stream movement. Typical oscillatory frequencies include a range from about 1,000 to about 2,150 regular oscillatory vibrations per minute. Typical vibration amplitudes include from about $\frac{1}{64}$ to about $\frac{1}{4}$ inch. It is apparent, however, that the energy loss during transmission of the vibratory energy from the energy source to the treatment housing should be considered when determining the particular amplitude to be employed. Generally, the circulating velocity of the bead stream increases with an increase in oscillatory energy frequency. Similarly, the velocity of the bead particles circumferentially positioned in the treatment housing increases with an increase in bead mass.

Any suitable well-known coated or uncoated electrostatographic carrier material may be employed as the core of the beads of this invention. Typical carrier core materials include sodium chloride, ammonium chloride, aluminum potassium chloride, Rochelle salt, sodium nitrate, granular zircon, granular silicon, glass, silicon dioxide flintshot, iron, steel, ferrite, nickel, Carborundum and mixtures thereof. Many of the foregoing and other typical carriers are described by L. E. Walkup in U.S. Patent 2,618,551; L. E. Walkup et al. in U.S. Patent 2,638,416, and E. N. Wise in U.S. Patent 2,618,552. An

ultimate homogenous or coated carrier bead diameter between about 30 microns to about 1,000 microns is preferred for electrostatographic use because the carrier bead then possesses sufficient density and inertia to avoid adherence to the latent electrostatic images during the cascade development process. Adherence of carrier beads to an electrostatographic drum is undesirable because of the formation of deep scratches on the drum surface during image transfer and drum cleaning steps, particularly where cleaning is accomplished by a web cleaner such as the web cleaner disclosed by W. P. Graff, Jr. et al. in U.S. Patent 3,186,838.

Any suitable natural resin, thermoplastic resin, or partially cured thermosetting resin may be used. Typical natural resins include: caoutchouc, colophony, copal, dammar, dragon's blood, jalap, storax, and mixtures thereof. Typical thermoplastic resins include: the polyolefins such as polyethylene, polypropylene, chlorinated polyethylene, and chlorosulfonated polyethylene; polyvinyls and polyvinylidenes such as polystyrene, polymethylstyrene, polymethylmethacrylate, polyacrilonitrile, polyvinylacetate, polyvinylalcohol, polyvinylbutyral, polyvinylchloride, polyvinylcarbazole, polyvinyl ethers, and polyvinyl ketones; fluorocarbons such as polytetrafluoroethylene, polyvinylfluoride, polyvinylidene fluoride; and polychlorotrifluoroethylene; polyamides such as polycaprolactamo and polyhexamethylene adipimide; polyesters such as polyethylene terephthalate; polyurethanes; polysulfides; polycarbonates; and mixtures thereof. Typical thermosetting resins include: phenolic resins such as phenol formaldehyde, phenol furfural and resorcinol formaldehyde; amino resins such as urea formaldehyde and melamine formaldehyde; polyester resins; epoxy resins; and mixtures thereof.

Styrene-n-butylmethacrylate is preferred because of its excellent triboelectric characteristics.

Any suitable solvent may be used. Typical solvents include carbon tetrachloride, petroleum ether, Freon 214 (tetrafluorotetrachloropropane), chloroform, methylene chloride, trichloroethylene, perchloroethylene, chlorobenzene, trichloromonofluoromethane, tetrachloridifluoroethane, trichlorotrifluoroethane, amides such as formamide, dimethyl formamide, esters such as ethyl acetate, isopropyl acetate, butyl acetate, amyl acetate, cyclehexyl acetate, isobutylpropionate and butyl lactate, ethers such as diethyl ether, diisopropyl ether, dioxane, tetrahydrofuran, ethylene glycol, monoethyl ether, aromatic and aliphatic hydrocarbons such as benzene, toluene, xylene, hexane, cyclohexane, gasoline, mineral spirits and white mineral oil, ketones such as acetone, methylethyl ketone, methylisobutyl ketone, and cyclohexanone. Toluene is preferred because it is readily available and because it is highly volatile.

Typical combinations of solute and solvent are available in most handbooks of chemistry. Typical combinations of resin solution and solvent include: styrene/methylmethacrylate/vinyltriethoxysilane reaction product and toluene; vinylchloride/vinylacetate copolymer and methylethylketone; nitrocellulose and methylethylketone; tetrahydrofuran and polyhydroxy ether; styrene-n-butylmethacrylate and toluene; polybutadiene and cyclohexane; polychloroprene and benzene; polyvinylalcohol and piperazine; polyvinylacetate and carbontetrachloride; polyvinylchloride and methylethylketone; polystyrene and methylcyclohexane; polymethylacrylate and toluene; and polyacrylonitrile and dioxanone.

Styrene-n-butylmethacrylate and toluene is preferred because of the excellent triboelectric properties of the polymer and because of the relatively high volatility of the toluene.

BRIEF DESCRIPTION OF THE DRAWINGS

The advantages of this improved method of coating will become apparent upon consideration of the detailed disclosure of the invention, especially when taken in conjunction with the accompany drawings wherein:

FIG. 1 is a schematic sectional view of one preferred form of apparatus for carrying out the method of this invention.

FIG. 2 is a schematic sectional view taken along line 2—2 of FIG. 1.

Referring now to FIG. 1, treatment chamber **1** adapted for continuous coating is shown. Treatment chamber **1** is axially tilted from the horizontal. Feed material is fed continuously through funnel **2** and flexible tube **4**. Solvent from pressure vessel **6** is sprayed onto the carrier material through spray nozzle **8**. Centrifugal blower **10** supplies air which is heated by heating means **12** and directed into treatment chamber **1** by flexible hose **14**. Air-solvent mixture is exhausted through flexible tube **15**, preferably to a solvent recovery system. Additional means may be used for providing heat to the treatment chamber. For example, the treatment chamber may be jacketed and hot fluids pumped through the jacket. The mixture of carrier material and solvent moves in a generally cyclical movement around the axis of treatment chamber **1**. However, because of the axial tilt of treatment chamber **1** and the influence of gravity, the circulating beads gradually work their way to the opposite end of treatment chamber **1** where they fall through flexible tube **22** into a suitable collecting means **24**. The counter current flow of hot air removes solvent from the beads and dries the carrier material as it progresses toward the lower end of the treatment chamber **1**. In addition, where prepolymer coatings are applied, the hot air can be used to cure the carrier bead coating. Vibrating treatment chamber **1** is insulated from rigidly secured supporting members **26** and **28** by means of helical springs **30** and **32**. Oscillatory energy is provided to treatment chamber **1** by a suitable source not shown.

FIGURE 2 is a cross sectional view taken through lines 2—2 of FIGURE 1.

The cyclical and vibrating movement of the individual carrier beads is provided by any suitable source of oscillatory energy such as the schematically illustrated means **41** of FIGURE 2. The oscillatory energy source **41** is securely fastened to the treatment chamber and may comprise an electric motor having unequal eccentric weights **42** mounted on the motor drive shaft **44**.

Other cross sectional shapes and baffles may be used where desired. For example, baffles and shapes as disclosed in U.S. Ser. No. 585,875, filed Oct. 11, 1966 in the U.S. Patent Office may be used. U.S. Ser. No. 585,875 discloses the use of vibrating barrel type equipment for impacting particulate material into the surface of coated carrier materials. The disclosure of U.S. Ser. No. 585,875 does not suggest, however, that the carrier materials may be coated in apparatus of this type. The agitating means described therein are also suitable for the process of this invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples further specifically illustrate the present invention. The examples below are intended to illustrate the various preferred embodiments of the improved carrier coating method. The parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A treatment chamber having a cross sectional shape as shown in FIGURE 2 is charged with about 25 pounds of 600 micron glass beads. An electric vibrator securely attached to an external surface of the treatment housing is operated to provide an oscillatory vibration frequency of about 1,800 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower (Master Heat Gun, model HG 301) to preheat the beads to a temperature of about 75° C. Upon completion of the preheating step, the application of oscillatory energy to the treatment

housing is terminated and about 2 pounds of a resin solution of 1 part diallylphthalate in 9 parts methylethylketone is poured into the treatment chamber. Oscillatory energy is again supplied to the treatment chamber simultaneously with the application of sufficient heated air to remove the solvent. After a coating period of about 10 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. Vibration is then terminated. An examination of the coated carrier beads after termination of the coating treatment reveals that they are free flowing and have a relatively thick uniform smooth coating over the surface of the carrier beads.

EXAMPLE II

A treatment chamber having a cross sectional shape as shown in FIGURE 2 is charged with about 10 pounds of 500 micron quartz sand. An electric vibrator securely attached to an external surface of the treatment housing is operated to provide an oscillatory vibration frequency of about 2,000 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower (Master Heat Gun, model HG 301) to preheat the beads to a temperature of about 65° C. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and about ¼ pounds of a resin solution of 2 parts polystyrene in 8 parts methylethylketone is poured into the treatment chamber. Oscillatory energy is again supplied to the treatment chamber simultaneously with the application of sufficient heated air to remove the solvent. After a coating period of about 5 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. Vibration is then terminated. An examination of the coated carrier beads after termination of the coating treatment reveals that they are free flowing and have a relatively thick uniform smooth coating over the surface of the carrier beads.

EXAMPLE III

A treatment chamber having a cross sectional shape as shown in FIGURE 2 is charged with about 50 pounds of 250 micron steel beads. An electric vibrator securely attached to an external surface of the treatment housing is operated to provide an oscillatory vibration frequency of about 2,000 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower (Master Heat Gun, model HG 301) to preheat the beads to a temperature of about 70° C. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and about 1.4 pounds of a resin solution of 1 part 65/35 styrene-n- butylmethacrylate in 9 parts toluene is poured into the treatment chamber. Oscillatory energy is again supplied to the treatment chamber simultaneously with the application of sufficient heated air to remove the solvent. After a coating period of about 10 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. Vibration is then terminated. An examination of the coated carrier beads after termination of the coating treatment reveals that they are free flowing and have a relatively thick uniform smooth coating over the surface of the carrier beads.

EXAMPLE IV

A treatment chamber having a cross sectional shape as shown in FIGURE 2 is charged with about 25 pounds of 250 micron glass beads. An electric vibrator securely attached to an external surface of the treatment housing is operated to provide an oscillatory vibration frequency of about 1,800 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower (Master Heat Gun, model HG 301) to preheat the beads to a temperature of about 60° C. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and about 1 pound of a resin solution of polyvinylchloride is poured into the treatment chamber. Oscillatory energy is again supplied to the treatment chamber simultaneously with the application of sufficient heated air to remove the solvent. After a coating period of about 10 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. Vibration is then terminated. An examination of the coated carrier beads after termination of the coating treatment reveals that they are free flowing and have a relatively thick uniform smooth coating over the surface of the carrier beads.

EXAMPLE V

A treatment chamber having a cross sectional shape as shown in FIGURE 2 is charged with about 50 pounds of 250 micron lead beads. An electric vibrator securely attached to an external surface of the treatment housing is operated to provide an oscillatory vibration frequency of about 2,100 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower (Master Heat Gun, model HG 301) to preheat the beads to a temperature of about 70° C. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and about 1.5 pounds of a resin solution of 2 parts ethyl cellulose dissolved in 8 parts of a ⅓ methanol, ⅓ butanol, ⅓ xylene mixture is poured into the treatment chamber. Oscillatory energy is again supplied to the treatment chamber simultaneously with the application of sufficient heated air to remove the solvent. After a coating period of about 10 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. Vibration is then terminated. An examination of the coated carrier beads after termination of the coating treatment reveals that they are free flowing and have a relatively thick uniform smooth coating over the surface of the carrier beads.

EXAMPLE VI

A treatment chamber having a cross sectional shape as shown in FIGURE 2 is charged with about 20 pounds of 600 micron quartz sand. An electric vibrator securely attached to an external surface of the treatment housing is operated to provide an oscillatory vibration frequency of about 1,800 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower (Master Heat Gun, model HG 301) to preheat the beads to a temperature of about 70° C. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and about 2 pounds of a resin solution of 1.5 parts ethylacetatebutyrate in 8.5 parts ethylene dichloride is poured into the treatment chamber. Oscillatory energy is again supplied to the treatment chamber simultaneously with the application of sufficient heated air to remove the solvent. After a coating period of about 10 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. Vibration is then terminated. An examination of the coated carrier beads after termination of the coating treatment reveals that they are free flowing and have a relatively thick uniform smooth coating over the surface of the carrier beads.

EXAMPLE VII

A treatment chamber having a cross sectional shape as shown in FIGURE 2 is charged with about 27 pounds of 450 micron glass beads. An electric vibrator securely attached to an external surface of the treatment housing is operated to provide an oscillatory vibratory frequency of about 2,000 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower (Master Heat Gun, model HG 301) to preheat the beads to a temperature of about 85° C. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and about 1.5 pounds of a resin solution of 0.5 part of styrene/methylmethacrylate/vinyltriethoxysilane made in accordance with the process disclosed in copending application U.S. Ser. No. 571,509, filed Aug. 10, 1966 in the U.S. Patent Office in 9.5 parts toluene is poured into the treatment chamber. Oscillatory energy is again supplied to the treatment chamber simultaneosuly with the applictaion of sufficient heated air to remove the solvent. After a coating period of about 10 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. Vibration is then terminated. An examination of the coated carrier beads after termination of the coating treatment reveals that they are free flowing and have a reltaively thick uniform smooth coating over the surface of the carrier beads.

EXAMPLE VII

A treatment chamber having a cross sectional shape as shown in FIGURE 2 is charged with about 10 pounds of 100 micron glass beads. An electric vibrator securely attached to an external surface of the treatment housing is operated to provide an oscillatory vibration frequency of about 1,800 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower (Master Heat Gun, model HG 301) to preheat the beads to a temperature of about 70° C. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and about 1 pound of a resin solution of 1 part styrene/methylmethacrylate/vinyltriethoxysilane of Example VII in 9 parts toluene is poured into the treatment chamber. Oscillatory energy is again supplied to the treatment chamber simultaneously with the application of sufficient heated air to remove the solvent. After a coating period of about 10 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. Vibration is then terminated. An examination of the coated carrier beads after termination of the coating treatment reveals that they are free flowing and have a relatively thick uniform smooth coating over the surface of the carrier beads.

EXAMPLE IX

A treatment chamber having a cross sectional shape as shown in FIGURE 2 is charged with about 15 pounds of 50 micron glass beads. An electric vibrator securely attached to an external surface of the treatment housing is operated to provide an oscillatory vibration frequency of about 2,000 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower (Master Heat Gun, model HG 301) to preheat the beads to a temperature of about 75° C. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and about 1.5 pounds of a resin solution of 1.5 parts styrene/methylmethacrylate/vinyltriethoxy of Example VII in 8.5 parts toluene is poured into the treatment chamber. Oscillatory energy is again supplied to the treatment chamber simultaneously with the application of sufficient heated air to remove the solvent. After a coating period of about 10 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. Vibration is then terminated. An examination of the coated carrier beads after termination of the coating treatment reveals that they are free flowing and have a relatively thick uniform smooth coating over the surface of the carrier beads.

Although specific components, proportions, apparatus and procedures have been stated in the above description of the preferred embodiments of the novel bead coating system, other suitable materials as listed above may be used with similar results. Further, other materials and procedures may be employed to synergize, enhance, or otherwise modify the method of this invention. For example, a polymerization initiator may be added to the mixture to speed polymerization of the coating were polymerizable materials are used.

Other modifications and ramifications of the present invention will occur to those skilled in the art upon the reading of this disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. The method of coating carrier beads comprising the steps of:
   (a) contacting said carrier beads with a solvent solution of a resin in a container;
   (b) agitating said beads and said resin solution by simultaneously vibrating the individual beads and moving said beads and said solvent solution as a stream in a cyclical path with oscillatory motion;
   (c) evaporating said solvent while said beads and said solution are being agitated as in step b; and
   (d) recovering free flowing carrier beads coated with a resin coating.

2. The method of claim 1 wherein said evaporation is aided by blowing a hot gas onto said beads and said solution.

3. The method of claim 1 wherein said evaporation is aided by heating said container.

4. The method of claim 1 wherein said agitating is accomplished by simultaneously vibrating each of said beads and moving said beads and said solution in a cyclical path with oscillatory energy having a frequency of from about 1,000 to about 3,000 vibrations per minute.

5. The method of claim 1 wherein said agitating is accomplished by simultaneously vibrating each of said beads and moving said beads and said solution in a cyclical path with oscillatory energy having a frequency of from about 1,000 to about 3,000 vibrations per minute and having a vibration amplitude of from about 0.0156 inch to about 0.25 inch.

6. The method of claim 1 wherein said resin comprises styrene copolymers.

7. The method of claim 1 wherein said resin comprises styrene-n-butyl methacrylate copolymers.

8. The method of claim 1 wherein said solution comprises styrene copolymers in toluene.

9. The method of coating carrier beads comprising the steps of:
   (a) preheating said carrier beads in a container;
   (b) contacting said carrier beads with a solvent solution of a resin in the container;
   (c) agitating said beads and said resin solution by simultaneously vibrating the individual beads and moving said beads and said solution as a stream in a cyclical path with oscillatory motion;
   (d) evaporating said solvent while said beads and resin solution are being agitated as in step b; and

(e) recovering said carrier beads coated with a resin coating.

References Cited

UNITED STATES PATENTS

3,117,027	1/1964	Lindlof et al.	118—303
3,385,724	5/1968	Grün	117—100
3,386,182	6/1968	Lippert	118—303

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U.S. Cl. X.R.

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