United States Patent [19]

Madrid

[11] **3,789,796**

[45] **Feb. 5, 1974**

[54] **APPARATUS FOR PRODUCING DEVELOPER MATERIAL**

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[73] Assignee: **Xerox Corporation,** Rochester, N.Y.

[22] Filed: **Jan. 20, 1971**

[21] Appl. No.: **107,913**

Related U.S. Application Data

[62] Division of Ser. No. 585,875, Oct. 11, 1966, abandoned.

[52] **U.S. Cl.** **118/612,** 34/164, 117/DIG.8, 118/418, 118/DIG. 5

[51] **Int. Cl.** **G03g 13/08**

[58] **Field of Search** ..... 118/612, DIG. 5, 637, 303, 118/417, 418, 19; 34/57 D, 58, 59, 164, 34/179; 117/DIG. 8, 100 M, 17.5, DIG. 6; 51/163, 314, 6, 7

[56] **References Cited**

UNITED STATES PATENTS

2,143,610	1/1939	Muller et al.	259/2
2,997,814	8/1961	Brandt	51/7
392,556	11/1888	Harris	51/6
2,840,923	7/1958	Behrens	34/164
2,860,598	11/1958	Loesche	118/418
3,285,223	11/1966	Sahlin	118/64
3,097,958	7/1963	Morris	117/20
3,058,235	10/1962	Morris et al.	34/164
3,202,537	8/1965	Norman et al.	117/100
3,197,328	7/1965	Jung et al.	118/DIG. 5
3,574,660	7/1966	Hagenbach	118/637
3,117,064	1/1964	Friedrich	118/DIG. 5
3,152,005	10/1964	Tuttle	118/DIG. 5
3,241,520	3/1966	Wurster et al.	118/DIG. 5
3,233,584	2/1966	Angstadt	118/DIG. 5
2,880,118	3/1959	Taylor	118/612

FOREIGN PATENTS OR APPLICATIONS

646,627	6/1937	Germany	34/164

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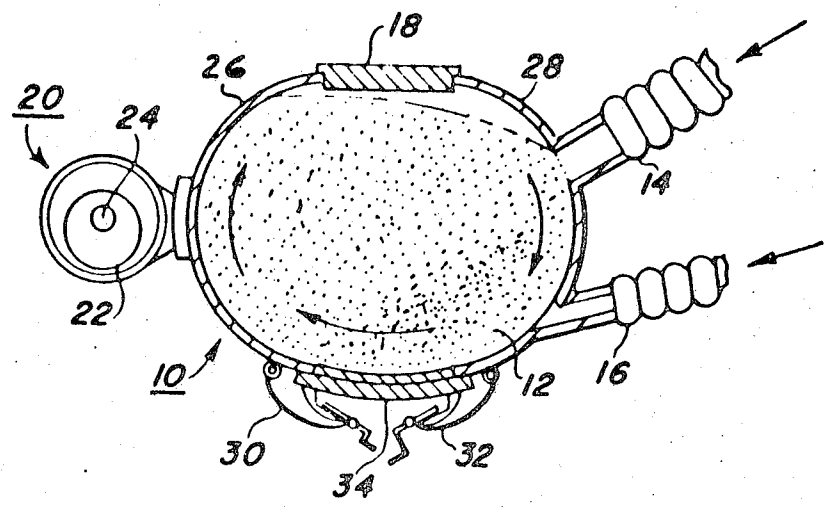
Assistant Examiner—Leo Millstein

[57] **ABSTRACT**

Carrier beads for electrostatographic developer mixtures having substantially smooth surfaces and having finely divided particulate material imbedded in a soft-enable surface are made by softening the external surface of the bead material and contacting the softened bead with finely divided particulate material and subjecting the beads to multiple collisions with other beads.

7 Claims, 9 Drawing Figures



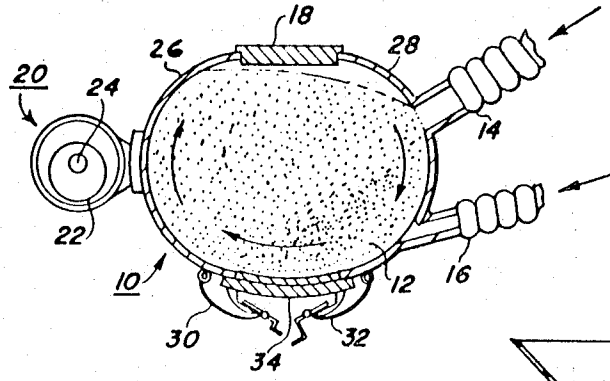


FIG. 1

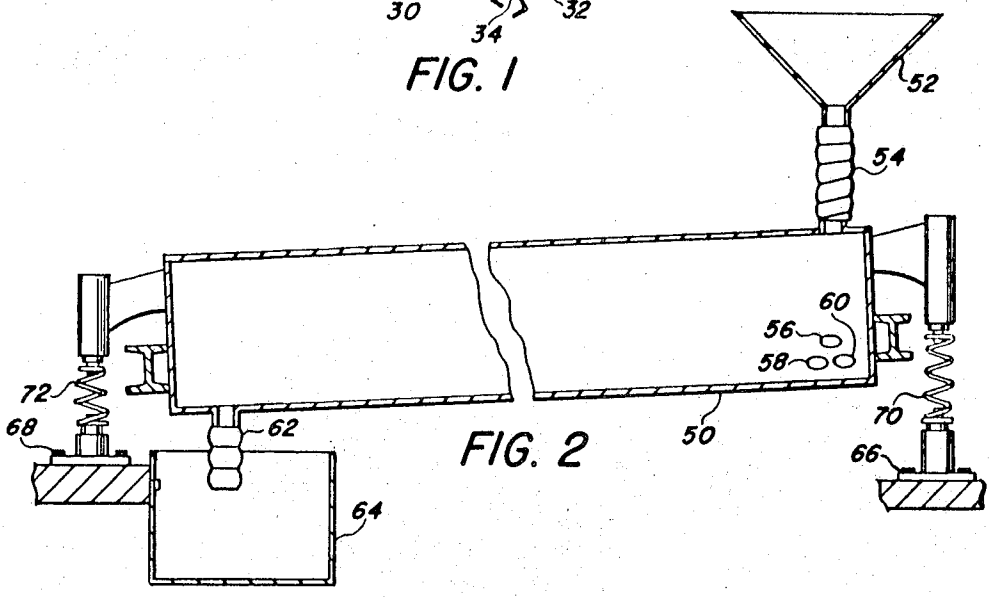


FIG. 2

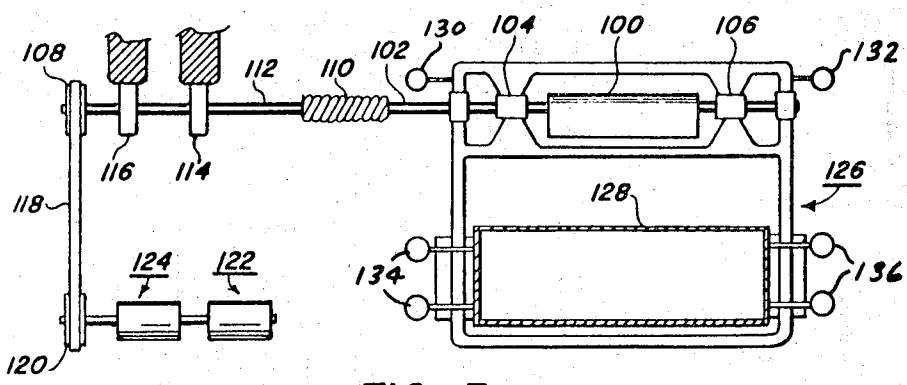


FIG. 3

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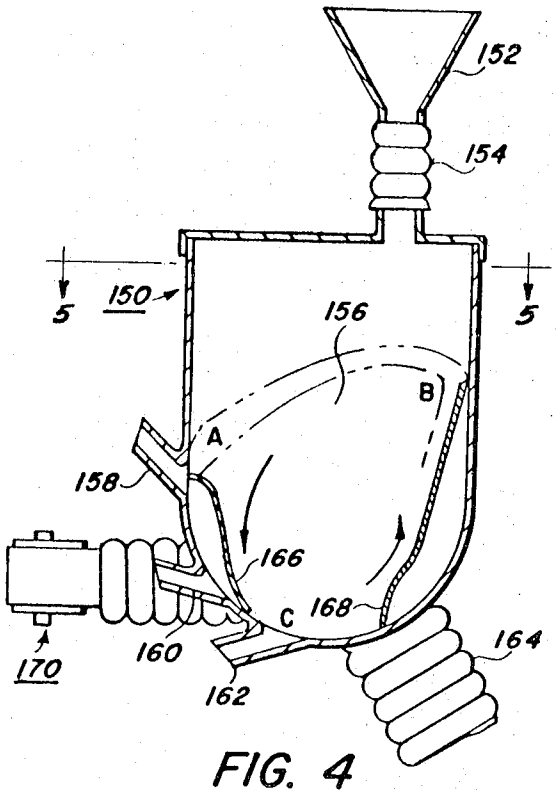

FIG. 4

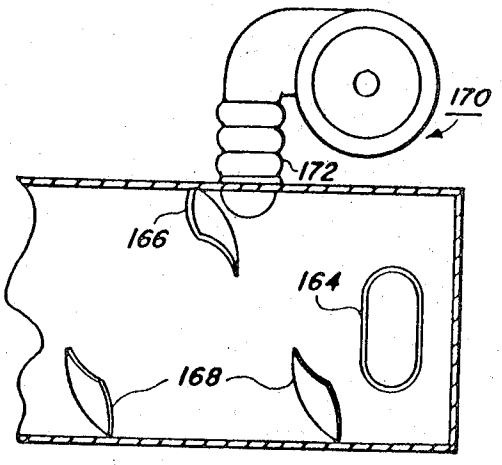

FIG. 5

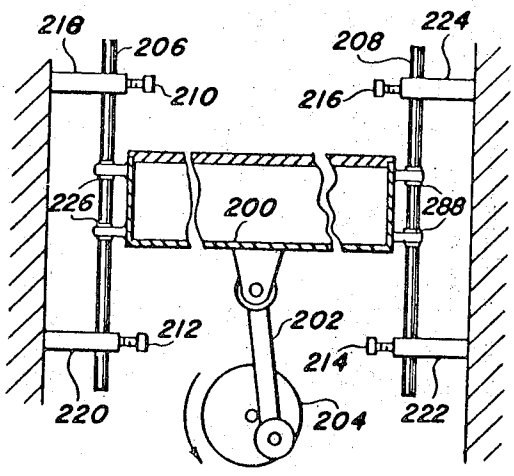

FIG. 6

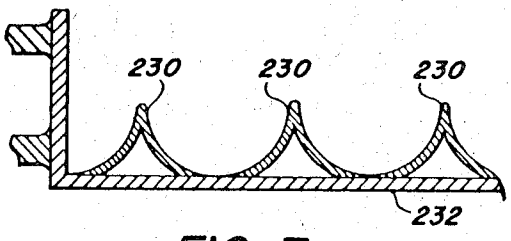

FIG. 7

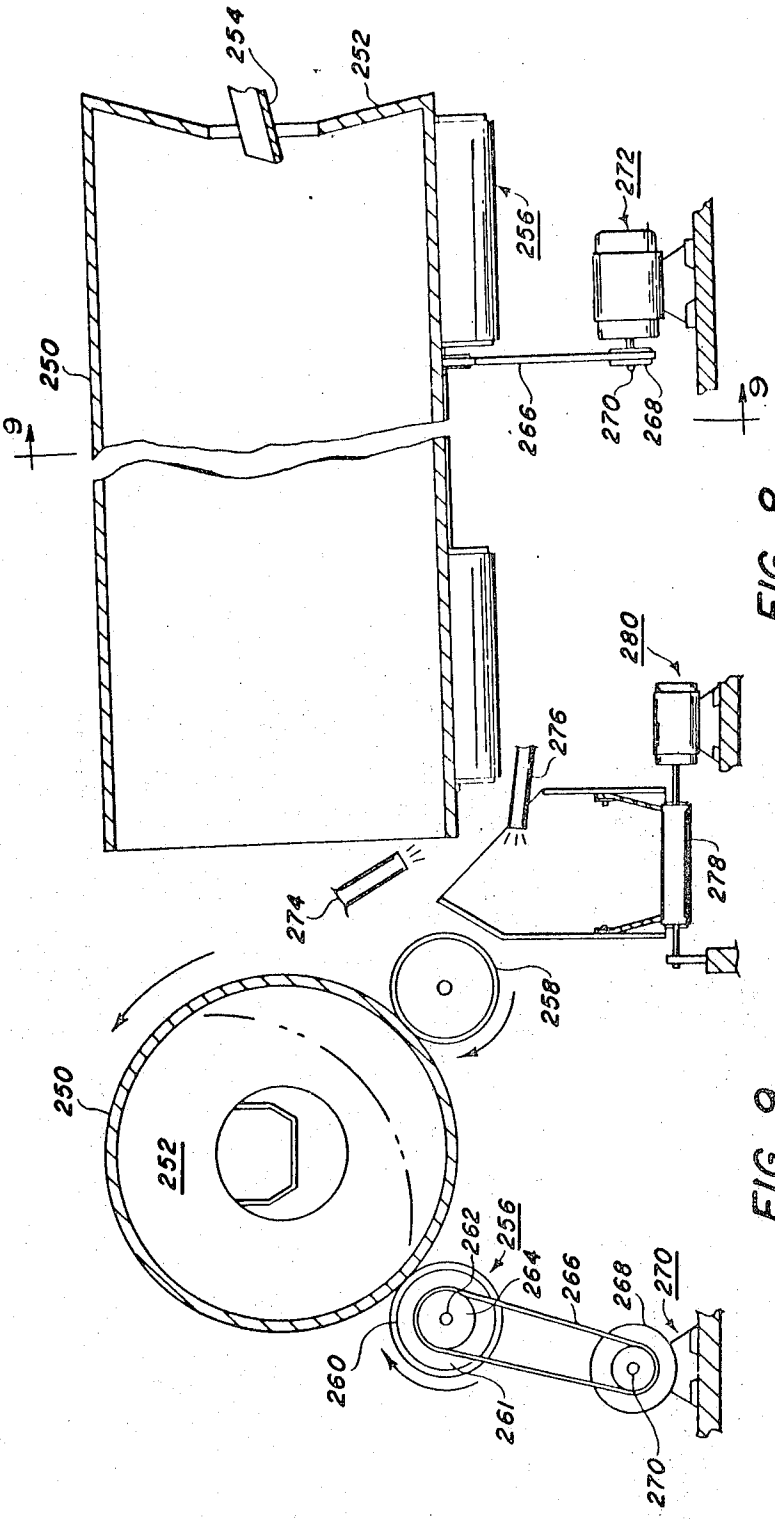
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FIG. 8

FIG. 9

APPARATUS FOR PRODUCING DEVELOPER MATERIAL

This application is a division of copending parent application, Ser. No. 585,875, filed Oct. 11, 1966 in the United States Patent Office, and now abandoned.

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

Electrostatography is best exemplified by the process of xerography as first described in U.S. Pat. No. 2,297,691 to C. F. Carlson. In this process, a photoconductor is first provided with a uniform electrostatic charge over its surface and is then exposed to an image of 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 surface as by heat. Instead of latent image formation by uniformly charging the photoconductive layer and then exposing the layer to a light and shadow image, one may form the latent image by directly charging the layer in image configuration. The powder image may be fixed to the photoconductive layer 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. Pat. No. 2,874,063. In this method, a developer material containing toner and magnetic carrier beads is carried by magnets. A 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 electrostatic attraction.

Another technique for developing electrostatic latent images is the "cascade" process disclosed by L. E. Walkup in U.S. Pat. No. 2,618,551 and E. N. Wise in U.S. Pat. No. 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 uncharged 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 coatings should be characterized by smooth outer surfaces, high tensile strength, stable triboelectric charactistics, strong adhesion to substrates, and good solubility in conventional solvents. Uncoated carrier beads must also posses 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 added 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 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 core. The separation may be in the form of chips, flakes, or entire layers and is primiarly 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 distintegration 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. The addition of particulate additives as suspensions in carrier coating mixtures to alter the triboelectric characteristics thereof often adversely affect the adhesive properties of the coating material. The triboelectric values of some carrier materials fluctuate with changes in relatively humidity and ordinarily are not desirable for employment in xerographic systems, particularly in automatic machines which require carriers having stable predictable triboelectric properties. Attempts to incroporate hydrophobic particulate materials into uncoated carrier beads or carrier coatings to stabilize the triboelectric characteristics of the carrier often fail because the hydrophobic particulate materials are incompatible with the carrier or carrier coating materials and cannot be suspended therein. Further, hydrophobic

particulate materials frequently act as "release" points between the carrier core and the film-forming portion of a carrier coating mixture. These "release" points reduce the interfacial contact area between the film forming component of the carrier coating material and the carrier core thereby proportionately reducing the carrier core surface area available for adhesive contact with the film-forming component of the carrier coating mixture. In addition, where a particulate additive is found which can be suspended in a carrier or carrier coating mixture, the particulate additive is often dispersed throughout the thickness of the ultimate cured or dried carrier or carrier coating. Since, in most cases, it is only the particulate material adjacent the external surface of the carrier which serves any useful function, the subsurface particles are not necessary, and in some cases tend to add to the cost of the carrier materials. Although some particulate materials may be successfully supended in carrier or carrier coating materials with the aid of supplementary dispersing agents, the presence of dispersing agents in the resulting carrier bead often adversely affect the triboelectric properties of the dried or cured product. Often, the outer surfaces of suspension coatings are lumpy and uneven due to the presence of the finely-divided additive, particularly when the film-forming component of the carrier coating mixture shrinks upon drying or curing or when the additive particles tend to form agglomerates. Carriers having rough and uneven surfaces are occasionally unsuitable because, they tend to cake, bridge and agglomerate and are especially undesirable in high speed precision copying machines because accurate metering and even distribution of the developer mixture is adversely affected. Also, uneven concentrations of particulate material at the surface of a carrier is undesirable in high quality electrostatographic developing systems because non-uniform images are produced. In addition, suspensions of finely-divided particulate materials are difficult to apply to beads by conventional coating techniques because the particles tend to clog the nozzles of spray guns. Thus, there is a continuing need for a better coated electrostatographic carrier and an improved method and apparatus for forming same.

It is, therefore, an object of this invention to provide a coating technique and a resulting product which overcome the above noted deficiencies.

It is another object of this invention to provide treated beads which flow freely.

It is a further object of this invention to provide a coating technique which promotes the tenacious adherence of coating material to particulate cores.

It is still a further object of this invention to incorporate particulate material into a bead surface without adversely affecting the resistance of the bead material to chipping, flaking and the like.

It is yet another object of this invention to reduce the quantity of particulate additives required in a coated or uncoated bead.

It is another object of this invention to provide carrier beads having physical and chemical properties superior to known carrier beads.

The foregoing objects and others are accomplished, generally speaking, by bringing finely-divided particulate additives into contact with the soft hardenable external surface of grossly larger coated or uncoated beads and impacting the particulate additives therein by causing other beads to collide and roll across the soft surface thereof. Each bead is subjected to thousands of collisions and rolling contacts with other beads during the impaction treatment. Any suitable means may be employed to impact the finely-divided particulate additives into the soft bead surface. Satisfactory treatment is obtained with systems which tumble a mixture of additives and beads having a soft surface in hollow rotating cylinders and systems which vibrate a mixture of additives and beads having a soft surface linearly in high frequency reciprocating chambers. Optimum impaction treatment is achieved with a system which utilizes high frequency oscillatory energy because smoother treated carrier surfaces are obtained and because treatment is effectuated more quickly.

In a preferred embodiment, the finely-divided particulate additives are incorporated into at least the outer surface of relatively large coated or uncoated beads by bringing the finely-divided particles into contact with the soft external surfaces of individually vibrating coated or uncoated beads moving as a mass in a generally cyclical or orbital path. Movement of both the individual beads and the stream mass in this preferred embodiment is effected by a device which imparts regular oscillatory molten to the bead treatment chamber. Rapid and uniform distribution of the finely-divided particulate additives throughout the mass of beads to be treated is promoted by moving the bead mass 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 vigratory 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, a great number of different beads and particulate additives are brought into contact with each incremental surface area of each bead during a given unit of time. The circulating bead bath is contained within a rapidly oscillating chamber or housing having a concave bottom surface. Although the axial 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 impaction 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, tilting the chamber axis and the like. Further, baffles may be employed in the chamber to promote uniform flow of the beads 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 oscillator 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 ajdustable 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 particulate additive material in the treatment housing, the bead material stream velocity desired, the shape of the treatment housing, the frictional characteristics of the particular bead and additive materials being employed, and the total mass of equipment actually being vibrated all affect 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 4,000 regular oscillatory vibrations per minute. Typical vibration amplitudes include from about 0.001 to about 0.25 inches. It is apparent, however, that the energy loss during tranmsission 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. Although it is not entirely clear, the formation of smooth impacted surfaces on each bead without an attendant hammered or peened finish may be due, at least in part, to the effects of rolling contact with many thousands of carrier beads and the resilient highly viscous state of the soft coating material surrounding the carrier core.

The entire carrier or merely the coating during the treatment process may comprise any soft material which is capable of being hardened. Thus, materials such as soft curable prepolymer resins, gelled plastisols, or certain softened materials may be employed in the bead or bead coatings. The softened materials may comprise materials softened by heat or solvents. The solvent or heat softenable materials may include natural resins, thermoplastic resins, and hard partially cured thermosetting resins. The soft curable prepolymers may comprise any suitable partially polymerized thermoplastic or thermosetting resin. Typical natural resins include: caoutchoac, colophony, copal, dammar, Dragon's Blood, jalap, storax, and the like. Typical thermoplastic resins include: the polyolefins such as polyethylene, polypropylene, chlorinated polyethylene, and chlorosulfonated polyethylene; polyvinyls and polyvinylidenes such as polystyrene, polymethylstyrene, polymethyl methacrylate, polyacrylonitrile, polyvinyl acetate, polyvinyl alochol, polyvinyl butyral, polyvinyl chloride, polyvinyl carbazole, polyvinyl ethers, and polyvinyl ketones; fluorocarbons such as polytetrafluoroethylene, polyvinylfluroide, polyvinylidenefluoride; and polychlorotrifluoroethylene; polyamides such as polycoproloctamo and polyhexamethylene adipamide; polyesters such as polyethyleneterephthalate; polyurethanes; polysulfides; polycarbonates; and the like. Typical thermosetting resins include: phenolic resins such as phenol-formaldehyde, phenolfurfural and resorcinol formaldehyde; amino resins such as ureaformaldehyde and melamineformaldehyde; polyester resins; epoxy resins; and the like.

The heat or solvent softenable material may be applied as a coating to a bead core by any conventional coating method such as spraying, dipping, or brushing. Similarly, the soft resin prepolymers may be applied in a solution by the foregoing techniques or by partially polymerizing monomers in situ on the surface of the beads. Alternatively, plastisols may be applied to the surface of the beads and gelled to a non-flowable state in situ. Especially good results are obtained with plastisols because a coating having a hardness gradient can be obtained. This hardness gradient is achieved by coating preheated bead cores. The heat supplied by the bead cores gell the plastisol coating from the coating-bead interface rather than from the external coating surface as in conventional hardening techniques. The speed of gellation and hardening, of course, depends upon the temperature difference between the plastisol coating and the bead core. Generally, plastisols such as polyvinyl chloride reesin plastisols begin to fuse at about 350° F. (Difference in temperature as well as heat transfer characteristics determine the gellation rate).

Any suitable wel 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, methyl methacrylate, 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. Pat. No. 2,618,551; L.E. Walkup et al, in U.S. Pat. No. 2,638,416 and E.N. Wise in U.S. Pat. No. 2,618,522. An ultimate homogeneous 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. Pat. No. 3,186,838.

Any suitable finely-divided particulate material may be impacted into the soft surface of the beads. The choice of materials would depend on the particular properties desired in the ultimate carrier bead. For example, where wear resistance is desired in the ultimate treated bead, hard finely-divided particles such as diamond dust, carborundum, stainless steel and the like may be impacted into the softened surface of the carrier bead. The triboelectric properties of the bead may be modified by impacting finely-divided incompatible material above or below the bead or bead coating material in the triboelectric series. The impaction technique of this invention uniformly alters the surface triboelectric properties of the carrier bead. The size of the finely-divided particles to be incorporated into the bead surface generally depends upon the diameter of the carrier bead, or if a coated bead is used, the thickness of the carrier coating. Generally, an average particulate additive diameter of less than about 15 microns is preferred because the height to which some of the particles extend above the external bead surface is reduced and less additive material is required to achieve a dense impacted surface. The degree of distribution of the finely-divided particles in the treated bead surface

depends upon the period of subjection to impaction conditions, the quantity of finely-divided materials available in the treatment housing and the radial depth of the soft material. Where a relatively small quantity of finely-divided particles having a diameter substantially less than the thickness of the bead coating is employed, the ultimate treated bead coating will contain a cross-sectional gradient of the finely-divided particles consisting of a concentrated region of particles near the external surface of the coating; the concentration diminishing in the direction of the bead core. Employment of even smaller quantities of finely-divided particles will result in a monolayer of particles adjacent the surface of the treated bead. When relatively large quantities of finely-divided particles are available, impaction may be continued until the finely-divided particles are evenly dispersed throughout the coating layer from the outer surface to the interface between the coating and the inner core. As discussed above, the degree of particule distribution in the bead coating depends, at least in part, upon the diameter of the particles and the thickness of the carrier coating. A monolayer of particles adjacent the external surface of the coating or a gradient of particles comprising a dense region of particles adjacent the external surface of the coating is preferred because less additive material is consumed and maximum adhesion between the bead core and the coating layer is maintained. The carrier beads formed by the process of this invention permits the use of many coating materials having near-marginal adhesion to a bead core which would ordinarily be adversely affected by the incorporation of finely-divided particulate additives which decrease the contact area between the coating material and the bead core surface. The particulate additive impacted into bead surfaces by the process of this invention are tenaciously held by the bead coating or bead material. Although it is not entirely clear, it appears that the particles are at least partially locked within the matrix comprising the periphery of the bead. Apparently, as each particulate additive penetrates the external surface of the bead, the soft coating or bead material begins to creep around and behind the particle. As the advancing edge of the soft material closes around the particle, the edge is kneaded and flatened by rolling contact with thousands of rapidly moving beads, particularly in the preferred oscillatory treatment system. It is postulated that it is this mechanism which causes the smooth outer surface of the carrier products of this invention. Where desired, loss of impacted additive particles from the surface of the carrier bead surface may be substantially eliminated by a thin overcoating of any suitable film forming material.

The soft carrier bead or coating on a carrier core is preferably a material softened by heat or by solvents prior to impaction with the particulate additives. The quantity of heat energy or solvent employed should not exceed that quantity necessary to soften the carrier coating to a tacky or highly viscous state. When excessive quantities of heat energy or solvent is applied to the carrier coating, the coating material tends to flow and collect on the treatment chamber walls and, in some cases, cause agglomeration of the carrier particles. Thus, it is preferred that the coating is not liquified. The carrier beads may be heated or treated with solvent prior to, during and/or subsequent to placement in the treatment chamber. Heating of the carrier beads may be effected by convection, conduction and/or radiation. Generally, heating by convection or radiation is preferred because the danger of coating removal by hot heat transfer surfaces is eliminated. Conventional hot air blower systems and/or infrared heater banks may be employed to heat the carrier particles. Solvents or partial solvents may be employed to soften the external surface of the bead. Generally, greater control of the softening process is achieved when solvent vapors or partial solvents for the coating material are employed. The use of solvents which rapidly dissolve external bead surface materials is less desirable because uniform surface softening of all the beads is difficult to attain, particularly at temperatures at which the solvents are most effective. Since the particulate additives to be incorporated into the bead surface are solids, care must be taken in selecting a solvent which will not completely dissolve the particulate additive. Any suitable solute bead material and solvent combination may be employed. Solvents for the solvent soluble beads or bead coatings employable in this invention are available in most handbooks of chemistry. Typical combinations of bead solute and solvent include: styrene/methyl methacrylate/vinyl triethoxy silane reaction product and toluene; vinyl chloride-vinyl acetate copolymer and methyl ethyl ketone; nitrocellulose and methyl ethyl ketone; polyhydroxy ether and tetrahydrofuran; styrene-n-butyl methacrylate and toluene; polybutadiene and cyclohexane; polychloroprene and benzene; polyvinyl alcohol and piperazine; polyvinyl acetate and carbon tetrachloride; polyvinyl chloride and methyl ethyl ketone; polystyrene and methylcyclohexane; polymethyl arcylate and toluene; and polyacrylonitrile and dioxanone and the like.

The advantages of this improved coating system will become even further apparent upon consideration of the following disclosure of the invention, particularly when taken in conjunction with the accompanying drawings wherein:

FIG. 1 is a schematic sectional view of one preferred form of apparatus for carrying out the novel method set forth in the specification.

FIG. 2 is a schematic sectional front elevation of a modified preferred form of apparatus for carrying out the novel method set forth in the specification.

FIG 3 is a schematic plan view of modified preferred arrangement of apparatus for effecting cyclical movement of the beads.

FIG. 4 is a schematic sectional side elevation of an alternative preferred form of the apparatus shown in FIG. 2.

FIG. 5 is a schematic sectional view taken along line 5—5 of FIG. 4.

FIG 6 is a schematic sectional view of an alternative form of apparatus for carrying out the novel treatment method set forth in the specification.

FIG. 7 is a schematic sectional view of a modified arrangement of apparatus for promoting rolling movement of the beads.

FIG. 8 is a schematic sectional front elevation of another alternative form of apparatus for carrying out the novel treatment method set forth in the specification.

FIG. 9 is a schematic sectional view taken along line 9—9 of FIG. 8.

Referring now to FIG. 1, reference character 10 designates a treatment housing containing a stream 12 of circulating beads and finely-divided particulate mate-

rial. The treatment housing **10** is charged with pre-softened beads through flexible tube **14.** The finely-divided particulate additive material is supplied as needed through flexible tube **16** or through an opening covered by hatch **18.** Both the generally cyclical movement of the total means **12** of beads and additive particles and the vibratory movement of individual beads in the mass are effected by any suitable source of regular oscillatory energy such as the schematically illustrated means **20** securely fastened to treatment housing **10.** The oscillatory energy source **20** may comprise an electric motor having unequal eccentric weights **22** mounted on the motor drive shaft **24.** The vibratory motion of individual beads circulating in the housing **10** promote rapid and uniform mixing of the beads and newly added particulate additives. Preferably, the beads in treatment housing **10** should be moving in a cyclical path when the fully-divided particulate additives are supplied to the housing **10** through flexible tube **16.** However, if the treatment housing **10** is charged with the additives through the opening covered by hatch **18,** the finely-divided particles are preferably gently folded into the bead mass prior to setting the bead mass into motion. This folding procedure is preferred because more uniform distribution of the additives material throughout the bead mass promotes uniformity of impaction treatment.

The geometry of treatment housing **10** and the direction of orbital vibration imparted to the housing **10** may be altered to control the direction of movement of the carrier system. High speed bead treating machines require rapidly moving streams of bead material. In order to avoid non-uniform impaction treatment, stagnant areas in the treatment housing **10** are preferably avoided. When a uniform and rapidly moving bead stream is desired, curved lips **26** and **28** should be employed to impart a "bottle" configuration to the housing **10.** The curved lips **26** and **28** eliminate the formation of stagnant areas which often occur in the bead material on one or both sides of the housing **10.** The curved lips **26** and **28** function as guides which promote gradual rather than abrupt changes in direction of the bead material thereby eliminating any eddy currents.

Where heating or solvent treatment of the beads is to be effected in the treatment housing **10,** the solvent or heated air may be supplied to the housing **10** through flexible tube **16** and exhausted through flexible tube **14** or through the opening covered by hatch **18.** Uniform softening of the bead surfaces is promoted and bead agglomeration is substantially eliminated when heat or solvent is supplied to chamber **10** while the beads are circulating. If desired, heat or solvent may be continued to be supplied to soften the circulating beads after chamber **10** is charged with the finely-divided particulate additive material. Upon termination of the impaction process, the treated beads are removed from the bottom chamber **10** by releasing latches **30** and **32** and removing hatch **34.** If a soft curable prepolymer coating is to be treated, heated air may be admitted into chamber **10** through flexible tube **10** immediately prior to termination of the impaction treatment to harden and polymerize the prepolymer.

In FIG. **2,** another embodiment of the invention is shown wherein a treatment chamber adapted for continuous treatment processes is employed. The cross section of treatment chamber **50** is similar to that of the treatment chamber of FIG **1** except that it is elongated axially and also axially tilted from the horizontal. Pre-softened beads are continuously fed into treatment chamber **50** through funnel **52** and flexible tube **54.** The finely-divided particulate additive material is continuously supplied to treatment chamber **50** through inlets **56, 58** and **60.** As in the chamber of FIG **1,** the mixture of finely-divided particulate additive material and pre-softened beads move in a generally cyclical movement around the axis of treatment chamber **50.** However, because of the axial tilt of treatment chamber **50** and the influence of gravity, the circulating beads granually work their way to the opposite end of treatment chamber **50** where they fall through flexible tube **62** into a suitable collecting means **64.** Vibrating treatment chamber **50** is insulated from rigidly secured supporting members **66** and **68** by means of helical springs **70** and **72.** Oscillatory energy is provided to treatment chamber **50** by a suitable source such as the device described with reference to FIG. **3** below.

In FIG. **3,** the oscillatory energy source for the treatment chamber is, unlike the oscillatory energy source described with reference to FIG. **1** above, is driven by means remote from the treatment housing. In this embodiment, eccentric weight **100** is mounted on a shaft **102** which in turn is journaled in support bearings **104** and **106.** Shaft **102** is connected to pulley **108** by a flexible spring or cable **110** and shaft **112.** Shaft **112** is supported by bearings **114** and **116.** Rotation of pulley **108** is effected by belt **118** driven by pulley **120.** Pulley **120** is connected to a reversible motor **122** through a variable speed drive mechanism **124.** The oscillatory energy created by rotation of eccentric weight **100** is transmitted through shaft **102** to bearings **104** and **106.** Since bearings **104** and **106** are rigidly secured to frame **126,** the frame **126** oscillates at the same frequency as the bearings **104** and **106.** Treatment housing **128** is rigidly secured to frame **126** by suitable means not shown. The oscillatory energy transmitted from the eccentric weight **100** through bearings **104** and **106** to the frame **126** is further transmitted to treatment housing **128.** To facilitate oscillation with minimum restraint, frame **126** is suspended from a supporting member (not shown) by means of elastic mounts **130, 132, 134** and **136.** Spring or cable **110** also functions as a means to minimize loss of oscillatory energy.

The apparatus illustrated in FIGS. **4** and **5** are a modified form of the treatment housing shown in FIG **2.** The modified housing **150** has a generally U-shaped configuration wherein the sides of the U do not contain a curved lip. The pre-softened beads are supplied through the top of one end of axially elongated treatment chamber **150** through funnel **152** and flexible tube **154.** Axial circulatory movement of the mass of pre-softened beads **156** is effected by oscillatory energy from a source (not shown) transmitted through the walls of chamber **150** to the mass of beads **156.** The small arrows in the circulating bead mass **156** indicate the direction of bead flow of bead material. Due to the configuration of housing **150,** zones of different bead velocities occur in the circulating bead mass. These zones are indicated by the letters A, B and C. The velocity of the mass of beads in Zone A is very high as a result of the influence of gravity and the oscillatory energy provided by the vibrating walls of housing **150.** The rapidly moving bead stream in Zone A promotes the rapid and uniform mixing of finely-divided particulate additive material supplied to the circulating bead

mass through inlet **158**. The bead particles in Zone B move at a relatively low velocity and reduce loss of additive material by arresting particle cloud formation. Where relatively large quantities of finely-divided particulate additive materials are to be impacted in the soft surface of the beads, additional additive material may be supplied as needed to chamber **150** through inlets **160** and **162**. The gradual movement of the mass of beads along the axis of chamber **150** from the inlet end of chamber housing **150** to the outlet **164** is promoted by a plurality of baffles **166** and **168**. Where desired, the treated beads may be cooled or heated in chamber **150** prior to discharge. This cooling or heating may be effected by a blast of air at the proper temperature forced into the circulating beads near the discharge end of chamber **150** by means of a centrifugal blower **170** operatively connected to chamber **150** through flexible tube **172** as shown in FIGS. **4** and **5**.

In FIG. **6**, another embodiment of the invention is shown wherein the treatment housing is supplied with reciprocatory energy rather than oscillatory energy. The reciprocatory energy is supplied to treatment housing **200** through connecting rod **202** driven by rotating crank shaft **204**. Guide rods **206** and **208** are rigidly secured by set screws **210, 212, 214** and **216** to supports **218, 220, 222** and **224**, respectively. Treatment housing **200** is journaled fo linear reciprocatory movement along guide rods **206** and **208** by means of sleeve bearings **226** and **228**, respectively, secured to brackets attached to housing **200**.

FIG. **7** is a modified form of the treatment housing shown in FIG. **6**. Since the treatment housing described above with refernece to FIG. **6** vibrates with a linear reciprocatory motion rather than in an oscillatory motion, less bead rolling action is achieved. To promote a rolling action of the carrier beads, baffles **230** are positioned along the bottom surface of chamber **232**. The baffles **230** are preferably curved to facilitate a gradual rather than abrupt change of direction of the beads during the impaction treatment process. The operational procedure of the apparatus described with reference to FIGS. **6** and **7** is similar to that described with reference to FIG. **1** where the beads are pre-softened before charging the treatment chamber or first simultaneously vibrated and softened in the chamber and then impacted with finely-divided particulate additive materials. Further, the reciprocatory impaction treatment apparatus illustrated in FIGS. **6** and **7** may also be tilted or appropriately baffled for continuous rather than batch type treatment.

In FIGS. **8** and **9**, another embodiment of the invention is shown wherein a mixture of additives and beads is rolled in a hollow rotating cylinder having an axis inclined with respect to the horizontal. In this embodiment, a mixture of beads having soft surfaces and finely-divided particulate additives are supplied to treatment cylinder **250** through an opening in conical end plate **252** by means of a chute **254**. Treatment cylinder **250** is supported by idler rollers **258** and drive roller **256**. Drive roller **256** is provided with a frictional surface such as rubber tread **260** bonded to support cylinder **261** to provide maximum frictional contact with treatment cylinder **250**. Drive roller **260** is mounted on a shaft **262** which in turn is connected to pulley **264**. Rotation of pulley **264** is effected by belt **266** driven by pulley **268**. Pulley **268** is connected to the drive shaft **270** of electric motor **272**. As the treatment cylinder **250** rotates, the mixture of beads and finely-divided particulate additives are tumbled from the raised end of inclined cylinder **250** towards the lower discharge end. As the impacted beads flow out of the lower end of cylinder **250**, they may be subjected to a blast of cooling or curing gas from nozzles **274** and **276**. The discharged impacted beads are collected on a conveyor belt **278** driven by electric motor **280**. The internal surface speed of treatment cylinder **250** may be varied through a considerable range. However, the internal surface speed should not exceed the point where centrifugal force maintains the beads in a motionless state along the circumference of the cylinder. Factors which determine the circumferential cylinder velocities to be employed include cylinder diameter; bead diameter; bead mass; and the frictional surface characteristics of the beads, additives, and cylinder interior. Generally, the impaction rate decreases with a decrease in the circumferential velocity of the cylinder.

As discussed above, the oscillatory treatment apparatus of this invention is preferred because smoother treated carrier bead surfaces are obtained at higher production rates. However, other suitable systems which bring the finely-divided particulate additives into contact with the soft external surface of coated or uncoated beads and impact the particular additives therein by causing other beads to collide and roll across the softened surface of the bead may be employed. Illustrative satisfactory systems are described above with reference to FIGS. **6** through **9**.

The following examples further specifically define and describe the system of the present invention for impacting finely-divided particulate additives into the softened surface of carrier beads. Parts and percentages are by weight unless otherwise indicated. The examples below are intended to illustrate the various preferred embodiments carrying out the invention.

EXAMPLE I

A control sample is produced by applying a mixture of about 10 parts finely-divided particles of carbon black (Neo Spectra Mark II) having an average particle size of about 13 millimicrons and about 20 parts of a 10 percent toluene solution of butyl methacrylate terpolymer onto glass beads having an average diameter of about 600 microns. About 20 grams of the carbon black and terpolymer solids is applied to about 5 pounds of glass cores. An examination of the coated beads after drying reveals a lumpy and mottled coating which is easily removed by firmly rubbing the beads together in the palm of the hand with a moistened thumb.

EXAMPLE II

A treatment chamber similar to that illustrated in FIG. **1** is charged with about 5 pounds of 600 microns glass beads coated with the same butyl methacrylate solution described in Example I, but without the carbon black. 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 bead coating to a temperature of about 90° C. in order to render the coating

surface tacky. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and finely-divided particles of carbon black (Neo Spectra Mark II) having an average particle size of about 13 millimicrons is gently folded into the preheated bead mass. Oscillatory energy is again supplied to the treatment chamber simultaneously with the application of sufficient heated air to maintain the bead surfaces in a tacky state. After an impaction treatment period of about 30 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. An examination of the treated mass after termination of the treatment reveals no free additive particles. The outer surfaces of the treated beads are smooth and appear to be uniformly impacted with the additive particles. Further, the treated butyl methacrylate coating cannot be removed by firmly rubbing the beads together in the palm of the hand with a moistened thumb.

EXAMPLE III

A treatment chamber similar to that illustrated in FIG. 1 is charged with about 7 pounds of 500 micron steel beads coated with a layer of phenoxy polyhydroxy ether having a thickness of about 0.1 mils. An electric vibrator securely attached to an external surface of a treatment housing is operated to provide an oscillatory vibration frequency of about 1,750 cycles per minute. Upon activation of the vibrator, the resulting stream of vibratory carrier beads is subjected to a continuous blast of heated air from a heated resistance wire type blower to preheat the bead coating to a temperature of about 150° C. in order to render the coating surface tacky. Upon completion of the preheating step, the application of oscillatory energy to the treatment housing is terminated and finely-divided particles of Pumice having an average particle size of about 1 micron is gently folded into the preheated bead mass. Oscillatory energy is again supplied to the treatment housing simultaneously with the application of sufficient heated air to maintain the bead surfaces in a tacky state. After an impaction treatment period of about 30 minutes, application of heated air is discontinued and the vibrating material is allowed to cool to room temperature. An examination of the treated mass after termination of the treatment reveals no free additives particles. The outer surfaces of the treated beads are smooth and uniformly impacted with the additive particles. Further, the treated polyhydroxy ether coating cannot be removed by firmly rubbing the beads together in the palm of the hand with a moistened thumb.

EXAMPLE IV

A treatment chamber similar to that illustrated in FIG. 1 is charged with about 5 pounds of 600 micron glass beads coated with the same butyl methacrylate terpolymer solution described in Example I, but without the carbon black. 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 stream of trichloromethane vapors heated to about 70° C. The vapor stream is supplied to the chamber interior through an inlet beneath the surface of the flowing beads and exhausted through an outlet located above the surface of the following beads. After the coating surface is sufficiently tacky, vapor treatment and application of oscillatory energy to the treatment chamber is terminated and finely-divided particles of carbon black (Molacco H) having an average particle size of about 70 millimicrons is gently folded into the solvent treated bead mass. The bead mass is then again subjected to oscillatory energy for about 30 minutes. Prior to termination of the oscillatory treatment, warm dry air is circulated through the flowing bead stream to drive off any solvent remaining in the coating. An examination of the dry impacted carrier beads reveals no free additive particles. The outer surfaces of the treated beads are smooth and appear to be uniformly impacted with the additive particles. In addition, the treated butyl methacrylate coating retains its excellent adhesion to the glass core.

EXAMPLE V

A treatment chamber similar to that illustrated in FIG. 1 is charged with about 5 pounds of uncoated 600 micron polystyrene beads. An electric vibrator securely attached to an external surface of a treatment housing is operated to provide an oscillatory vibration frequency of about 1,750 cycles per minute. Upon activation of the vibrator, the resulting stream of vibrating carrier beads is subjected to a stream of methyl ethyl ketone vapors heated to about 80° C. The vapor stream is supplied to a chamber interior through an inlet beneath the surface of the flowing beads and exhausted through an outlet located above the surface of the flowing beads. After the coating surface is sufficiently tacky, vapor treatment and application of oscillatory energy to the treatment chamber is terminated and finely-divided particles of lead dioxide having an average particle size of about 4.5 microns is gently folded into the solvent treated bead mass. The bead mass is then again subjected to oscillatory energy for about 30 minutes. Prior to termination of the oscillatory treatment, warm dry air is circulated through the flowing bead streams to drive off any solvent remaining in the coating. An examination of the dry impact carrier beads reveals no free additive particles. A treated bead is cut in half and examined for additive particle penetration. A particle concentration gradient having maximum lead dioxide concentration at the surface of the bead is observed.

EXAMPLE VI

A treatment chamber similar to that illustrated in FIGS. 4 and 5 is continuously fed with 250 micron glass beads coated with a heat softened layer of vinyl chloride-vinyl acetate copolymer having a thickness of about 0.2 mils and colloidal silica (Cab-O-Sil S-5). The treatment housing is supplied with oscillatory energy having a vibration frequency of about 1,750 cycles per minute. Resident time of each carrier bead is about 10 minutes. As the flowing stream of impacted beads approaches the outlet end of the treatment chamber, the beads are subjected to a continuous blast of air at room temperature sufficient to render the outer surface of the coating non-tacky. An examination of the cooled treated mass after termination of the impaction treatment reveals no free particulate additives. The outer surface of the treated beads are smooth and appear to be uniformly impacted with the additive particles. Further, the treated coating retains its excellent adhesion to the core.

EXAMPLE VII

A cylindrical treatment chamber having an internal diameter of about 6 centimeters and an internal length of about 14 centimeters is charged with about 200 grams of 600 micron flintshot beads coated with a layer of pre-softened nitrocellulose having a thickness of about 0.1–0.2 mils and talc powder having an average particle size of about 1 micron. The treatment chamber is simultaneously heated and rotated at an internal linear speed of about 2,400 centimeters per minute. After an impaction treatment of about 30 minutes, application of heat is discontinued and the tumbled impacted bead material is allowed to cool while rotation of the cylinder is continued. As examination of the treated mass after termination of the impaction process reveals no free additive particles. The outer surfaces of the treated beads are relatively smooth and substantially uniformly impacted with the finely-divided talc particles. Further, the treated coating adheres well to the core.

EXAMPLE VIII

A cylindrical treatment chamber having an internal diameter of about 6 centimeters and an internal length of about 14 centimeters is charged with about 200 grams of 250 micron glass beads coated with a layer of pre-softened styrene-methylmethacrylate-vinyl silane reaction product having a thickness of about 0.1 to 0.2 mils and powdered bauxite having an average particle size of about 0.1 mil. The treatment chamber is simultaneously heated and rotated at an internal linear speed of about 1,500 centimeters per minute. After an impaction treatment of about 30 minutes, application of heat is discontinued and the tumbled impacted bead material is allowed to cool while rotation of the cylinder is continued. An examination of the treated mass after termination of the impaction process reveals no free additive particles. The cutter surfaces of the treated beads are relatively smooth and substantially uniformly impacted with the finely-divided bauxite particles. Further, the treated coating adheres well to the core.

Although specific components, proportions, apparatus and procedures have been stated in the above description of the preferred embodiments of the novel bead treatment 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 novel system.

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

What is claimed is:

1. An apparatus for incorporating finely divided particulate material into at least the softenable external surfaces of beads which are grossly larger than said finely divided particulate material, said apparatus comprising a treatment housing for said beads having an arcuate bottom, means coupled with said housing to soften said external surfaces of said beads, and means coupled to said housing for imparting oscillatory motion including a rotatable eccentric weight mounted on a shaft journaled in support bearings, said bearings being secured to a frame bearing of said housing, said shaft being connected to a pulley by a flexible spring and a shaft supported by another set of bearings wherein said pulley is rotatable by a belt driven by a second pulley connected to a reversible motor through a variable speed drive mechanism, whereby said beads impact said finely divided particulate material into said external surfaces of said beads.

2. An apparatus according to claim **1** wherein said oscillating means provides oscillatory frequencies between about 1,000 and about 4,000 regular oscillatory vibrations per minute and vibration amplitudes from about 0.001 to about 0.25 inches.

3. An apparatus according to claim **1** wherein said treatment housing includes a chamber having curved lips to guide the direction of said beads.

4. An apparatus according to claim **1** wherein said treatment housing includes a chamber which is elongated axially

5. An apparatus for incorporating finely divided particulate material into at least the softenable external surfaces of beads which are grossly larger than said finely divided particulate material, said apparatus comprising a treatment housing for said beads wherein said treatment housing is provided with reciprocatory energy means through a connecting rod driven by a rotating crank shaft and wherein said treatment housing is journaled for linear reciprocatory movement along guide rods by means of sleeve bearings secured to brackets attached to said treatment housing, and means coupled with said housing to soften said external surfaces of said beads whereby said beads impact said finely divided particulate material into said external surfaces of said beads.

6. An apparatus for incorporating finely divided particulate material into at least the softenable external surfaces of beads which are grossly larger than said finely divided particulate material, said apparatus comprising a treatment housing for said beads wherein said treatment housing is provided with oscillating means situated remote from said treatment housing and said oscillating means comprises a rotatable eccentric weight mounted on a shaft journaled in support bearings, said shaft being connected to a pulley by a flexible spring and a shaft supported by another set of bearings wherein said pulley is rotatable by a belt driven by a pulley connected to a reversible motor through a variable speed driven mechanism, and means coupled with said housing to soften said external surfaces of said beads whereby said beads impact said finely divided particulate material into said external surfaces of said beads.

7. An apparatus according to claim **6** wherein said support bearings are rigidly secured to a frame bearing said treatment housing.

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