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PROCESS OF COATING FINELY DIVIDED SOLID MATERIAL

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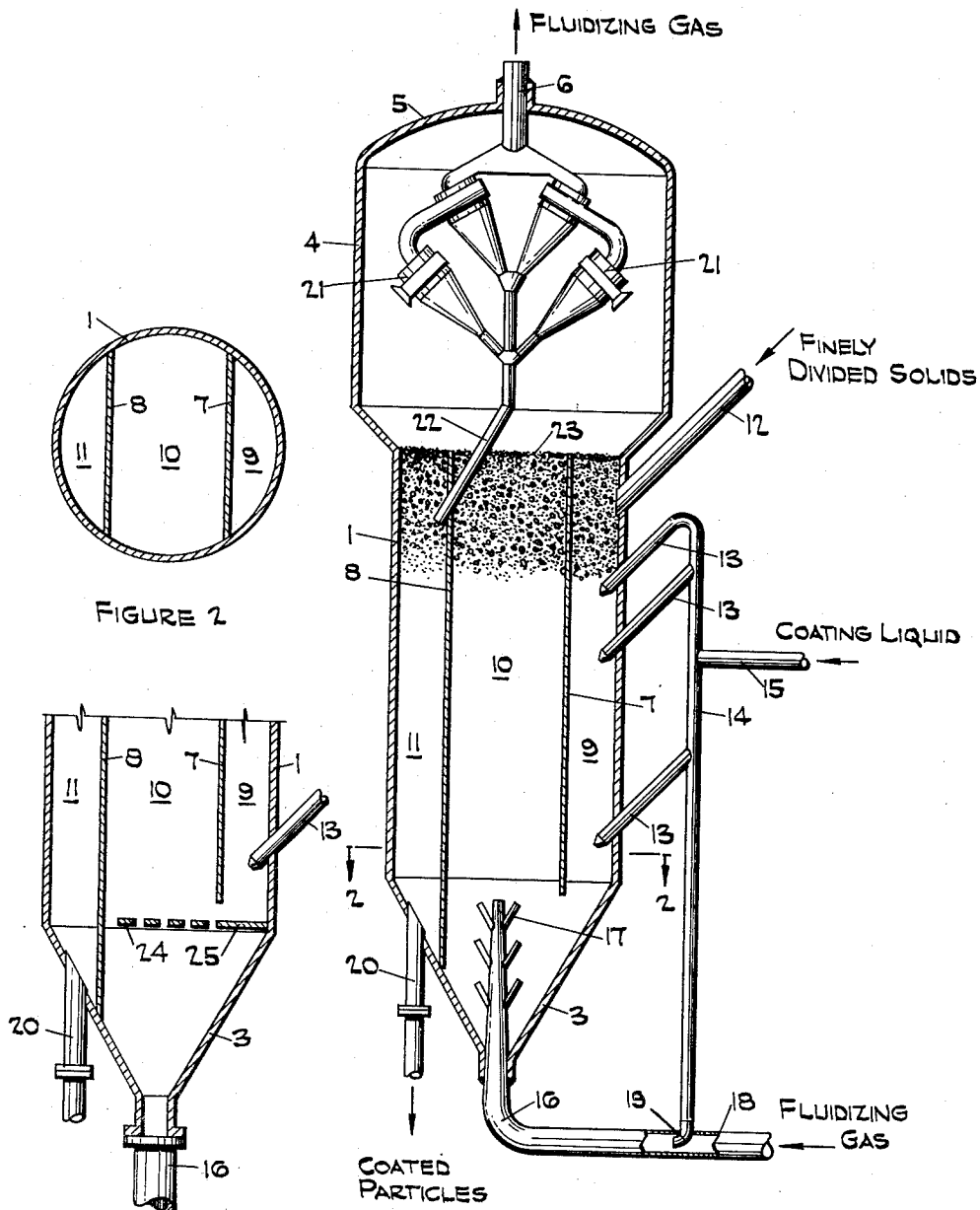


FIGURE 2

FIGURE 3

FIGURE 1

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This invention relates to methods of distributing liquids on solid material. It deals particularly with an improved procedure for achieving uniform distribution of liquids on solids in finely divided form and especially with the coating of such solids in a more efficient and economical manner.

A variety of different methods have been proposed for distributing liquids on solids. None of these methods has proven entirely satisfactory in all respects. One widely used method, for example, is to spray the coating material on to the solid particles while agitating the particles in a tumbling drum, for instance, or in other ways. Uniform distribution is difficult to achieve in this way and, especially in the case of solid particles which tend to adhere to each other on contact, great irregularities are encountered. More uniform distribution can be obtained by dissolving the material which is to be added in a solution in which the solid to be treated is also dissolved. By drying the mixture, for example, by spraying into hot gases, one may obtain solid particles of quite uniform composition. This adds greatly to the cost of production, however, unless the drying step is an otherwise necessary step in the process and even then it is an unsatisfactory method of incorporating additives which have a substantial vapor pressure at the drying temperature since the losses by evaporation during drying can be quite serious. These losses can be somewhat reduced by spraying the coating liquid into the stream of powdery product formed in the drying chamber by spray drying a solution of the solid material to be treated. The losses are still undesirably high in this method of operation, however.

It is an object of the present invention to overcome the foregoing disadvantages of the prior methods of coating finely divided solids with liquids. An important object is to provide a method for uniformly distributing liquids in finely divided solids without substantial loss of materials. Another object is the provision of a method of coating finely divided solids with liquid materials with minimized loss of coating material. A special object is to treat heat-sensitive materials so as to uniformly coat them with liquids in an efficient manner. A further object is the provision of a process whereby relatively small amounts of liquids can be distributed throughout a finely divided solid uniformly and without loss. Still other objects and advantages of the invention will be apparent from the following description in which some of the more important applications of the new method will be emphasized by way of illustration but without limiting the invention to these exemplary procedures.

The new process can be used successfully in applying a wide variety of different types of liquid materials to solids of any kind. The liquid applied can be a normally liquid material or mixture of such materials, or can be a liquefied gas or fused solid, or solution of one or more materials in a suitable solvent, depending on the conditions of operation and the purpose for which the treatment is intended. Typical applications are, for instance, in pre-

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paring fillers or reinforcing agents for rubber, as in the application of stearic acid as a coating for calcium sulfate intended for use in compounding rubber, for example; in the preparation of paint pigments as in surface coating silica gel particles with water-soluble fluorides to reduce or prevent settling in the paints made therewith; and in the application of protective layers on powders which tend to agglomerate or require protection from the atmosphere, as in the addition of magnesium sulfate to table salt or in coating asphalt or resin particles with solutions of surface-active agents, etc. The invention is also useful, for example, in powder metallurgy for applying lubricants to improve moldability, and in the manufacture of sand cores for molding use where it can be employed in applying fillers to at least partially fill the voids and hence reduce the amount of more expensive binder required. The coating of abrasive particles for grinding wheel manufacture is another example of an advantageous application of the process of the invention in uniform coating of abrasives, particularly those separated by elutriation, with bonding agents, whereby one can not only realize substantial reductions in the amount of bonding agent required but also can produce more porous wheels of better grinding properties.

As previously indicated, the invention is especially advantageous in the treatment of heat-sensitive powders. It is thus useful in applying additives to foodstuffs such, for instance, as dried milk, instant coffee, and the like where very careful handling is necessary for proper preservation of flavor or other properties. A particularly important application of the invention is in the addition of builders or other agents for improving the foaming and/or detergent activity of detergents and cleansing compositions and the like consisting wholly or partially of heat-sensitive surface-active substances. For the sake of simplicity, this special application of the invention will be emphasized in the following detailed description as the preferred exemplification of the new process.

When preparing products intended for washing, cleansing and the like, based on synthetic surface-active substances, as for example sulfuric acid ester salts of higher (that is to say, containing at least 7 carbon atoms) primary or secondary alcohols, alkyl sulfonates and alkyl-arylsulfonates, it is often desirable, in addition to any inorganic salts (such as phosphates, sulfates, borates and silicates), cellulose derivatives and the like, to add organic substances which improve the foaming and detergent action. As such, in addition to the higher primary and secondary alcohols, the higher 1,2-alkane diols and also the higher fatty acid amides are very effective. Only relatively small amounts, for example a few percent (for instance, about 1.5% to 4%) calculated on the weight of finished product, of these additives are generally needed. The uniform incorporation of additives in the solid product by prior methods is very difficult. Homogeneous end products can be obtained by dissolving the additives in a solution of the product to be improved, for example, an aqueous solution of sulfuric acid ester salts such as is obtained by sulfating higher alkenes or primary or secondary alcohols and converting the sulfuric acid esters formed into the corresponding alkali alkyl sulfates. Other components, if desired, can also be added and the solution worked up to a dry product, for which a spray-drying process or drying-roller process is generally applied. An objection to such a method of working, however, is that losses occur in the higher alcohols or other substances added. This loss is due either to evaporation of the additives at the high temperatures required for drying or, particularly during spray drying for example, to entrainment of a part of the additive in the steam formed and/or in the drying gas used. In many cases these losses

may be so considerable that only a small part of the substance originally added is present in the dry end product. Thus, for example, during the working up of an aqueous solution of secondary sodium alkyl sulfates (prepared from a C_8 — C_{18} -alkene fraction of a paraffin was cracked product), to which technical lauryl alcohol had been added to improve the foaming action, into a dry end product by means of spray drying or drying rollers, losses in lauryl alcohol were observed which, depending on the conditions prevailing during drying, varied from 25% to 75%. In the case, too, when coconut oil fatty acid amides were added instead of lauryl alcohol, serious losses amounting to as much as 70% were found to occur during drying. These losses can be somewhat reduced by adding the lauryl alcohol, not to the solution to be dried, but only at a later stage, namely by spraying it into the stream of the powdery product formed in the drying chamber, before conducting it to a cyclone or other separating device, but even then the losses are still so great that the process is uneconomical.

It has been found that the foregoing difficulties can be avoided and that the addition of liquids of all kinds to finely divided solid substances of various types can be carried out in a simple and particularly efficient manner by injecting the liquid in an atomized form beneath the upper bed boundary of a fluidized bed of the finely divided solid material. In this way a solid end product can be obtained having the liquid homogeneously distributed on the particles.

To obtain the desired homogeneous distribution of the liquid on the particles of the solid substance, it is necessary for these particles to be fluidized in such a manner that intensive mixing of the solid particles takes place in the fluid bed. As is known, this condition is satisfied when the rate of flow of the gas is high and the bed has a sufficiently large diameter as explained, for example, in Chem. Eng. Progress, vol. 47, pp. 401-404 (1951). Under the preferred conditions, known as aggregative fluidization, the bubbles rise to the surface in the middle of the fluid bed, while the mixture of gas and solid substance, having a greater density, flows along the walls in a downward direction.

When mention is made here of a "liquid," this refers not only to a substance which is liquid at room temperature, but also to a substance which, although solid or semi-solid at room temperature, is fusible without being decomposed, preferably at temperatures below 200° C. By a "liquid" should also be understood here a solution of a substance in a solvent which is preferably volatile.

By "finely divided solid substances" should be understood here solid substances whose individual particles, which may be either regular or irregular in shape, have dimensions or average dimensions of not more than 10 mm.; in the case of detergents, the dimensions of the particles are generally not larger than 1 mm.

The atomization of the liquid to be injected, and also the fluidization of the finely divided solid substance, can be effected by means of any gaseous substance which is inert towards the said liquid and solid substance. In most cases air can be used for this purpose. If, however, owing to the nature of the solid substance to be treated or of the liquid used, the presence of oxygen is undesirable, gases which contain no free oxygen, such as nitrogen or carbon dioxide, can be used instead of air. In order to obtain uniform coating of the particles, it is desirable that the liquid be sprayed in the form of small droplets, preferably less than 100 microns in diameter. With such fine sprays, considerable losses of the coating material by entrainment in the fluidizing gas are unavoidable if the spray is directed on to the surface of the fluidized bed, but, by introducing the coating liquid beneath the surface of the bed in accordance with the present invention, such losses can be substantially or completely eliminated.

The sprayed liquid can be injected at one or more points which may lie at the same level, for example half-

way up, or at varying levels within the fluid bed. It has been found that to insure a rapid and even distribution of the liquid on the particles of the solid substance, it is preferable to select the place (or places) of injection beneath the surface of the fluid bed in such a way that it lies, or they lie, mainly in the downward-flowing stream of the fluid power. To this end it is therefore necessary to dispose the atomizer or atomizers for the liquid close to the side wall of the apparatus in which the solid substance is fluidized when using the preferred aggregative fluidization. The direction in which the liquid is sprayed into the fluid bed preferably runs counter to the gas stream used for the fluidization, but it may also be in parallel flow.

An alternative method of introducing the coating liquid beneath the surface of the fluidized bed is by spraying the liquid into the fluidizing gas before the gas is fed into the finely divided solid material to be fluidized.

The process according to the invention produces particularly favorable results at low, e. g. room, temperature of about 20° C. or at only moderately elevated temperatures, i. e. below 100° C. This is naturally a very important advantage in the case of liquids with a comparatively high vapor tension at high temperatures, and of heat-sensitive solid substances. In the case of liquids which have a relatively high viscosity and can therefore be atomized less easily at room temperature, it may be advisable and sometimes even necessary to work at a slightly raised temperature, namely in those cases where the substance to be atomized is not yet liquid at room temperature. Also, when the substance to be atomized is dissolved in a volatile solvent before application, it may be desirable to carry out the treatment of the solid material at an elevated temperature to promote removal of the solvent.

As the purpose of the process according to the invention is the homogeneous covering of the particles of the solid substance with a liquid while maintaining the finely divided state of the solid substance, those liquids which under the conditions of the treatment have the property of dissolving the latter substance are naturally less suitable. Moreover, the quantity of the liquid distributed on the solid substance should not be so great that a cohesive, paste-like product is formed. Usually amounts of 10% or less based on the weight of the fluidized solids are satisfactory.

By means of the process according to the invention, which can take place either under atmospheric pressure or at pressures deviating therefrom, for example at elevated pressure, solid substances in powder form can be covered in a short time and in a very uniform manner with the liquid sprayed therein (the quantity of which may be slight, for example only a few percent).

The present process can be carried out batchwise, intermittently or continuously. In batchwise operation the liquid to be added can be sprayed into a fluidized quantity of the finely divided solid substance and the treatment ended after the desired quantity of liquid has been distributed on the solid substance. The process, however, lends itself particularly well to a continuous operation in which the liquid is sprayed continuously in the desired dosage into a fluid bed of the finely divided solid substance, the solid substance being fed continuously to the bed and an equivalent part of the fluid being discharged continuously. Any particles of the solid substance entrained from the fluid bed with the gas stream may, if desired, be separated therefrom, for example by means of a cyclone.

The attached drawings illustrate by means of conventional figures, not drawn to scale, the more important elements of apparatus adapted for carrying out the new process on a continuous basis. For the sake of clearness and simplicity, such auxiliary items as vents, gauges, temperature control means, aeration lines, valves, supporting means, etc. have been omitted from the drawing.

Figure 1 is a vertical sectional view of the treating

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vessel as a whole with its main inlet and outlet lines.

Figure 2 is a horizontal section on line 2—2 of Figure 1.

Figure 3 is a sectional view of the lower portion of a modified form of the vessel shown in Figure 1.

The treating vessel comprises an outer shell 1 mounted vertically and having a conical lower end 3 and an enlarged upper portion 4 having a semispherical head 5 through which an outlet line 6 passes. Partitions 7 and 8 divide shell 1 into three sections 9, 10 and 11. Partition 7 is in spaced relation to cone 3 and extends no further than the enlarged upper portion 4 of the treater to provide communication between sections 9 and 10 around both the top and bottom of partition 7. Partition 8 is affixed at its lower end to cone 3 and provides communication between sections 10 and 11 only at its upper end which extends no further than the upper enlarged portion 4 of the treater. An inlet 12 for finely divided solids to be treated leads into the upper portion of section 9 into which project one or more downwardly disposed inlet lines 13 for the treating liquid. Lines 13 are each provided with suitable nozzles for injecting the liquid in the form of a fine spray. Lines 13 receive treating liquid from header 14 supplied by line 15. An inlet line 16 having a distributing nozzle 17 enters the bottom of cone 3 and is attached to a supply line 18 for fluidizing gas. Treating liquid from header 14 can be fed into the fluidizing gas in line 18 by means of nozzle 19. A draw-off line 20 at the bottom of section 11 provides for removal of the treated solids. Enlarged upper section 4 functions as a disengaging space for the fluidizing gas and contains one or more cyclone separators 21, shown in the present case as two banks of two separators, each connected in series and discharging gas by outlet 6. The solids discharge legs 22 of the cyclones are arranged to return recovered solid particles to section 11 below the level of the fluidized bed indicated in Figure 1 by line 23.

In the modification illustrated in Figure 3 in which like numerals indicate parts identical with those of Figure 1, a grill or screen, or perforated plate or the like 24 serves as the fluidized gas distributing means instead of nozzle 17. With such an arrangement, which is preferably positioned as shown at the top of cone 3, although it may also be somewhat lower or higher in the treater, it is desirable to have a baffle 25 to promote the flow of solids from section 9 to section 10.

In normal operation a fluidized bed of the solids to be treated is maintained in sections 9, 10 and 11 with the upper bed boundary somewhat above the upper ends of partitions 7 and 8. The fluidized solid particles in the bed pass under turbulent flow generally upward in section 10 and overflow into sections 9 and 11. In section 9 they pass downward together with the newly added solid particles introduced by line 12 and are sprayed with the atomized liquid introduced by lines 13. The fluidized solids and unabsorbed liquid particles circulate from the bottom of section 9 back into the central mixing section 10 and the absorption of the liquid on the solids is completed by the time the particles return to the top of the fluidized bed 23. The particles overflowing partition 8 into section 11 contain the liquid very uniformly distributed throughout the mass due to the intensive mixing to which the particles have been subjected. This uniform product is removed by line 20 at a rate corresponding to the rate of addition of finely divided solids by line 12. By varying the positions of partitions 7 and 8 so as to control the relative volumes of sections 9 and 11, the fluidized solids can be circulated through section 9 one or more times before withdrawal through section 11. When the coating liquid is to be introduced solely with the fluidizing gas, via nozzle 19, partition 7 can be dispensed with. Also, instead of returning the solids collected in the cyclone separator or separators to draw-off section 11, as shown, they may, by suitable relocation of discharge leg 22, be returned to either mixing section 10 or spraying section 9. In any

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case, the gases removed by line 6 will be substantially free from the added coating material due to the completeness of the absorption which is achieved without sacrifice of uniformity in the product by introducing the added liquid in finely divided form beneath the surface of the fluidized bed in accordance with the invention.

The process of the invention is also illustrated by the following examples:

Example I

A powdered detergent (1400 grams), obtained by spray-drying and which contained 25% of secondary sodium-C₈-C₁₈-alkyl sulfates and for the rest consisted of sodium sulfate, was introduced into a vertical tube with an inner diameter of about 10 cm. and a height of 100 cm., which at the bottom had a constriction with a sieve plate. This powder, the particles of which had an average size of about 0.1 mm., was fluidized by blowing in air at the bottom through the sieve plate at a rate of about 750 liters per hour. The fluid bed thus formed was about 35 cm. high.

By heating it to about 80° C., liquefied technical lauryl alcohol (which consisted of about 70% of primary C₁₂-alcohol and 30% of primary C₁₄-alcohol) was fed dropwise at the rate of about 4 cc. of liquid per minute into an atomizer, by means of which the liquid was injected in spray form into the fluid bed. Spraying took place in a downward direction with an air flow of about 500 liters per hour. The spraying nozzle was fitted about half-way up the fluid bed and at a distance of about 2 cm. from the inner wall of the tube with the fluid bed; in this way the lauryl alcohol could be sprayed mainly into the stream of fluidized powder circulating from top to bottom.

After 40 cc. of lauryl alcohol has been sprayed into the fluid bed in this way, the experiment was terminated. The lauryl alcohol supplied was dispersed very evenly on the powdered detergent, as was confirmed by determining the foam figures of samples taken at various places in the powder by the known method of Ross and Miles. Substantially no losses of lauryl alcohol were found to have occurred. During the experiment only a very small quantity (about 0.05%) of the powder was entrained with the air stream; this could easily be recovered by means of a cyclone fitted into the discharge line of the air supply.

Example II

Rapeseed (3500 grams) was fluidized by blowing in air through the sieve plate at a rate of about 390 liters per minute into a vertical tube with an inner diameter of 15 cm. and a height of 100 cm. which was fitted with a sieve plate in the constricted part at the bottom.

A solution of about 1% of chloranil in benzene was injected in spray form into the fluid bed of rapeseed thus formed at a rate of about 20 cc. per minute by means of a downwardly directed spraying nozzle which was fitted close to the inner wall of the tube about half-way up in the fluid bed. Spraying took place with an air flow of about 1.7 liters per minute.

The experiment was terminated after 5.25 grams of the fungicidal chloranil had been sprayed into the fluid bed in the manner described above. An analysis made of samples taken at various places in the rapeseed thus treated established that a completely homogeneous distribution of the chloranil on the rapeseed had been achieved without any losses of chloranil having occurred in the operation. Nor were there any losses of rapeseed.

Similar favorable results were obtained in distributing in the same way DDT on an inert carrier, namely talcum powder, the DDT being fed as a solution in benzene beneath the upper surface of the fluidized bed of the finely divided carrier.

As previously pointed out, although the process of the invention is particularly important for the addition to detergents and cleansing agents of liquids improving the foaming and detergent action, it is by no means restricted thereto, but can be quite generally applied in all cases in

which it is desired to cover the particles of finely divided solid substances homogeneously with a thin layer. Examples of such other fields of application which may be mentioned are: the coating of hydrophilic finely divided solid substances, such as calcium chloride and certain artificial fertilizers, with a thin layer of oil, wax, paraffin wax, and the like, in order to protect them against the action of water; bringing of insecticidal, fungicidal or other biocidal substances on to solid carriers; adding plasticizers to finely divided resins, such as polyvinyl chloride and the like; incorporation of flavoring substances and/or dyes into powders in the foodstuffs industry or of perfumes into cosmetic powders; and covering of plant seeds with biocidal substances, growth-promoting substances; and the like.

The new process can be varied not only with regard to the type of finely divided solids which can be treated and to the liquids which may be applied thereto but also in regard to the manner in which the treatment is carried out and the conditions of operation which can be employed. Thus, for example, when applying coating material dissolved in a suitable solvent, it is feasible to carry out the coating treatment at a temperature at which the solvent is evaporated, and for this purpose heat can be supplied by preheating the finely divided solid material to be treated or the fluidizing gas, or both, with or without direct heating of the treating vessel 1 or its contents. In such cases it is often desirable to provide means for cooling the treated solid particles before removing them from the system. Still other changes can be made in the process without departing from the invention, which will be seen to offer many advantages over prior methods of distributing liquids on solids, especially in the uniformity of the products which can be obtained and in the freedom from losses of material by evaporation and entrainment during treatment. A further advantage of the process of the invention is that, with regard to the nature of the liquids to be added, the choice is no longer restricted to those which are sufficiently soluble in a solution of the solid substance, but it is now also possible to apply, without any difficulty, liquids which are only partly soluble or insoluble therein.

We claim as our invention:

1. A process for homogeneously distributing a liquid on a surface of finely divided solid particles which comprises establishing in a first zone a fluidized bed of pulverulent solid comprising the solid to which the said liquid is applied, the fluidized bed in said first zone moving in fluidized flow upwardly, establishing and introducing into a second zone downward flow of said pulverulent solid which is introduced at the vicinity of the upper end of said second zone, introducing atomized liquid coating material into said second zone, circulating coated particles from the lower portion of said second zone into the lower portion of said first zone and removing coated particles from the system from a point near the top of said first zone, the system being maintained at a temperature below the decomposition temperature of said pulverulent solid.

2. A process in accordance with claim 1 wherein the atomized liquid is injected within the fluidized bed by spraying it into a gas stream with which the fluidized bed is maintained before bringing said fluidizing gas into contact with the finely divided solid particles.

3. A process in accordance with claim 1 wherein said atomized liquid is introduced into the said second zone in the form of droplets of less than 100 microns in diameter, said droplets and fluidized particles being maintained in intimate contact until deposition of the liquid on said particles is substantially complete and separately with-

drawing from the said first zone the thus coated particles and said fluidizing gas.

4. A process in accordance with claim 3 wherein the liquid injected is a fused, normally solid material.

5. A process in accordance with claim 3 wherein the liquid is a solution of a solid in a solvent.

6. In a process for distributing a liquid on heat sensitive solid particles wherein the particles are maintained in the form of a fluidized bed and material to be coated on the particles is introduced into the bed, the improvement which comprises establishing in a first zone a fluidized bed of pulverulent solid comprising the solid to which the said liquid is applied, the fluidized bed in said first zone moving in fluidized flow upwardly, establishing and introducing into a second zone downward flow of said pulverulent solid which is introduced at the vicinity of the upper end of said second zone, introducing atomized liquid coating material into said second zone, circulating coated particles from the lower portion of said second zone into the lower portion of said first zone and removing coated particles from the system from a point near the top of said first zone, the fluidized bed not being at a temperature higher than 50° C.

7. A process for incorporating a builder in detergents by the process of claim 6 wherein the builder is the atomized liquid and the fluidized bed is a bed of solid detergent powder.

8. A process in accordance with claim 7 wherein the detergent comprises an alkyl sulfate salt.

9. A process in accordance with claim 7 wherein the detergent comprises an alkyl aryl sulfonate.

10. A process in accordance with claim 7 wherein the builder is a foam promoting agent for said detergent.

11. A process in accordance with claim 10 wherein the foam promoting agent is an alcohol of 10 to 16 carbon atoms per molecule.

12. A process for depositing a biocide on a heat sensitive solid at a temperature below the decomposition temperature of said solid which comprises establishing in a first zone a fluidized bed of pulverized solid comprising the solid to which said biocide is applied, the fluidized bed of said first zone moving in fluidized flow upwardly, establishing and introducing into a second zone downward flow of said pulverulent solid which is introduced at the vicinity of the upper end of said second zone, introducing liquid atomized biocide solution into said second zone, circulating coated solid particles from the lower portion of the second zone into the lower portion of the said first zone and removing particles coated with biocide from the system from a point near the top of said first zone.

13. A process in accordance with claim 12 wherein the solid material is plant seeds.

14. A process in accordance with claim 12 wherein the biocide is introduced into the fluidized bed as a solution in an organic solvent boiling below 200° C.

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