EUROPEAN PATENT SPECIFICATION

WATER-IN-OIL EMULSION SPRAY DRYING PROCESS
VERFAHREN ZUR SPRÜHTROCKNUNG VON WASSER-IN-ÖL-EMULSIONEN
PROCÉDE DE SECHAGE PAR PULVERISATION D’UNE EMULSION EAU DANS HUILE

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References cited:
EP-A- 0 252 897
US-A- 4 035 317

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This invention relates generally to processes for spray drying dispersions emulsions and microemulsions containing water-soluble or water-swellable polymers to obtain substantially dry water-soluble or water-swellable polymer particles, compositions of substantially dry water-soluble or water-swellable polymer particles.

High molecular weight, water-soluble and water-swellable polymers produced from such monomers as acrylamide are commercially important materials. These polymers find use as flocculants for mining operations to recover ore from slurries, water treating to remove suspended impurities etc., in agriculture as soil conditioners, and also in paper making to aid paper formation and in oil recovery industries.

Water-soluble and water-swellable polymers are generally commercially available in solution, dry, dispersion, water-in-oil emulsion, and water-in-oil microemulsion forms. In many cases polymer solutions are convenient, but may be limited to low molecular weight polymers and/or low solids levels because of the problem of handling viscous solutions of high solids, high molecular weight polymers. At very high solids and/or molecular weights, the solutions form gels that can be comminuted to form fine polymer gel particles that may be dissolved into water by the end-user. Although these comminuted gels typically contain up to about 20% water, they are frequently called "dry" polymers to distinguish them from the other product forms. In many cases the dry polymers exhibit long dissolution times and poor handling characteristics e.g. dusting. Although some handling problems may be mitigated by agglomeration see e.g. EP 0 277 018 A2; U.S. Patent Nos. 3,279,924; 3,275,449, 4,696,762; 5,171,781; both solutions and gels of water-soluble and water-swellable polymers may also suffer from the lack of a convenient method for post-reacting or functionalizing the polymer.

Another problem relates to blends of dry polymers, particularly when blending dry polymers having different particle sizes or particle size distributions. It is well known that dry polymer particles tend to stratify on handling and storage, with the larger particles tending to settle towards the bottom of the container, and the smaller particles tending to be concentrated towards the top. Stratification may be inconvenient because differences in handling characteristics are encountered as a function of container depth. The stratification problem may be exacerbated when two different dry polymers are blended together, because the particle size distributions of the two products are generally not identical. Stratification on storage may affect blend product performance as the top of the container tends to become enriched in the polymer having the smaller particle size. For obvious reasons, changes in product performance as a function of storage depth are to be avoided, and it is generally preferred that each polymer be of similar particle size, see e.g. EP 479 616 A1 and U.S. Patent No. 5,213,693. However, when producing dry polymer by spray-drying, changes in production e.g. changes in dryer size, dryer temperature, bulk viscosity of the feed, atomizer type, etc. may affect particle size, and it may be difficult or impossible to achieve a desired particle size while simultaneously maintaining some other production parameter, so blends of spray-dried polymers may be adversely affected by stratification.

The advent of water-in-oil emulsion and water-in-oil microemulsion forms of water-soluble and water-swellable polymers solved some of these problems, e.g. blends of water-in-oil emulsions and water-in-oil microemulsions as disclosed in US-A Nos. 5,883,181 and 5,763,530 do not tend to stratify, and high solids, high molecular weight, and relatively fast dissolution times may all be obtained simultaneously. In addition, unique functionalized polymers may be produced that cannot be practically manufactured by polymerization in solution. For instance, U.S. Patent Nos. 4,956,399; 4,956,400; 5,037,881; and 5,132,023, teach that functionalization of a water-soluble polymer contained in a water-in-oil microemulsion can be carried out to produce high molecular weight charged polymers with advantageous flocculation performance. The use of microemulsions, as opposed to emulsions, in polymer production provides improved polymer performance properties among other benefits. Hydrolyzed polyacrylamides with uniquely high molecular weight are disclosed in U.S. Patent No. 5,286,806. In U.S. Patent No. 4,767,540, very high molecular weight hydroxamate-functionalized polyacrylamide is disclosed, and novel charged organic polymer microbeads are disclosed in U.S. Patent Nos. 5,274,055 and 5,167,766. In addition, methods for esterifying (meth)acrylic acid polymer and, optionally, hydroxamating said polymers are disclosed in U.S. Patent No.5,847,056.

Despite the many benefits provided by emulsion and microemulsion polymers, transportation costs associated with such materials remain high and disposal of the oil and emulsifier in the emulsions may pose environmental concerns as secondary pollution. Moreover, many emulsion and microemulsion polymers tend to exhibit stability problems, e.g. detrimental changes in polymer properties and/or performance as a function of time. Although US-A-Nos. 5,883,181, 5,763,530, 4,956,399; 4,956,400; 5,037,881; 5,132,023; 5,274,055; and 5,167,766 mention non-solvent precipitation and stripping as methods of recovering dry polymer products from water-swellable or water-soluble polymer microemulsions or microemulsion-containing blends, these methods may produce a dry polymer with undesirable handling properties, poor dissolution times, low bulk density, etc. Practically, non-solvent precipitation and stripping may be inconvenient and expensive.

Water-soluble polymers may also be prepared in the form of suspensions or dispersions of polymer beads or droplets in a non-aqueous liquid e.g. oil. The reverse phase polymerization process described in U.S. 4,528,321 is said to form dispersions of water-soluble polymers. Water-soluble polymer dispersions, which may be azeotropically
dried, are disclosed in U.S. Patent No. 4,628,078. U.S. Patent 4,506,062 discloses a reverse phase suspension polymerization process for the production of high molecular weight, water-soluble polymers and also reports that dry polymer beads may be obtained by azeotropic distillation followed by filtration. However, a problem remains in that azeotropic distillation tends to be energy-intensive, and the filtering process may be hazardous or inconvenient.

Although dry polymers may be obtained from vinyl-addition polymer-containing water-in-oil emulsions, water-in-oil microemulsions or dispersions by such methods as precipitation in a non-solvent, stripping, etc., these methods may also be impractical for economic and environmental reasons because of difficulties in recovering, purifying and recycling the oil. Although the oil recovered from an emulsion or suspension polymerization may occasionally be recycled without further purification, as disclosed in U.S. 4,212,784 and JP 50-124979, in other cases e.g. United States Statutory Invention Registration H915 additional purification steps are necessary. The level of impurities in the oil is an important consideration, as certain polymerizations e.g. chain-growth polymerizations, or polymerizations used to make very high molecular weight polymers, are especially sensitive to even trace amounts of polymerization-debilitating substances. Particular problems are also encountered where the polymer has been formed from monomers in the presence of the oil or the oil has been heated or subjected to processing steps, which may have a tendency to deposit polymerization-debilitating impurities in the oil.

Spray-drying is the transformation of feed from a fluid state to a dried particulate form by spraying the feed into a hot drying medium, typically a hot gas. Spray-drying is widely used to produce a diverse range of products e.g. instant coffee, dried eggs, instant milk, household detergents, pharmaceutical products, pigments, cosmetics, starch, plastics, ceramics, etc. Typical spray-drying equipment, drying procedures, etc. are described in detail in known references e.g. "Spray Drying Handbook," by K. Master, 5th Ed., Longman Scientific, 1991.


U.S. Patent No. 4,035,317 teaches that water-in-oil emulsions of water-soluble vinyl-addition polymers may be spray dried, under specific conditions including an outlet temperature of at least 100°C and a residence time of 40-180 seconds, to produce free-flowing, non-dusting polymer particles which rapidly dissolve in water. Powders of polyacrylamide, acrylamide/ acrylic acid copolymer, and acrylamide/dimethylaminopropyl methacrylate copolymers are described therein. The size range of the spray-dried products is such that none are smaller than about 325 mesh (about 40 microns), at least about 50% are larger than about 120 mesh (about 122 microns), and substantially none of the particles are larger than about 20 mesh (about 841 microns). These particles do not clump when added to water and dissolve much faster than traditional dry or gel particles of water-soluble polymers. When the spray-dried particles are either larger or smaller than this size range, however, they dissolve with difficulty. Although the invention of U.S. 4,035,317 was a significant advance in the art, a difficulty nevertheless remains with respect to certain polymers, in that the spray-drying methods of said patent gives polymers whose properties are undesirably changed relative to the emulsion or microemulsion form. Attempts to spray-dry Mannich polyacrylamides according to the teachings in the art resulted in polymer powder exhibiting reduced flocculation performance, compared to that of the corresponding polymers used in the microemulsion form. Furthermore, the viscosities of solutions of the spray-dried products tended to be significantly lower than desired.

Accordingly, there exists a need for a method of recovering water-soluble and water-swellable polymers from water-in-oil dispersions, water-in-oil emulsions or water-in-oil microemulsions to produce rapidly dissolving water-soluble polymers without adversely affecting polymer properties. It would also be advantageous to provide blending of two or more spray-dried dry polymers and methods for production thereof wherein 90% or greater of the particles in the blend are each individually comprised of two or more polymers, so that the effect of stratification on the blend is minimized. There also exists a need for an economical method for producing substantially dry polymers having good handling and dissolution properties. It would also be advantageous to provide methods for spray-drying water-in-oil emulsions and water-in-oil microemulsions which eliminate or reduce undesirable product changes, and enable component recycling or reuse.

An improved method has now been discovered for producing substantially dry water-soluble and water-swellable vinyl-addition polymers by spray-drying the corresponding polymer water-in-oil dispersion, water-in-oil emulsion, or water-in-oil microemulsion. Surprisingly, dry polymer products are obtained whose properties and/or performance are not detrimentally changed by the spray-drying process. Surprisingly, substantially dry polymers produced by methods of the instant invention tend to have improved stability relative to the corresponding dispersion, water-in-oil emulsion, or water-in-oil microemulsion polymers. Advantages blends of two or more spray-dried dry polymers are also produced, wherein 90% or more of the particles in the blend are each individually comprised of two or more polymers. Surprisingly, the dissolution and handling characteristics of the spray-dried polymer particles obtained by the instant
invention are improved by agglomeration.

[0014] The present invention broadly provides a process for producing by spray-drying substantially dry water-soluble or water-swellable vinyl-addition polymer particles comprising the steps of:

(a) spray-drying a water-in-oil dispersion, water-in-oil emulsion or water-in-oil microemulsion containing said vinyl-addition polymer into a gas stream with a residence time of 8 to 120 seconds and an outlet temperature of 70°C to less than 100°C, the oil phase of said dispersion, emulsion or microemulsion containing a volatile oil whose boiling point, or the upper end of whose boiling point range, is 200°C or less; and

(b) collecting resultant polymer particles containing 12% or less volatiles, based on the weight of the spray-dried polymer as measured by determining the weight loss on drying the polymer at 105°C for 30 minutes.

[0015] The present invention also provides a process for producing by spray-drying a substantially dry blend of water-soluble or water-swellable vinyl-addition polymer particles, comprising the steps of:

(a) spray-drying a blend comprised of (i) a first water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, water-in-oil emulsion or water-in-oil microemulsion and (ii) a second water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, water-in-oil emulsion or water-in-oil microemulsion, the oil phases of said dispersions, emulsions or microemulsions comprising a volatile oil whose boiling point, or the upper end of whose boiling point range, is 200°C or less, into a gas stream with a residence time of 8 to 120 seconds and an outlet temperature of 70°C to less than 100°C, and

(b) collecting resultant blend of polymer particles containing 12% or less volatiles, based on the weight of the spray-dried polymer as measured by determining the weight loss on drying the polymer at 105°C for 30 minutes.

[0016] In accordance with the instant invention, vinyl-addition polymer-containing water-in-oil dispersions, water-in-oil emulsions, and water-in-oil microemulsions are sprayed-dried by a suitable means into a large chamber through which a hot gas is blown, thereby removing most or all of the volatiles and enabling the recovery of the dried polymer. Surprisingly, the means for spray-drying the water-in-oil dispersion emulsion, or microemulsion into the gas stream are not particularly critical and are not limited to pressure nozzles having specified orifice sizes; in fact, any known spray-drying apparatus may be used. For instance, means that are well known in the art such as rotary atomizers, pressure nozzles, pneumatic nozzles, sonic nozzles, etc. can all be used to spray-dry the water-in-oil dispersion, emulsion, or microemulsion into the gas stream. The feed rate, feed viscosity, desired particle size of the spray-dried product, droplet size of the water-in-oil dispersion, emulsion or microemulsion, etc. are factors which are typically considered when selecting the spraying means. The size and shape of the chamber, the number and type of spraying means, and other typical operational parameters may be selected to accommodate dryer conditions using common knowledge of those skilled in the art.

[0017] Although open cycle spray-dryers may be used, closed cycle spray-drying systems are preferred. Gas flow may be cocurrent, countercurrent or mixed flow, cocurrent flow being preferred. The hot gas, or inlet gas, may be any gas that does not react or form explosive mixtures with the feed and/or spray-dried polymer. Suitable gases used as the inlet gas are gases known to those skilled in the art, including air, nitrogen, and other gases which will not cause undesirable polymer degradation or contamination, preferably gases containing 20% or less oxygen, more preferably 15% or less oxygen. Most preferably, inert gases such as nitrogen, helium, etc. that contain 5% or less of oxygen should be used.

[0018] The dried polymer may be collected by various means such as a simple outlet, classifying cone, bag filter, etc., or the polymer may be subjected to further stages of drying, such as by fluid beds, or agglomeration. The means for collecting the dry polymer product is not critical. The hot gas that remains after substantially all of the polymer is recovered from the feed generally contains volatiles such as oil, water, etc. and may be vented to the atmosphere or recovered, preferably recovered and most preferably thereafter recycled. The oil is generally recovered from a vinyl-addition polymer-containing water-in-oil dispersion, water-in-oil emulsion, and water-in-oil microemulsion spray-drying process by condensing spray-dry process-generated oil, preferably cocondensing spray-dry process-generated oil and spray-dry process-generated water, and separating condensed or recovered oil from condensed water. Said separating is easily accomplished by simply draining off the lower layer, and/or pumping off the upper layer, as water and oil are essentially immiscible. The difference in boiling points between water and oil may be such that the condenser may be operated at a temperature so as to only condense the oil, reducing the energy costs associated with condensing the vaporized water. However, it has been surprisingly discovered that cocondensation of both the water and oil may be beneficial, as the recovered or cocondensed oil is generally substantially free of non-gaseous polymerization-debilitating substances. The volatiles are preferably condensed or cocondensed with a spray condenser. Spray condensers are well-known to those skilled in the art and function by spraying a liquid into hot gas, causing the hot gas to cool and
causing the volatile oil, water, etc. contained in the hot gas to condense. The spray condenser may utilize an aqueous liquid, preferably water, more preferably aqueous acid, most preferably aqueous inorganic acid e.g. aqueous sulfuric acid. Polymerization-debilitating substances are those that inhibit or retard polymerization, or act as chain-transfer agents. Polymerization-debilitating chain-transfer agents may have chain transfer constants of about $10^{-4}$ or greater. Preferably, the condensed, cocondensed, or recovered oil contains less than 0.1% of such polymerization-debilitating substances, more preferably less than 0.05%, by weight based on total weight.

In some cases, recovered oil, which may be cocondensed or condensed oil, may not be as free of impurities or polymerization-debilitating substances as desired. Recovered oil may be purified by intermixing said recovered oil with aqueous liquid to obtain purified oil and separating said purified oil from the resultant aqueous liquid. Oil purified in this manner is typically substantially free of non-gaseous polymerization-debilitating substances, and is generally suitable for use in subsequent polymerizations. Said aqueous liquid is preferably water, more preferably aqueous acid. Said acid is preferably an inorganic acid, more preferably sulfuric acid. In a preferred embodiment, a vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion is comprised of an oil recovered from a polymer-containing water-in-oil emulsion or water-in-oil microemulsion spray-drying process. Both purified oil and recovered oil may be treated to remove gaseous polymerization-debilitating substances such as ammonia, oxygen, methylchloride, dimethylamine, formaldehyde, etc. by known means such as by sparging with an inert gas e.g. nitrogen, helium, etc.

One way to determine whether a treated, recovered, or purified oil is substantially free of non-gaseous polymerization-debilitating substances is to use a particular oil to prepare a vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion which is subsequently spray-dried, and then to recover the condensed or cocondensed oil and, optionally, to purify the recovered oil. If the resultant recovered or purified oil is substantially free of non-gaseous polymerization-debilitating substances, the molecular weight or solution viscosity of polyacrylamide prepared by polymerizing or copolymerizing acrylamide in a water-in-oil emulsion or water-in-oil microemulsion using said particular oil will generally be substantially the same as the molecular weight or solution viscosity of polyacrylamide prepared by polymerizing acrylamide in a dispersion, water-in-oil emulsion or water-in-oil microemulsion using virgin oil in an oil, under otherwise substantially identical conditions.

In one embodiment of the instant invention, the level of formaldehyde in the recovered or purified oil obtained by spray-drying a water-in-oil dispersion, emulsion or microemulsion, preferably a quaternized Mannich poly(alk)acrylamide microemulsion, is typically less than one hundred milligrams formaldehyde per kilogram of recovered or purified oil, preferably less than ten milligrams formaldehyde per kilogram of recovered or purified oil, and most preferably less than ten milligram formaldehyde per kilogram of recovered or purified oil. Formaldehyde may be detrimental to certain types of polymerization processes, so that a very much reduced level of formaldehyde in the recovered or purified oil is a substantial advantage. It is economically and environmentally advantageous to recycle the oil for use in other processes, including the same or other polymerization processes. The lack of oil and certain residual chemical reagents from the post-reaction step, in particular formaldehyde, in the polymer particles are also substantial environmental advantages.

There are four interrelated operating parameters in the instant spray-drying process: gas inlet temperature, gas outlet temperature, product volatiles and residence time in the dryer. The outlet temperature generally should be less than 100°C, preferably 95°C or below, more preferably 90°C or below, but 70°C or higher, preferably 75°C or higher. Therefore, outlet temperatures are generally 70°C to less than 100°C, preferably 70°C to 95°C, more preferably 75°C to 90°C.

Generally, the dryer should be operated at the lowest possible outlet temperature consistent with obtaining a satisfactory produce. In accordance with this invention, to facilitate operating at the lowest possible operating temperature, the vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion is comprised of a volatile oil. "Volatile", for purposes of this invention, means that the boiling point or upper end of the boiling point range of the oil is 200°C or below, preferably 190°C or below, most preferably 180°C or below. The use of a volatile oil allows for spray drying of the vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion to be carried out at low outlet temperatures so that polymer degradation is avoided or substantially reduced. Although in theory an oil with a very low boiling point, say room temperature or below, would be most preferable to avoid produce degradation, in practice oils with low boiling points in this range may, under some circumstances, be unacceptable for other reasons related to handling and flammability. Thus, oils having a boiling point within the range from 70°C to 190°C, preferably from 130°C to 185°C, most preferably from 160°C to 180°C are used. Suitable oils useful herein include any organic hydrocarbon liquids such as halogenated hydrocarbons, aliphatic hydrocarbons, aromatic hydrocarbons, mixtures of aromatic and aliphatic hydrocarbons, etc. usually containing about 6 to about 12 carbon atoms. Preferred examples of suitable hydrocarbons include perchloroethylene, benzene, xylene, toluene, mineral oil fractions, kerosenes, naphthas, petroleum fractions and the like. A most preferred oil is a material called Isopar G manufactured by Exxon Chemical. Isopar G is a mixture of synthetic isoparaffinic hydrocarbons having a boiling point range of 160°C to 177°C.

The inlet temperature, the feed rate, and the composition of the polymer emulsion may all affect outlet tem-
peratures. These parameters may be varied to provide a desired outlet temperature. Feed rates are not critical, and generally will vary depending on the size of the dryer and the gas flow rate. Inlet gas temperature is less critical than outlet gas temperature, and is generally 140°C or above, preferably 160°C or above. The inlet gas temperature is preferably 200°C or below and more preferably 180°C or below. Thus, preferred inlet gas temperature ranges from 140°C to 200°C, more preferably from 160°C to 180°C. Proper inlet gas temperatures tend to avoid product degradation on the high side and to avoid inadequate drying on the low side.

[0025] Residence time is a nominal value obtained by dividing the volume of the dryer by the volumetric gas flow. Residence time is generally at least 8 seconds, preferably at least 10 seconds. Residence time is generally no more than 120 seconds, preferably no more than 90 seconds, more preferably no more than 60 seconds, and most preferably no more than 30 seconds. Therefore, the general range of residence time is 8 to 120 seconds, preferably 10 to 90 seconds, more preferably 10 to 60 seconds, and most preferably 10 to 30 seconds. It is known to those skilled in the art that longer residence times are to be expected when larger dryers are used or when the dryer is run in a less efficient manner. For instance, at the cost of efficiency, longer residence times would be expected at very low inlet temperatures and slow gas flow rates.

[0026] Any water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, water-in-oil emulsion or water-in-oil microemulsion may be spray-dried by the processes of the instant invention. For purposes of this invention, water-swellable polymers are generally those that have been crosslinked to a certain degree, preferably by forming the polymer in the presence of certain amounts of crosslinking or branching agents. Preferably, water-swellable polymers include microbeads of U.S. Patent Nos. 5,274,055 and 5,167,766. Water-soluble, branched polymers generally result when smaller amounts of crosslinking agent are used to formulate the polymer, as in EP-A-374,458. Most preferably, the water-soluble or water-swellable vinyl-addition polymer-containing dispersion, water-in-oil emulsion or water-in-oil microemulsion is as described in U.S. Pat. Nos. 4,956,399; 4,956,400; 5,037,881; 5,132,023; 5,286,806; 4,767,540; 5,274,055; 5,167,766; and 5,847,056; and EP-A-374,458. The vinyl-addition polymer content of the water-in-oil dispersion, emulsion or microemulsion is generally about 10% or greater, preferably greater than 15%, more preferably about 17% or greater, and most preferably 20% or greater, by weight based on total weight.

[0027] Preferably, the vinyl-addition polymer-containing, water-in-oil dispersions, emulsions or microemulsions are comprised of a polymer having pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, hydroxamic acid salt, dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate. Thus the polymer may be Mannich poly(alk)acrylamide, quatemized Mannich poly (alk)acrylamide, hydroxamated polyacrylamide, esterified (meth)acrylic acid polymer, esterified (meth)acrylic acid copolymer, and hydrolyzed polyacrylamide. Hydrolyzed polyacrylamide may be formed by inadvertent hydrolysis during production, but is preferably post-reacted e.g. deliberately reacted with acid or base to a degree of hydrolysis of 5 mole% or more, preferably 10 mole% or more, based on total moles of recurring units, most preferably as disclosed in U.S. Patent No. 5,286,806. The polymer may contain recurring units selected from the group consisting of acrylamide, dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, quaternized dialkylaminoalkyl(alk)acrylate, (meth)acrylic acid, and salts of (meth)acrylic acid. Preferred polymers included (1) a polymer containing 10 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt and having a standard viscosity of at least 8.0 cps, (2) a polymer containing 20 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt and having a standard viscosity of at least 9.0 cps, (3) a polymer containing at least 1 mole % of tertiary aminomethyl groups, (4) an acrylamide polymer containing at least 1 mole% of quaternized tertiary aminomethyl groups, (5) an acrylamide polymer containing at least 1 mole% of hydroxamic acid or hydroxamic acid salt groups, (6) an esterified polymer containing hydroxamic acid groups and carboxylic acid groups or salts thereof, and (7) an ionic, organic, polymer microbead being less than 750 nanometers in diameter if crosslinked and less than 60 nanometers in diameter if non-crosslinked and water-insoluble, the ionicity of the microbead being at least 1%, preferably having 1 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt. Polymers and copolymers of acrylamide are particularly preferred.

[0028] In a preferred embodiment, the vinyl-addition polymer-containing water-in-oil emulsion or microemulsion is a Mannich poly(alk)acrylamide or quaternized Mannich poly(alk)acrylamide-containing water-in-oil emulsion or microemulsion. Mannich polyacrylamide and quaternary Mannich polyacrylamide water-in-oil microemulsions may be heat treated prior to spray drying according to methods described in U.S. Patent No. 5,627,260.

[0029] The instant invention is of particular value for preparing substantially dry, functionalized or post-reacted polymers. In many cases functionalized polymers are those that may be or have been post-reacted, e.g. a chemical reaction has been performed on the polymer after the formation of the polymer from the corresponding monomers, see e.g. U.S. Patent No. 4,956,400. The chemical reaction is generally deliberate or purposeful, and polymers which are inadvertently or indifferently reacted e.g. slightly hydrolyzed during the course of production are not generally considered to be functionalized. For example, Mannich poly(alk)acrylamides, quaternized Mannich poly(alk)acryla-
The water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersions emulsions or microemulsions used in the instant invention are generally prepared by polymerization of the corresponding monomers, preferably as described in U. S. Pat. Nos. 4,956,399; 4,956,400; 5,037,881; 5,132,023; 5,286,806; 4,767,540; 5,274,055; 5,167,766; and 5,847,056; and EP-A-374,458. The monomers may be polymerized in a water-in-oil dispersion, emulsion or microemulsion. Water-in-oil emulsions or water-in-oil microemulsions are preferred. All dispersions, emulsions and microemulsions described herein are inverse or water-in-oil. An emulsion, for purposes of this invention, is generally defined as a composition comprising two liquids or phases which are insoluble in each other along with a surfactant, surfactant mixture or emulsifier. A microemulsion, for purposes of this invention, is generally defined as a thermodynamically stable composition comprising two liquids or phases which are insoluble in each other along with a surfactant, surfactant mixture or emulsifier. Polymeric inverse microemulsions which contain a continuous oil phase and a polymer-containing discontinuous phase (usually aqueous) are prepared from thermodynamically stable monomer microemulsions. Inverse microemulsions have a narrow droplet size distribution and are usually, but not always, optically transparent. The discontinuous polymer-containing phase of a microemulsion forms droplets or micelles, which are usually aqueous and usually have a volume average droplet diameter which is less than 2500 Å, preferably less than 2000 Å, and most preferably less than 1000 Å. Some microemulsions may have a volume average droplet diameter as large as 3000 Å.

Water-in-oil emulsions are well-known in the art, see e.g. Vanderhoff U.S. Patent No. 3,284,393. For the purposes of this invention, dispersions are compositions comprises of polymer beads or droplets that are dispersed in oil, generally with reduced surfactant levels, but generally including other types of stabilizers, as described in e.g. U. S. Patent Nos. 4,528,321; 4,628,078 and 4,506,062.

Homopolymers and copolymers of the monomers enumerated herein are fully encompassed by the instant invention. Preferred nonionic monomers are water-soluble monomers such as (meth)acrylamide, N-vinyl pyrrolidone, N,N-dialkyl(meth)acrylamide, hydroxyalkyl(meth)acrylate, N-vinylformamide and the like. Small quantities e.g. about 10% or less, of other monomers having limited water solubility e.g. methyl acrylate, styrene, methyl methacrylate, acrylonitrile, vinyl acetate, etc. may also be used, provided that the resulting polymer is water-soluble or water-swellable. Generally, water-swellable polymers are crosslinked polymers, not polymers containing so many water-insoluble recurring units that they swell without dissolving in water. Acrylamide and methacrylamide are especially preferred nonionic monomers. Although, in some instances, the polymer may contain 80% or even 100% nonionic monomer, preferably, the polymer contains 50% or less of nonionic monomer, preferably about 40% or less, most preferably 30% or less, by mole based on total moles of polymer repeat units.

Water-swellable polymers or water-soluble, branched polymers may be produced by copolymerization with multifunctional branching agents e.g. methylenebisacrylamide.

Useful cationic monomers include salts and quaternaries of dialkylaminoalkyl(alk)acrylate and dialkylaminoalkyl(meth)acrylamide, and diallyldialkylammonium halide. Preferred quatemizing agents are methyl chloride, ethyl chloride, benzyl chloride, dimethylsulfate, and diethylsulfate. Preferred cationic monomers include the methyl chloride salt of dimethylaminoethyl(meth)acrylate, the methyl chloride salt of dimethylaminopropyl(meth)acrylamide, and diallyldimethylammonium chloride. Preferably, the polymer contains 5% or more of cationic monomer, preferably 10% or more, most preferably 30% or more, by mole based on total moles of polymer repeat units.

Preferential anionic monomers include (meth)acrylic acid, fumaric acid, crotonic acid, maleic acid, 2-acrylamido-2-methylpropanesulfonic acid, styrenesulfonic acid, and salts thereof. Sodium and ammonium salts are preferred. Preferred anionic monomers include sodium acrylate, potassium acrylate, ammonium acrylate, and the sodium salt of 2-acrylamido-2-methylpropanesulfonic acid. Generally, the polymers contain enough of the salt form of the acid such that the polymer is water-soluble or water-swellable, preferably greater than 50% of the acid monomers are in the salt form, more preferably 60% or greater, by weight based on total weight. Preferably, the polymer contains 5% or more of anionic monomer, preferably 50% or more, more preferably 70% or more, most preferably 75% or more, by mole based on total moles of polymer repeat units.

The polymerization may be carried out in the presence of such conventional additives as are desired. For example, the polymerization may contain chelating agents to remove polymerization inhibitors, chain transfer agents, pH adjusters, initiators and other conventional additives. Polymerization of the monomers may be carried out in any manner known to those skilled in the art. Initiation may be effected with a variety of thermal and redox free radical initiators, including peroxides, e.g. t-butyl peroxide; azo compounds, e.g. azobisisobutyronitrile; inorganic compounds, such as potassium persulfate and redox couples, such as ferrous ammonium sulfate/ammonium persulfate. A preferred initiator is sodium bromate/sulfur dioxide. Initiator addition may be effected any time prior to the actual polymerization per se. Polymerization may also be effected by photochemical irradiation processes, such as ultraviolet irradiation or by ionizing irradiation from a cobalt 60 source.
Surfactants and/or dispersing agents are generally helpful and sometimes necessary for the formation and continued stability of vinyl-addition polymer-containing water-in-oil dispersions, emulsions and microemulsions. As spray-drying is contemplated, ongoing stability may not be required, and it may be advantageous to reduce or eliminate the surfactants and/or dispersing agents. Vinyl-addition polymer-containing water-in-oil dispersions, emulsions and microemulsions may be prepared using little or no surfactants and/or dispersing agent and spray-dried soon thereafter, preferably during the period of continued stability. Preferably, the vinyl-addition polymer-containing water-in-oil dispersion emulsions and microemulsions contain 2% or less of surfactant and/or dispersing agent, more preferably 1% or less, by weight based on total weight. The spray-dried polymer particles made by the processes of instant invention preferably contain 6% or less of surfactant and/or dispersing agent, preferably 4% or less.

Substantially dry water-soluble or water-swellable polymer particles may be produced from a blend by (a) spray-drying a blend comprised of, or made by intermixing, (i) a first water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion and (ii) a second water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion, and (b) collecting resultant polymer particles. Preferred blends of water-in-oil emulsions and water-in-oil microemulsions are disclosed in U.S.-A.-5,883,161 and 5,763,530.

Blending of water-in-oil emulsions and water-in-oil microemulsions may advantageously provide a product with improved performance by e.g. providing a property such as charge or molecular weight that is different from the individual emulsions or microemulsions from which the blend is derived. The different property may result from averaging of the properties of the blend components, or occasionally synergistic results may be observed. For instance, when treating substrates that are themselves blends or mixtures of various components, each of the blend components may have a specific role in product performance. Accordingly, although two identical water-in-oil emulsions and water-in-oil microemulsions could be blended, it generally preferred to blend emulsions or microemulsions that are different from each other e.g. different performance, different charge, different viscosity, different molecular weight, different physical form, different chemical identity, different aging characteristics, different costs, etc.

Spray-drying of blends is advantageous because typically 90% or greater, preferably 95% or greater, most preferably substantially all, of the resultant spray-dried polymer particles each individually contains two or more water-soluble or water-swellable vinyl-addition polymers, so that stratification effects may be minimized. Spray-drying a blend may be particularly advantageous when the first water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion has a viscosity that is different from the viscosity of the second water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion. This is because viscosity generally impacts the particle size distribution of the spray dried polymer particles, so that the particle size distribution of the particles obtained from the first water-in-oil emulsion or water-in-oil microemulsion may be different from the particle size distribution of the particles obtained from the second water-in-oil emulsion or water-in-oil microemulsion. A dry blend of the two different polymers is thus likely to exhibit greater stratification than a dry blend obtained by spray-drying a blend of the first and second water-in-oil emulsions or water-in-oil microemulsions.

In an embodiment of the instant invention, the Mannich and quaternary Mannich polymer particles obtained have, in some cases, substantially reduced residual contamination by certain chemical reagents added during the functionalization step e.g. formaldehyde, methyl chloride and amines. Typically, the residual level of methyl chloride in the polymer particles is below 500 parts per million parts (ppm), based on the total weight of the particles, and preferably below 100 ppm, same basis. Formaldehyde is typically below 2000 ppm and preferably below 1000 ppm, same basis. Individual residual amines, which may be present as their hydrochloride salts, are typically present at below 20,000 ppm and preferably below 10,000 ppm, same basis.

With respect to the various spray-dried and agglomerated polymer products described herein, the optimum standard viscosity for a particular polymer is very dependent on the application e.g. flocculation of suspended solids, paper making, oil recovery, mining, etc. For instance, for many applications, it is preferred that the standard viscosity of the polymer particles be 1.5 centipoise or greater, more preferably 2.0 centipoise or greater, most preferably 2.5 centipoise or greater. However, applications other than flocculation may require polymers with standard viscosities higher or lower than those given above. One advantage of the instant invention is that the standard viscosity of the polymer particles reduced according to the processes described herein is generally within 15% of the standard viscosity of the corresponding polymer water-in-oil dispersion, emulsion or microemulsion. This indicates that the polymers are not substantially altered by the spray-drying process.

Generally, the polymers of the instant invention have a molecular weight of 100,000 or greater, preferably greater than 1,000,000; more preferably greater than 10,000,000, most preferably greater than 20,000,000. The optimum molecular weight or molecular weight range for a particular polymer is also very dependent on the application e.g. flocculation of suspended solids, paper making, oil recovery, mining, etc. For instance, for many flocculant applications, Mannich polyacrylamide and quaternized derivatives thereof have a molecular weight greater than 100,000 and preferably greater than 1,000,000. However, applications other than flocculation may require polymers with molecular
weights higher or lower than those given above. The water-soluble polymers produced by the processes described herein may contain small amounts of insoluble polymer. Such small amounts of insoluble polymer do not generally affect the performance of the polymer in, for instance, the applications mentioned above. In some cases, water-swellable polymers are desired for applications such as fluid thickening, papermaking, printing ink thickeners, etc.

[0043] When produced according to the spray drying processes disclosed herein, polymer particles of the instant invention are generally 10 microns or greater in diameter, preferably 40 microns or greater, more preferably 100 microns or greater, most preferably 200 microns or greater. It is preferred that the polymer particles be non-dusting. Dusting and flow problems are typically exacerbated when the polymer particles are small, so larger polymer particles are generally desirable. However, very large particles may dissolve more slowly. Therefore, it is generally desirable for the polymer particles to be 1200 microns or less in diameter, preferably 800 microns or less in diameter, more preferably 600 microns or less, most preferably 400 microns or less. Generally, at least 90% of the polymer particles range in size from 10 microns to 1200 microns, preferably at least 95%, more preferably at least 98%. The size of the polymer particles can be varied somewhat by altering the operational parameters e.g. spray configuration, emulsion viscosity, feed rate, etc. Particles may be substantially spherical or non-spherical; “diameter” of a non-spherical particle is the dimension along a major axis.

[0044] Although in some cases the particles are hollow, porous structures having at least one opening in their walls, it has been discovered that these features are not always necessary in order to obtain particles having desirable properties e.g. fast dissolution times. In many cases, the spray-drying parameters e.g. nozzle type, nozzle size, outlet temperature, etc. needed to produce particles that are hollow, porous structures having at least one opening in their walls are inconvenient or uneconomical, and it is advantageous to produce particles that lack some or all of these features.

[0045] The particles formed by the spray-drying processes of the instant invention may be screened to remove an oversize or undersize fraction. Oversize particles may be fragmented by e.g. grinding, whereas undersized particles are generally agglomerated. Sizes may be determined by methods known to those skilled in the art e.g. sieving, screening, light scattering, microscopy, microscopic automated image analysis, etc.

[0046] Surprisingly, the bulk densities of the spray-dried polymer particles of the instant invention are generally greater than the bulk densities of dry polymers prepared by precipitation of the corresponding water-in-oil dispersion, water-in-oil emulsion or water-in-oil microemulsion. Polymer particles having greater density may be advantageous because they occupy a smaller volume, resulting in e.g. lower shipping and storage costs. Whereas the densities of precipitated polymers are usually less than 0.35 grams per cubic centimeter (g/cc), the bulk densities of the spray-dried polymer particles of the instant invention are generally greater than 0.35 g/cc or greater, preferably 0.4 g/cc or greater, more preferably 0.45 g/cc or greater, most preferably 0.50 g/cc or greater. The bulk densities of the spray-dried polymer particles of the instant invention are generally 1.1 g/cc or less, preferably 1.0 g/cc or less, more preferably 0.95 g/cc or less, most preferably 0.90 g/cc or less. Therefore, the bulk densities of the spray-dried polymer particles of the instant invention generally range from 0.35 to 1.1 g/cc, preferably 0.4 to 1.0 g/cc, more preferably 0.45 to 0.95 g/cc, most preferably 0.50 to 0.90 g/cc.

[0047] Under the conditions of drying set forth herein, the polymer particles produced by the processes described herein are substantially dry. As used to describe the polymer produced herein, “substantially dry” generally means that the polymer contains 12% or less volatiles, preferably 10% or less by weight, based on the weight of the spray dried polymer. The polymer generally contains 2% or more volatiles, preferably 5% or more, by weight based on total weight, and most preferably contains from 8% to 10% volatiles by weight, same basis. The volatiles are measured by determining the weight loss on drying the polymer product at 105°C for 30 minutes.

[0048] Additional materials such as flow control agents, dust control agents, pH adjusting agents, surfactant, emulsifier, etc. and the like may be added to the emulsion or microemulsion before or during the spray drying process, or to the polymer particles after the spray drying process, or both, to enhance the production, distribution, packaging, handling, performance, etc. and the like of the polymer particles.

[0049] We have also discovered that mixing, in any order, an acid, base or buffer with the substantially dry water-soluble polymer particles that are the product of the spray drying processes described herein, may be advantageous. A buffer, for the purposes of this invention, is a substance or blend of substances that, when dissolved in water, gives a solution that resists changes in pH when small amounts of acid or base are added. Preferably, a buffer contains an acid and a base. For example, any solution of a weak acid plus a salt of that acid is a buffer solution. A base, for the purposes of this invention, is a substance or blend of substances that, when dissolved in pure water, gives a solution with a pH value greater than 7. An acid, for the purposes of this invention, is a substance or blend of substances that, when dissolved in pure water, gives a solution with a pH value less than 7. The addition of an acid, base or buffer to the polymer particles may enhance the flow properties of the dry polymer particles and adjusts the pH of the solution that the polymer particles are dissolved into so as to enhance the rate of dissolution and performance of the polymer particles in the desired application. Bases are preferred and buffers are most preferred. Acids, bases and buffers useful in the instant invention may be solid or liquid, though it is especially preferred to use an acid, base, or buffer that is
Any base known in the art may be used. Suitable powdered bases may include the alkali and alkaline earth metal salts of carbonate, bicarbonate, citrate, phosphate and acetate. Preferred bases may include sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, sodium acetate, potassium acetate, sodium citrate, potassium citrate, sodium phosphate, potassium phosphate, etc. and the like. Sodium carbonate and sodium bicarbonate are more preferred, and sodium bicarbonate is most preferred. The mixture of the base and the polymer particles is such that the base may be incorporated into the interior of the particles, or may coat the surface of the particles, or may be distinct from the particles, or any combination thereof.

Any acid known in the art may be used. Suitable acids may comprise inorganic acids e.g. hydrochloric acid, nitrous acid, nitric acid, carbonic acid, phosphoric acid, phosphorus acid, sulfurous acid, and sulfuric acid, as well as organic acids e.g. acetic acid, lactic acid, citric acid, formic acid, alkylsulfonic acids, etc. and the like. Acids such as KH₂PO₄, Na₂HPO₄ and hydrates thereof are preferred. In instances where a quaternary Mannich polyacrylamide is formed when a base is added to a water-in-oil emulsion or water-in-oil microemulsion before spray drying. The solution or slurry of the acid, base or buffer may be spray dried simultaneously or substantially simultaneously with the spray drying of the water-in-oil emulsion or water-in-oil microemulsion, or the acid, base, or buffer may be added directly to the spray dryer while simultaneously or substantially simultaneously spray drying the water-in-oil emulsion or water-in-oil microemulsion, to form polymer particles which comprise the acid, base, or buffer. In this case, the acid, base, or buffer need not be substantially dry. Another, also less preferred, way to add one or more acids, bases, or buffers to the polymer is to add part of the acid, base, or buffer before or during the spray dry process, and part of the acid, base, or buffer, or perhaps a different acid, base, or buffer, to the resulting polymer particles. The buffer may be formed when a base is added to an water-in-oil emulsion or water-in-oil microemulsion or polymer particle which already contains the corresponding base, or the buffer may be formed when an acid is added to a water-in-oil emulsion or water-in-oil microemulsion or polymer particle that already contains the corresponding base.

It is preferred to add the acid, base or buffer directly to the polymer particles. Alternatively, and less preferably, an acid, base or buffer may be dissolved in water or oil to form a solution or slurry and added to the water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil emulsion or water-in-oil microemulsion before spray drying. The solution or slurry of the acid, base or buffer may be spray dried simultaneously or substantially simultaneously with the spray drying of the water-in-oil emulsion or water-in-oil microemulsion, or the acid, base, or buffer may be added directly to the spray dryer while simultaneously or substantially simultaneously spray drying the water-in-oil emulsion or water-in-oil microemulsion, to form polymer particles which comprise the acid, base, or buffer. In this case, the acid, base, or buffer need not be substantially dry. Another, also less preferred, way to add one or more acids, bases, or buffers to the polymer is to add part of the acid, base, or buffer before or during the spray dry process, and part of the acid, base, or buffer, or perhaps a different acid, base, or buffer, to the resulting polymer particles. The buffer may be formed when a base is added to an water-in-oil emulsion or water-in-oil microemulsion or polymer particle which already contains the corresponding base, or the buffer may be formed when an acid is added to a water-in-oil emulsion or water-in-oil microemulsion or polymer particle that already contains the corresponding base.

The amount of base, acid or buffer to be added to the water-soluble Mannich acrylamide or quatemized Mannich acrylamide polymer particles of the present invention is preferably an amount sufficient to provide a solution pH of from 5 to 11, preferably from 5.5 to 9 and most preferably 6 to 8, when the particles or particle compositions are dissolved in water. Regardless of the manner in which acid, base or buffer is added (i.e., whether added to the emulsion prior to or during spray drying or to the particles after spray drying) the amount should be such that the resulting solution containing dissolved polymer particles has a pH at least 5, preferably at least 6 and below 11, preferably a pH below 8. It is understood that the pH of the resulting solution will depend on the pH of the water before the polymer particles are added. For instance, in order to produce a preferred pH in the resulting solution in the range of 5 to 9, more base should generally be present in the particles if the water is more acidic than if the water is less acidic. It is likewise understood that the preferred amount of base present in the polymer particles may depend on the pH of the water into which the polymer particles are to be dissolved. For example, for many waters of moderate acidity, the polymer particles should contain 0.1% to 3.5%, based on total weight, of a preferred base such as sodium bicarbonate. Generally, the polymer particles may contain base in an amount of at least 0.05% by weight, preferably at least about 0.1% and generally up to 10.0% preferably up to 20.0% by weight based on total particle weight. More preferably the amount of base ranges from 0.05% to 5.0%, based on total weight of particles. The aforesaid amounts also apply to acids. Similar reasoning is understood concerning the optimum amount of acid; i.e. the presence of more acid will be preferred in the particles when the water is more basic than when the water is less basic in order for the solution of the polymer to have the desired pH. Routine experimentation by one skilled in the art may be used to determine the appropriate amount of acid, base or buffer for a particular water.

Likewise, the amount of buffer will also depend on the pH of the water before the polymer particles are added. The amount of buffer present will tend to affect the ability of the polymer solution to resist changes in pH. For instance, for a preferred buffer system such as KH₂PO₄ / Na₂HPO₄, 12 H₂O, the buffer should be at least 0.1%, by weight, and preferably at least 5%, by weight, of the total weight of the particles. Although it would seem preferable to use as much...
buffer as possible so as to provide the polymer solution with the greatest ability to resist pH changes, it is also preferable for the polymer particles to contain as much polymer as possible. Thus, in practice, the buffer should comprise less than 50%, by weight, of the polymer particles, and preferably less than 30%, by weight, same basis. Therefore, the buffer should be present in the polymer particles at a level of at least 0.05%, generally from 0.1% to 50%, by weight, and preferably 5% to 30%, by weight, based on the total particle weight. The exact amount of buffer depends on the pH of the water and how strongly the polymer solution needs to be able to resist changes in pH.

[0057] In addition to pH, another factor which tends to influence the rate of dissolution of the polymer particles and the performance of the polymer is the temperature of the polymer solution or the solution into which the polymer particles are dissolved. Therefore, the amount of acid, base, or buffer present in the polymer particles may vary depending on the temperature of the water into which the polymer is to be dissolved. For instance, quaternized Mannich polyacrylamide tends to dissolve more readily at higher temperatures, so that a lower pH, such as 5, may be desired to dissolve the polymer when the temperature of the water is higher, such as 35°C, whereas a pH of 8 may be preferred if the water temperature is very low, such as 5°C. It is apparent, therefore, from the foregoing that less base, or more acid, might be preferred at high temperatures than at low temperatures, and that the selection of buffer will also depend on the temperature.

[0058] The particle size of the acid, base, or buffer is not particularly important, and may be varied to optimize the flow properties of the mixture with the polymer particles. For instance, a preferred range of particle sizes for sodium bicarbonate is from 10 to 500 microns, more preferably 50 to 300 microns. The means for adding and mixing the substantially dry base to the polymer particles are likewise not critical. Any mechanical mixing means known to those skilled in the art for mixing granular solids is suitable.

[0059] It has also been discovered that agglomeration of the polymer particles of the instant invention may improve the flow properties and dissolution times of the polymers. Agglomeration is a known process for increasing particle size and various methods for agglomerating particles are known to those skilled in the art, e.g. "Successfully Use Agglomeration for Size Enlargement," by Wolfgang Pietsch, Chemical Engineering Progress, April 1996, pp. 29-45;

"Speeding up Continuous Mixing Agglomeration with Fast Agitation and Short Residence Times," by Peter Koenig, Powder and Bulk Engineering, February 1996, pp. 67-84. Known agglomeration methods such as natural agglomeration, mechanical agglomeration, tumble or growth agglomeration, pressure agglomeration, binderless agglomeration, agglomeration with binders, etc. may be used to agglomerate the polymer particles of the instant invention. Agglomeration is preferably followed by drying e.g. fluid bed drying, to remove binder e.g. water. Pressure agglomeration is preferred, and mechanical agglomeration using a water binder, followed by fluid bed drying is most preferred.

[0060] The agglomerates formed by agglomerating the polymer particles tend to have improved flow properties and faster dissolution times when compared to the unagglomerated polymer particles. Preferably, the agglomerates are non-dusting. Flow properties may be measured by measuring flow times as described in the Examples. Dissolution rates may be determined by measuring the increase in viscosity of a polymer solution as a function of dissolution time, as described in the Examples. Typically, 90% of the agglomerates obtained by the instant invention have an aggregate size of 120 microns or greater, preferably 160 microns or greater, more preferably 200 microns or greater, most preferably 300 microns or greater. Generally, 90% of the agglomerates have an aggregate size of 1500 microns or less, preferably 1200 microns or less, more preferably 1100 microns or less, most preferably 1000 microns or less. Thus, 90%, preferably 95%, of the agglomerates have a size in the range of 120 to 1500 microns, preferably 160 microns to 1200 microns, more preferably 200 microns to 1100 microns, most preferably 300 microns to 1000 microns. Usually, at least 5% of the agglomerates, preferably at least 10%, most preferably at least 15%, are larger than 900 microns. The agglomerates formed by agglomerating the spray-dried particles obtained by the instant invention may be screened to remove an oversize or undersize fraction. Preferably, agglomerates larger than 1200 microns and smaller than 175 microns are removed by e.g. screening. Oversize agglomerates are generally fragmented by e.g. grinding, whereas undersized agglomerates are generally recycled into the agglomerator.

[0061] The bulk density values of the agglomerates obtained by the instant invention tend to be lower than the bulk density values of the spray-dried particles from which they are formed. The bulk densities of the agglomerates of the instant invention are generally 0.35 g/cc or greater, preferably 0.4 g/cc or greater, more preferably 0.45 g/cc or greater, most preferably 0.50 g/cc or greater. The bulk densities of the agglomerates are generally 1.0 g/cc or less, preferably 0.95 g/cc or less, more preferably 0.90 g/cc or less, most preferably 0.85 g/cc or less. Therefore, the bulk densities of the agglomerates generally range from 0.35 to 1.0 g/cc, preferably 0.4 to 0.95 g/cc, more preferably 0.45 to 0.90 g/cc, most preferably 0.50 to 0.85 g/cc.

[0062] In order to obtain agglomerates of a preferred size, it is preferred that the polymer particles themselves be of such a size that they are agglomerable. Agglomeration obviously tends to multiply the average particle size, so that it is frequently easier to cause large increases in particle size than it is to cause small increases in particle size. Therefore, to produce agglomerates of a preferred size or size range, it is generally preferred to agglomerate particles that are much smaller than the desired agglomerate size, rather than particles that are only slightly smaller. Agglomerable particles are generally those that may be conveniently agglomerated to produce agglomerates having a preferred size.
It is possible, but less preferred, to agglomerate larger particles to produce agglomerates that are larger than desired, then remove the oversize agglomerates as described above.

The substantially dry polymer particles and agglomerates obtained according to the present invention are generally comprised of the polymer that was contained in the water-in-oil emulsion, or water-in-oil microemulsion that was spray-dried, as discussed hereinabove. Preferably, the substantially dry polymer particles and agglomerates of the present invention are comprised of polymer having pendant groups selected from the group consisting of amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxyl, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid, hydroxamic acid salt, dialkylaminoalkyl(alk)acrylate, dialkylaminoalkyl(alk)acrylate salts, and quaternized dialkylaminoalkyl(alk)acrylate. Polymers and copolymers of acrylamide are preferred.

In a preferred embodiment, substantially dry water-soluble or water-swellable polymer particles and agglomerates are comprised of a polymer having 1 mole % or more of recurring units having pendant groups selected from the group consisting of tertiary aminomethyl, quaternized tertiary aminomethyl, glyoxal, hydroxamic acid, and hydroxamic acid salt, based on total moles of recurring units. In another preferred embodiment, substantially dry water-soluble polymer particles and agglomerates are comprised of a polymer having 1 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt, based on total moles of recurring units, said polymer having a standard viscosity of 7.0 cps or greater, and in another preferred embodiment, said polymer is further comprised of recurring units having pendant alkyl ester groups, wherein said alkyl ester groups contain from 2 to 12 carbon atoms. In another preferred embodiment, substantially dry water-soluble or water-swellable polymer particles and agglomerates are comprised of acrylamide, (meth)acryloxyethyltrimethylammonium chloride, copolymers thereof and, optionally, branching agent e.g. methylenebisacrylamide, as described in EP-A-374,458.

In another preferred embodiment, substantially dry water-soluble polymer particles and agglomerates are comprised of a polymer having 10 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt and wherein said polymer has a standard viscosity of at least 8.0 cps, or (b) wherein said polymer contains 20 mole % or more of recurring units having pendant groups selected from the group consisting of carboxylic acid and carboxylic acid salt and wherein said polymer has a standard viscosity of at least 9.0 cps.

In yet another preferred embodiment, substantially dry water-soluble polymer particles and agglomerates are comprised of an ionic, organic, polymer microbead being less than 750 nanometers in diameter if crosslinked and less than 60 nanometers in diameter if non-crosslinked and water-insoluble, the ionicity of the microbead being at least 1%.

The substantially dry polymer particles and agglomerates of the present invention generally exhibit improved stability relative to the water-in-oil emulsion, or water-in-oil microemulsion from which they were derived. For instance, Table 7 shows the change in standard viscosity as a function of time at 90°C for spray dried quatemized Mannich polyacrylamide, compared to a quaternized Mannich polyacrylamide microemulsion from which the spray dried polymer was derived. The standard viscosity of the microemulsion polymer changed substantially as a function of time, whereas the change in standard viscosity for the spray dried polymer was much less. Table 8 shows data obtained in a similar manner, except that the dry polymer and the microemulsion polymer were stored at ambient temperature. Once again, the standard viscosity of the microemulsion polymer changed substantially as a function of time, whereas the change in standard viscosity for the spray dried polymer was not substantial. In both cases, at room temperature and at 90°C, it is quite surprising that the spray dried polymer shows greater stability, as measured by standard viscosity, than the corresponding polymer contained in the microemulsion.

Surprisingly, the standard viscosities of the polymer particles and agglomerates that are the product of the process described herein are not substantially reduced by the spray drying process of the invention. Generally, the standard viscosity values of the polymer particles are not decreased by greater than 15 % of their initial value, preferably not greater than 10%, more preferably not greater than 8%, most preferably not greater than 5%, as a result of the spray drying process, even when the standard viscosity of the polymer in the polymer-containing water-in-oil microemulsions is observed to decrease quickly at elevated temperatures as described hereinabove. It is also surprising that the short residence times result in polymer particles with low volatile levels. Moreover, the residual level of oil in the finely divided polymer particles is typically very low, usually less than 1.0 % by weight, based on the total weight of the particles, and preferably less than 0.2% by weight, same basis.

The free flowing, substantially dry, water-soluble polymer particles and agglomerates that are the product of the invention described herein may be used in many applications, such as, for example, solids/liquids separation; flocculants for mining operations to recover ore from slurries; flocculants for water treating to remove suspended impurities etc.; in paper making as a flocculant and to aid paper formation e.g. retention aids; in oil recovery industries e.g. enhanced oil recovery, treatment of oily wastewater, etc., in agriculture e.g. soil stabilization or soil conditioning; in biotechnological applications e.g. treatment of enzyme broths; and in food processing e.g. flocculation of suspended food particles. The polymers of the present invention can conveniently be employed e.g. as flocculants in the form of dilute aqueous solutions. These solutions can be prepared by intermixing, dispersing, and/or dissolving the particles
in or with water. Concentrating dispersions of suspended solids is carried out by adding an effective amount of the
dilute aqueous solution to the suspension to produce an effluent of desired characteristics. For instance, a preferred
method of treating suspended solids comprises (a) dissolving, dispersing, or intermixing substantially dry water-soluble
or water-swellable polymer particles or agglomerates in or with water to form a polymer solution, polymer dispersion,
or aqueous mixture, (b) intermixing said polymer solution, dispersion or aqueous mixture with suspended solids, and
(c) separating resultant concentrated solids from resultant aqueous liquid.

[0070] The polymer products of this invention are useful in a wide range of solid-liquid separations. These polymers
may be used in the dewatering of biologically treated suspensions, such as sewage or other municipal and industrial
sludges, the drainage of cellulosic suspension such as those found in paper production, e.g. paper waste, the production
of paper e.g. retention aids, and the settlement of various organic or inorganic suspensions, i.e. refinery waste, food
waste, etc. Likewise, enzyme broths and suspended mineral solids may be treated similarly. The dose of polymer
effective for a particular application is generally found by routine experimentation in a manner well-known to those
skilled in the art. Preferred doses range from 0.1 parts of polymer per million (ppm) to 10,000 ppm, based on the weight
of the solids suspended in the substrate to be treated.

[0071] When the particles are produced in such a way that they are not water-soluble but are instead water-swellable,
they may be dispersed in water to form aqueous mixtures comprised of dispersions of water-swellable polymers. Water-
swellable polymers may be useful for applications such as thickening paint, in papermaking e.g. as described in U.S.

[0072] The following examples are set forth for illustration purposes only and are not to be construed as limits on
the present invention.

Test procedures

[0073] Standard viscosity is the viscosity of a 0.096% solution of water-soluble polymer in 1 N sodium chloride at
25°C, at a pH of 8.0 for nonionic and anionic polymers and at a pH of 7.0 for cationic polymers, except where noted.
The viscosity was measured by a Brookfield LVT viscometer with a UL adapter at 60 rpm. The polymer solution being
measured was made by preparing a 0.20% solution of polymer in deionized water during two hours and then diluting
with the appropriate amounts of deionized water and sodium chloride.

[0074] Volatiles content (% loss on drying; LOD) was determined using a Sartorius Model MA30 Moisture Analyzer.
The dry polymer sample was dried at a specified temperature either to a constant weight or for a specified time. A
period of 30 minutes at 105°C provided a reliable and reproducible indicator of product volatiles content. The results
are reported as weight percent volatiles based on the total weight.

[0075] Water analysis of the volatiles was performed by Karl Fisher titration. Residual oil levels in the dry products
were determined by sample extraction with supercritical carbon dioxide and gas chromatography analysis of the ex-
tactant. Residual formaldehyde in the recovered oil was determined by stirring the recovered oil with water for thirty
minutes, then analyzing the water extractant by ion chromatography.

[0076] The laboratory spray dryer used in the Examples below was obtained commercially. The chamber of the
laboratory spray dryer was 760 millimeters (mm) in diameter with a 860 mm vertical side and a 65 degree conical
bottom. Nominal gas flow through the dryer was about 180 cubic meters per hour. The emulsion or microemulsion feed
was fed at the center of the top of the chamber using a variable speed pump, through a two-fluid nozzle using air for
atomization. The outlet gas temperature was controlled by varying the inlet gas temperature and feed rate. To provide
an inert atmosphere, the dryer was supplied with nitrogen gas from a cryogenic storage tank. The dried polymer
product was discharged through the bottom of the dryer cone to a cyclone where the dry product was removed and
collected. Residence time in the dryer was generally about 10-15 seconds.

[0077] Some spray-drying Examples were performed with a commercial-scale 8.3 foot diameter closed cycle spray
dryer equipped with a direct contact spray condenser.

[0078] Spray-dried polymer particle products were agglomerated using a commercial mechanical agglomerator in
conjunction with a 10.76 square foot fluid bed dryer. The agglomerator had a vertical shaft and a flexible polymer
housing, with a single shaft rotor having 2 or 3 pin or paddle-type mixing elements that rotated at 1500 to 5200 revo-
lutions per minute (rpm). It was equipped with mechanically driven rollers that moved along the flexible polymer housing
to prevent accumulation of material along the walls. The spray-dried product and binder e.g. water were fed to the top
of the agglomerator; the spray-dried polymer by screw feeder, and the via spray nozzles. The agglomerates formed
by agglomerating the spray-dried polymer particles dropped out of the bottom of the agglomerator and directly into a
fluid bed-dryer, where the agglomerates were dried to the desired water content. Typical residence time in the agglom-
erator was about two seconds.

[0079] The purpose of the funnel flow test is to identify the funnel at which polymer particles and agglomerates fail
to flow, both uncompacted and compacted. The funnel flow test is conducted using 5 funnels, numbered 1-5, respec-
tively, having the following outlet diameters: 14 mm, 12 mm, 8 mm, 5 mm, 3.5 mm. The procedure is followed by starting
with funnel 5 (outlet 3.5 mm), blocking the outlet, filling the funnel with the polymer to be tested, and unblocking the outlet to allow the polymer to flow. If all of the polymer passed through the funnel, the polymer was given a score of +5. If the polymer failed to flow from the funnel when the outlet was unblocked, the procedure was repeated with funnel 4, funnel 3, etc. until flow was observed. The funnel number was recorded when flow was not observed. The process was then repeated to determine the flow of compacted polymer, by tapping the funnel about twenty times (or placed on a suitable vibrating plate) to create compaction. For example, a polymer with a score of +5, +5 flowed through the No. 5 funnel on both tests, whereas a polymer with a score of +5, 3 flowed through the No. 5 funnel uncompacted, but would not flow through the No. 3 funnel when compacted.

[0080] The bulk density of polymer particles and agglomerates was determined by adding the particles or agglomerates to a suitable preweighed measuring container and “tapping” or slightly agitating the container to cause the particles or agglomerates to settle. The volume of the polymer was then read from the measuring container, the measuring container weighed, and the bulk density calculated in units of grams per cubic centimeter (g/cc).

[0081] Dissolving times were determined by adding a 0.2 parts of polymer particles or agglomerates to 99.8 parts of deionized water in a suitable vessel and stirring with a magnetic stir bar. The bulk viscosity of the mixture was measured at regular intervals e.g. five or ten minutes, using a Brookfield LVT viscometer with a UL adapter at 60 rpm, until a maximum bulk viscosity was reached, e.g. until no further increase in bulk viscosity was observed. The time to achieve this maximum bulk viscosity was recorded as the dissolving time and was generally no more than a few hours.

[0082] In the following Examples, the quatemized Mannich polyacrylamide microemulsions (Cat.PAM) were prepared as in U.S. Patent No. 4,956,399, except that Isopar G was used as the oil. The hydrolyzed polyacrylamide emulsions were prepared as described in U.S. Patent No. 5,286,806, except that Isopar G was used as the oil. Highly crosslinked acrylamido/acrylic acid emulsion and microemulsion copolymer microbeads were prepared as described in U.S. Patent No. 5,274,055, except that Isopar G was used as the oil. Cationic emulsion copolymers of (meth)acryloxyethyltrimethylammonium chloride and acrylamide, and anionic copolymers of acrylic acid and acrylamide, were prepared by known methods e.g. Vanderhoff, U.S. Patent No. 3,284,393, and branched cationic polymers were prepared as in U.S. Patent Application Serial No. 08/455,419, except that isopar G was used as the oil in all cases. In all cases, the substitution of Isopar G for the other oil was on a volume basis.

[0083] Polymer particle and agglomerate sizes were determined by commercially available light scattering instrumentation and by conventional sieve techniques.

EXAMPLE 1

[0084] A quaternized Mannich polyacrylamide microemulsion (Cat.PAM) having a Standard Viscosity of about 2.5 was spray dried in a laboratory spray dryer using a two-fluid nozzle in a nitrogen atmosphere with gas inlet and outlet temperatures of 182°C and 92°C respectively. The volatiles were 7.65% and the residence time was 14 seconds. The Standard Viscosity of a solution of the dry product was 2.25 cps, 9.3% less than the standard viscosity of a solution of the microemulsion product. The polymer particles ranged in size from about 19 to about 900 microns. The level of residuals in the dry product were as follows: formaldehyde: 520 ppm; methyl chloride: less than 100 ppm; dimethylamine hydrochloride: 3724 ppm; trimethylamine hydrochloride: 6248 ppm; tetramethylammonium hydrochloride: 5219 ppm.

EXAMPLE 2 (Comparative)

[0085] The Cat.PAM of Example 1 was dried on a 12-inch by 18-inch vacuum double drum dryer with less satisfactory results. The steam temperature on the drum was 115°C. and the steam pressure on the drums was 10 psig. The drum was operated at 6 revolutions per minute with a drum clearance of 0.010 inches and with a vacuum of about 65 mm Hg. The feed rate was about 90 pounds of emulsion per hour. The percent volatiles and Standard Viscosity are set forth in Table 1. A comparison of the dry polymer produced herein to that of Example 1 shows that the Standard Viscosity was significantly reduced using the drum dryer.

<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>Emulsion Name</th>
<th>Gas Inlet/Outlet Temperature °C</th>
<th>Residence Time, sec.</th>
<th>Vofatiles (LOD), %</th>
<th>Polymer Emulsion Standard Viscosity, cps</th>
<th>Dry Product Standard Viscosity, cps</th>
<th>Change in Standard Viscosity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cat.PAM</td>
<td>182/92</td>
<td>14</td>
<td>7.65</td>
<td>2.48</td>
<td>2.25</td>
<td>-9.3</td>
</tr>
</tbody>
</table>
EXAMPLES 3-7

A Cat.PAM having a Standard Viscosity of about 2.5 was spray dried using an 8.3 foot diameter commercial spray dryer with a rotary (spinning disk) atomizer. The dryer was operated using air on a once-through basis. The various temperatures and residence time conditions used are described in Table 2; residence time was 30 seconds for all of the runs. Product was collected both at the base of the dryer (chamber) and at the discharge of a cyclone located immediately after the dryer. Table 2 also shows the analytical results of Examples 3-7; in each case, polymer product from each of the two collection points (chamber and cyclone) was analyzed with the results as shown. In each case, the Standard Viscosity of the polymer particles was within 15% of the Standard Viscosity of the corresponding Cat.PAM.

Table 2

<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>Emulsion Name</th>
<th>Gas Inlet/ Outlet Temperature °C</th>
<th>Atomizer Speed, rpm</th>
<th>Collection Point</th>
<th>Volatiles (LOD), %</th>
<th>Polymer Emulsion Standard Viscosity, cps</th>
<th>Dry Product Standard Viscosity, cps</th>
<th>Change in Standard Viscosity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Cat.PAM</td>
<td>138/86</td>
<td>19,500</td>
<td>chamber</td>
<td>8.59</td>
<td>2.44</td>
<td>2.45</td>
<td>+ 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cyclone</td>
<td>9.64</td>
<td>2.44</td>
<td>2.60</td>
<td>+ 6.6</td>
</tr>
<tr>
<td>4</td>
<td>Cat.PAM</td>
<td>178/93</td>
<td>17,100</td>
<td>chamber</td>
<td>8.91</td>
<td>2.44</td>
<td>2.44</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cyclone</td>
<td>9.71</td>
<td>2.44</td>
<td>2.59</td>
<td>+ 6.2</td>
</tr>
<tr>
<td>5</td>
<td>Cat.PAM</td>
<td>181/92</td>
<td>15,800</td>
<td>chamber</td>
<td>8.40</td>
<td>2.44</td>
<td>2.40</td>
<td>- 1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cyclone</td>
<td>9.42</td>
<td>2.44</td>
<td>2.58</td>
<td>+ 5.7</td>
</tr>
<tr>
<td>6</td>
<td>Cat.PAM</td>
<td>173/81</td>
<td>15,800</td>
<td>chamber</td>
<td>9.14</td>
<td>2.44</td>
<td>2.40</td>
<td>- 1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cyclone</td>
<td>10.93</td>
<td>2.44</td>
<td>2.58</td>
<td>+ 5.7</td>
</tr>
<tr>
<td>7</td>
<td>Cat.PAM</td>
<td>171/81</td>
<td>13,400</td>
<td>chamber</td>
<td>10.34</td>
<td>2.44</td>
<td>2.38</td>
<td>- 2.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cyclone</td>
<td>10.85</td>
<td>2.44</td>
<td>2.49</td>
<td>+ 2.1</td>
</tr>
</tbody>
</table>

EXAMPLES 8-12

A Cat.PAM having a Standard Viscosity of about 2.5 was spray dried using an 8.3 foot diameter commercial spray dryer with a pressure nozzle atomizer. The dryer was operated as a closed cycle system using nitrogen gas. Product was collected at the base of the dryer or chamber. After recovering the polymer, the outlet gas was passed through a direct contact condenser and the resulting aqueous and Isopar G layers were separated. The cooled gas was then reheated and returned to the inlet of the dryer; a very small fraction was vented. The level of residual formaldehyde in the recovered Isopar G was 0.09 milligrams/kilogram, as measured after the completion of the five runs. The quality of the recovered Isopar G was such that it could be recycled and used directly for further microemulsion or emulsion polymerizations. Table 3 provides the various process conditions; the residence time for all runs was 24 seconds. The properties of the resulting dry polymer particles are also shown in Table 3. One to three samples of the polymer product were collected for each run and analyzed as shown. In each case, the Standard Viscosity of the
polymer particles was within 15% of the Standard Viscosity of the initial Cat.PAM used to spray dry.

### Table 3

<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>Emulsion Name</th>
<th>Gas Inlet/Outlet Temperature °C</th>
<th>Nozzle Orifice Size, mm</th>
<th>Sample #</th>
<th>Volatiles (LOD), %</th>
<th>Polymer Emulsion Standard Viscosity, cps</th>
<th>Dry Product Standard Viscosity, cps</th>
<th>Change in Standard Viscosity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Cat.PAM</td>
<td>177/86</td>
<td>1.4</td>
<td>1</td>
<td>9.70</td>
<td>2.49</td>
<td>2.36</td>
<td>- 5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>9.64</td>
<td>2.49</td>
<td>2.16</td>
<td>- 13.3</td>
</tr>
<tr>
<td>9</td>
<td>Cat.PAM</td>
<td>183/90</td>
<td>1.3</td>
<td>1</td>
<td>11.76</td>
<td>2.49</td>
<td>2.57</td>
<td>+ 3.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>11.67</td>
<td>2.49</td>
<td>2.48</td>
<td>- 0.4</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
<td>10.28</td>
<td>2.49</td>
<td>2.46</td>
<td>- 1.2</td>
</tr>
<tr>
<td>10</td>
<td>Cat.PAM</td>
<td>184/91</td>
<td>1.3</td>
<td>1</td>
<td>8.12</td>
<td>2.49</td>
<td>2.20</td>
<td>- 11.7</td>
</tr>
<tr>
<td>11</td>
<td>Cat.PAM</td>
<td>145/91</td>
<td>0.8</td>
<td>1</td>
<td>9.15</td>
<td>2.49</td>
<td>2.21</td>
<td>- 11.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>9.57</td>
<td>2.49</td>
<td>2.42</td>
<td>- 2.8</td>
</tr>
<tr>
<td>12</td>
<td>Cat.PAM</td>
<td>164/93</td>
<td>1.04</td>
<td>1</td>
<td>6.80</td>
<td>2.49</td>
<td>2.32</td>
<td>- 6.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>8.53</td>
<td>2.49</td>
<td>2.30</td>
<td>- 7.6</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>No.</th>
<th>Emulsion Name</th>
<th>Gas Inlet/Outlet Temperature °C</th>
<th>Volatiles (LOD), %</th>
<th>Residence Time, sec.</th>
<th>Polymer Emulsion Standard Viscosity, cps</th>
<th>Dry Product Standard Viscosity, cps</th>
<th>Change in Standard Viscosity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>Cat.PAM</td>
<td>200/92</td>
<td>5.6</td>
<td>14</td>
<td>2.51</td>
<td>2.17</td>
<td>-13.5</td>
</tr>
</tbody>
</table>

### EXAMPLE 13

[A Cat.PAM having a Standard Viscosity of about 2.5 was buffered with urea/lactic acid to pH 4.5, then heat treated by heating to 67-70°C for 7-9 hours, then allowed to cool to ambient temperature. This heat treatment process is described in U.S. Patent No. 5,627,260. The resulting polymer microemulsion was then spray dried in a laboratory spray dryer using a two-fluid nozzle. The various temperatures and residence time conditions used are described in Table 4. As shown in the Table, the Standard Viscosity of the polymer particles was within 15% of the Standard Viscosity of the corresponding heat treated Cat.PAM. The levels of residuals in the dry product were as follows: formaldehyde: 510 ppm; methyl chloride: less than 100 ppm; dimethylamine hydrochloride: 7500 ppm; trimethylamine hydrochloride: 6928 ppm; tetramethylammonium hydrochloride: 4671 ppm.]

### EXAMPLE 14

[Cat.PAM polymer particles were obtained by the spray drying process of Example 1. To 97.5 parts of these granules was added 2.5 parts of sodium carbonate in a suitable vessel. The vessel was mechanically shaken for 30 minutes to form a composition containing substantially dry granules of quaternized Mannich polyacrylamide and sodium carbonate.]

### EXAMPLE 15

[Particles of Cat.PAM were obtained by the spray drying process of Example 13 and then sodium carbonate was added according to the process of Example 14. Solutions of the particles were prepared by dissolving 0.2 parts of the particles in 100 parts water. The dry particles took approximately 1 hour to dissolve. A sample of the heat treated...]

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polymer microemulsion described in Example 13 was also dissolved in water to produce a similar polymer concentration. Both polymers were allowed to stir in water for two hours, then were tested for their ability to flocculate suspended solids using a 2.0% solids digested sewage sludge. Approximately 200 parts of the sludge was mixed at about 1000 rpm with various amounts of the polymer solutions, ranging from 10 parts to 50 parts, for about 5 seconds. Thereafter, the drainage rates of the flocculated solids were measured at 10, 20 and 30 seconds. The polymer products both performed equally well in the dose range of 25 to 30 pounds of polymer per ton of sludge.

EXAMPLE 16

[0091] Particles of Cat.PAM were prepared according to Example 14, except that sodium bicarbonate was used in place of sodium carbonate. The Standard Viscosity of these particles was determined, without adjustment of the pH, to be 2.45 cps. In comparison, the Standard Viscosity (measured without pH adjustment) of particles of Cat.PAM prepared by the procedure of Example 1, which did not contain a base, was measured as 1.3 centipoise. Standard Viscosity is known in the art to directly correlate with polymer performance, e.g., flocculation.

EXAMPLES 17-21

[0092] A 20% hydrolyzed polyacrylamide emulsion having a polymer solids of 23.8% and a Standard Viscosity of 8.63 centipoise was prepared as described in U.S. Patent No. 5,286,806, except that Isopar G was used as the oil, then spray dried in a laboratory spray dryer using nitrogen. The inlet temperature, outlet temperature and feed rate were varied, and the LOD, Standard Viscosity (SV), and drying loss of the polymer particle product were measured as shown in Table 5. Smaller drying losses were observed at outlet temperatures of less than 100°C.

### Table 5

<table>
<thead>
<tr>
<th>No.</th>
<th>Inlet Temp., °C</th>
<th>Outlet Temp., °C</th>
<th>Feed Rate, ml/min.</th>
<th>LOD, %</th>
<th>Product SV, cp</th>
<th>Drying Loss, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>162</td>
<td>82</td>
<td>96</td>
<td>10.2</td>
<td>8.43</td>
<td>2.3</td>
</tr>
<tr>
<td>18</td>
<td>161</td>
<td>84</td>
<td>64</td>
<td>7.8</td>
<td>8.31</td>
<td>3.7</td>
</tr>
<tr>
<td>19</td>
<td>193</td>
<td>96</td>
<td>52</td>
<td>5.6</td>
<td>8.21</td>
<td>4.9</td>
</tr>
<tr>
<td>20C</td>
<td>227</td>
<td>115</td>
<td>44</td>
<td>3.6</td>
<td>8.11</td>
<td>6.0</td>
</tr>
<tr>
<td>21C</td>
<td>253</td>
<td>132</td>
<td>36</td>
<td>2.2</td>
<td>7.48</td>
<td>13.3</td>
</tr>
</tbody>
</table>

C. Comparative Example

EXAMPLES 22-34

[0093] A series of 13 water-soluble or water-swellable vinyl-addition polymer containing water-in-oil emulsions and water-in-oil microemulsions were prepared according to the methods referenced below (except that Isopar G was used as the oil), then spray dried in a laboratory spray dryer using nitrogen, and the results obtained in Table 6 were obtained. Hydrolyzed PAM emulsions were obtained by hydrolyzing polyacrylamide (PAM) emulsions as described in U.S. Patent No. 5,286,806 (Example 22-23). Acrylamide (AMD) and acrylic acid (AA) were emulsion copolymerized to yield AMD/AA emulsions by known methods e.g. Vanderhoff, U.S. Patent No. 3,284,393 (Examples 24-25). A hydroxamated acrylamide polymer with a degree of hydroxamation of about 40% (40% HX emulsion Example 26) was prepared by the methods of U.S. Patent No. 4,767,540. The acrylamide/acrylic acid microbead microemulsion of Example 27 was prepared by the methods of U.S. Patent No. 5,274,055. The water-soluble polyacrylate ester emulsion was prepared by the methods of U.S. Patent No. 5,847,056 (Example 28). Acrylamide and acryloxethyltrimethylammonium chloride (AETAC) were emulsion copolymerized to yield AMD/AETAC emulsions by known methods e.g. Vanderhoff, U.S. Patent No. 3,284,393 (Examples 29-32); small amounts e.g. about 4 molar parts per million, based on monomers, of methylenebisacrylamide were added to the AMD/AETAC polymers of Examples 30 and 32 to create branching, see e.g. EP-A-374,458. Mannich and quaternized Mannich microemulsions were prepared by the methods of U.S. Patent No. 4,956,399 (Examples 33 and 34). In each case, substantially dry, free flowing mixtures of polymer particles having drying losses of about 15% or less were obtained. As used herein, “drying loss” is the change in polymer viscosity resulting from spray-drying, and is not to be confused with “loss on drying” or LOD, which is a measure of volatiles. Drying loss may be expressed as the viscosity before spray-drying minus the viscosity after spray-drying, divided by the viscosity before spray-drying, and expressed as a percentage by multiplying by 100.
EXAMPLE 35-37

[0094] A 20% hydrolyzed polyacrylamide emulsion made with Isopar G was spray-dried on a commercial scale 8.3 foot diameter spray dryer using a direct contact spray condenser. Spray-dry process-generated water and oil were collected and acidified, the layers separated, and the upper Isopar G layer recovered. Side-by-side laboratory-scale acrylamide polymerizations were then performed using the recovered Isopar G and virgin Isopar G. The Standard Viscosity of the polyacrylamide made using the recovered oil was 6.58 cps, virtually the same as the Standard Viscosity of the polyacrylamide made using the virgin oil, 6.67 cps. Subsequently, an acrylamide polymerization was carried out on a 200-gallon scale using the same recovered Isopar G and the same recipe as the laboratory scale batch. The
resultant polyacrylamide had a Standard Viscosity of 6.55 cP, essentially the same as the laboratory batch.

**EXAMPLES 38-39**

[0095] A quaternized Mannich polyacrylamide microemulsion having a Standard Viscosity of about 2.1 was spray dried as in Example 1. Both the microemulsion and the polymer particles were placed into an oven at 90°C and the Standard Viscosities determined at various times, as shown in Table 7. The decrease in the Standard Viscosity of the microemulsion sample was much greater than the modest decrease observed for the spray-dried polymer, in spite of the relatively severe conditions.

### Table 7

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Example 38 Standard Viscosity of Spray-Dried Polymer</th>
<th>Example 39C (Comparative) Standard Viscosity of Microemulsion Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.86</td>
<td>2.1</td>
</tr>
<tr>
<td>15</td>
<td>1.66</td>
<td>1.25</td>
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<tr>
<td>30</td>
<td>1.52</td>
<td>1.15</td>
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<tr>
<td>60</td>
<td>1.47</td>
<td>1.10</td>
</tr>
</tbody>
</table>

**EXAMPLES 40-41**

[0096] A quaternized Mannich polyacrylamide microemulsion having a Standard Viscosity of about 2.5 was spray dried as in Example 1. Both the microemulsion and the polymer particles were stored at room temperature, and the Standard Viscosities determined at various times, as shown in Table 8. The Standard Viscosity of the spray-dried polymer was essentially unaffected by the passage of time, whereas the Standard Viscosity of the microemulsion polymer decreased noticeably.

### Table 8

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Example 40 Standard Viscosity of Spray-Dried Polymer</th>
<th>Example 41C (Comparative) Standard Viscosity of Microemulsion Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>2.44</td>
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<td>19</td>
<td></td>
<td>2.48</td>
</tr>
<tr>
<td>24</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>2.44</td>
<td>2.11</td>
</tr>
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<td>46</td>
<td>2.44</td>
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<td>1.90</td>
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<tr>
<td>103</td>
<td></td>
<td>1.84</td>
</tr>
<tr>
<td>215</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>257</td>
<td></td>
<td>1.70</td>
</tr>
</tbody>
</table>

**EXAMPLES 42-47**

[0097] An 20% anionic hydrolyzed PAM emulsion was obtained by hydrolyzing a polyacrylamide (PAM) emulsion as described in U.S. Patent No. 5,286,806. A 55% cationic emulsion was obtained by copolymerizing acrylamide and acryloxyethyltrimethylammonium chloride (AETAC) by known methods e.g. Vanderhoff, U.S. Patent No. 3,284,393. A Cat.PAM was obtained as in U.S. Patent No. 4,956,399. In each case, Isopar G was used as the oil. Part of each
sample was precipitated in hexane/acetone, then dried under vacuum to produce a polymer powder. Part of each sample was also spray-dried, and part of each spray-dried sample was agglomerated. Bulk density, flow properties (funnel flow test), dissolving time and particle size were determined and are shown in Table 9. Particle size was determined by light scattering for the precipitated and spray-dried polymers, and by sieve screening for the agglomerates.

**EXAMPLES 51-53**

[0098] The agglomerates of Examples 44, 47 and 50 were screened to remove agglomerates larger than about 1190 microns and smaller than about 177 microns. The resultant screened agglomerates had improved flow properties and dissolving times relative to the agglomerates of Examples 44, 47 and 50 as shown in Table 10.

### Table 9

<table>
<thead>
<tr>
<th>Ex. No.</th>
<th>Polymer</th>
<th>Bulk Density, g/cc</th>
<th>Funnel Flow</th>
<th>Dissolving Time, min.</th>
<th>Particle Size Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>42C</td>
<td>20% Anionic Precipitated</td>
<td>0.26</td>
<td>1,1</td>
<td>90</td>
<td>90% &lt; 109 microns, 50% &lt; 42 microns, 10% &lt; 8 microns</td>
</tr>
<tr>
<td>43</td>
<td>20% Anionic Spray-dried</td>
<td>0.79</td>
<td>1,1</td>
<td>85</td>
<td>90% &lt; 148 microns, 50% &lt; 65 microns, 10% &lt; 27 microns</td>
</tr>
<tr>
<td>44</td>
<td>20% Anionic Spray-dried and Agglomerated</td>
<td>0.53</td>
<td>4,3</td>
<td>20-25</td>
<td>90% &lt; 850 microns, 50% &lt; 350 microns, 10% &lt; 170 microns</td>
</tr>
<tr>
<td>45C</td>
<td>55% Cationic Precipitated</td>
<td>0.30</td>
<td>1,1</td>
<td>80</td>
<td>90% &lt; 18 microns, 50% &lt; 11 microns, 10% &lt; 5 microns</td>
</tr>
<tr>
<td>46</td>
<td>55% Cationic Spray-dried</td>
<td>0.86</td>
<td>1,1</td>
<td>60-65</td>
<td>90% &lt; 156 microns, 50% &lt; 68 microns, 10% &lt; 22 microns</td>
</tr>
<tr>
<td>47</td>
<td>55% Cationic Spray-dried and Agglomerated</td>
<td>0.52</td>
<td>4,3</td>
<td>25-30</td>
<td>90% &lt; 1500 microns, 50% &lt; 600 microns, 10% &lt; 260 microns</td>
</tr>
<tr>
<td>48C</td>
<td>Cat.PAM Precipitated</td>
<td>0.164</td>
<td>1,1</td>
<td>80</td>
<td>90% &lt; 58 microns, 50% &lt; 27 microns, 10% &lt; 17 microns</td>
</tr>
<tr>
<td>49</td>
<td>Cat.PAM Spray-dried</td>
<td>0.86</td>
<td>1,1</td>
<td>60-65</td>
<td>90% &lt; 152 microns, 50% &lt; 72 microns, 10% &lt; 20 microns</td>
</tr>
<tr>
<td>50</td>
<td>Cat.PAM Spray-dried and Agglomerated</td>
<td>0.52</td>
<td>4,3</td>
<td>25-30</td>
<td>90% &lt; 1600 microns, 50% &lt; 560 microns, 10% &lt; 280 microns</td>
</tr>
</tbody>
</table>

C: Comparative Example
Anionic hydrolyzed PAM emulsions were obtained by hydrolyzing polyacrylamide (PAM) emulsions as described in U.S. Patent No. 5,286,806, an 80% anionic emulsion was obtained by copolymerizing acrylamide and acrylic acid (AMD/AA) by known methods e.g. Vanderhoff, U.S. Patent No. 3,284,393, and a Mannich microemulsion was obtained as described in U.S. Patent No. 4,956,399, except that Isopar G was used as the oil in all cases. Each emulsion and microemulsion was spray-dried according to the conditions shown in Table 11. Smaller drying losses and faster dissolving times were observed when spray-drying was conducted at outlet temperatures lower than 100°C in accordance with this invention.

### Table 10

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Screened Agglomerate</th>
<th>Bulk Density, g/cc</th>
<th>Funnel Flow</th>
<th>Dissolving Time, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>20% Anionic</td>
<td>0.5</td>
<td>5,4</td>
<td>20</td>
</tr>
<tr>
<td>52</td>
<td>55% Cationic</td>
<td>0.51</td>
<td>5,4</td>
<td>20-25</td>
</tr>
<tr>
<td>53</td>
<td>Cat.PAM</td>
<td>0.51</td>
<td>5,4</td>
<td>&lt; 15</td>
</tr>
</tbody>
</table>

### Table 11

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Polymer</th>
<th>Inlet/Outlet Temperature, °C</th>
<th>Drying Loss, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>54</td>
<td>20% Hydrolyzed Anionic PAM emulsion</td>
<td>162/82</td>
<td>4.6</td>
</tr>
<tr>
<td>55C</td>
<td>20% Hydrolyzed Anionic PAM emulsion</td>
<td>253/132</td>
<td>15.4</td>
</tr>
<tr>
<td>56</td>
<td>40% Hydrolyzed Anionic PAM emulsion</td>
<td>162/84</td>
<td>4.0</td>
</tr>
<tr>
<td>57C</td>
<td>40% Hydrolyzed Anionic PAM emulsion</td>
<td>265/127</td>
<td>18.8</td>
</tr>
<tr>
<td>58</td>
<td>20/80 AMD/AA emulsion</td>
<td>163/86</td>
<td>4.8</td>
</tr>
<tr>
<td>59C</td>
<td>20/80 AMD/AA emulsion</td>
<td>225/120</td>
<td>14.5</td>
</tr>
<tr>
<td>60</td>
<td>Mannich microemulsion</td>
<td>155/83</td>
<td>6.8</td>
</tr>
<tr>
<td>61C</td>
<td>Mannich microemulsion</td>
<td>265/130</td>
<td>62.5</td>
</tr>
</tbody>
</table>

**EXAMPLES 62-63**

A blend of a Cat.PAM and a cationic copolymer is prepared as in U.S. Patent No. 5,883,181, and a cationic polymer dispersion is prepared according to the procedures of U.S. Patent No. 4,506,062 (without distillation), except that Isopar G is used as the oil. The blend and the dispersion are spray-dried in a laboratory spray-dryer as in Examples 22-34. Substantially dry polymer particles are obtained, with drying losses of about 15% or less. Greater than 90% of the spray-dried blend particles contain both the Cat.PAM and the cationic copolymer.

### Claims

1. A process for producing by spray-drying substantially dry water-soluble or water-swellable vinyl-addition polymer particles comprising the steps of:
   
   (a) spray-drying a water-in-oil dispersion, water-in-oil emulsion or water-in-oil microemulsion containing said vinyl-addition polymer into a gas stream with a residence time of 8 to 120 seconds and an outlet temperature of 70°C to less than 100°C, the oil phase of said dispersion, emulsion or microemulsion comprising a volatile oil whose boiling point, or the upper end of whose boiling point range, is 200°C or less; and
   
   (b) collecting resultant polymer particles containing 12% or less volatiles, based on the weight of the spray-dried polymer as measured by determining the weight loss on drying the polymer at 105°C for 30 minutes.

2. A process as claimed in Claim 1, wherein said outlet temperature is from 75°C to 90°C.
3. A process as claimed in Claim 1 or Claim 2, wherein said residence time is 90 seconds or less.

4. A process as claimed in Claim 3, wherein said residence time is from 10 to 60 seconds.

5. A process as claimed in any preceding claim, wherein said boiling point or upper end of the boiling point range of said volatile oil is in the range from 70° to 190°C.

6. A process as claimed in Claim 5, wherein said range is from 130° to 185°C.

7. A process as claimed in any preceding claim, wherein said volatile oil is a mixture of synthetic isoparaffinic hydrocarbons having a boiling point range of 160° to 177°C.

8. A process as claimed in any preceding claim, wherein said vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion is comprised of a polymer having pendant groups selected from amide, tertiary aminomethyl, quaternized tertiary aminomethyl, hydroxy, glyoxal, sulfonate, sulfonate salt, carboxylic acid, carboxylic acid salt, hydroxamic acid and hydroxamic acid salt groups, or a polymer having recurring units selected from dialkylaminocarbonyl(alk)acrylate, dialkylaminocarbonyl(alk)acrylate salt and quaternized dialkylaminocarbonyl(alk)acrylate groups.

9. A process as claimed in any preceding claim, wherein said vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion is comprised of a polymer having recurring units selected from acrylamide, dialkylaminocarbonyl(alk)acrylate, dialkylaminocarbonyl(alk)acrylate salt, quaternized dialkylaminocarbonyl(alk)acrylate, acrylic acid, and acrylic acid salt.

10. A process as claimed in Claim 9, wherein said water-soluble polymer is branched.

11. A process as claimed in any preceding claim, wherein said vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion is comprised of a polymer selected from Mannich poly(alk)acrylamide, quaternized Mannich poly(alk)acrylamide, hydroxamated polyacrylamide, esterified (meth)acrylic acid polymer, esterified (meth)acrylic acid copolymer, and hydrolyzed polyacrylamide.

12. A process as claimed in any preceding claim, wherein the oil phase of said dispersion, emulsion or microemulsion comprises volatile oil recovered from a polymer-containing water-in-oil dispersion, emulsion or microemulsion spray-drying process.

13. A process as claimed in any preceding claim, wherein said vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion contains 2% or less of surfactant, by weight based on total weight.

14. A process for producing by spray-drying a substantially dry blend of water-soluble or water-swellable vinyl-addition polymer particles, comprising the steps of:

(a) spray-drying a blend comprised of (i) a first water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, water-in-oil emulsion or water-in-oil microemulsion and (ii) a second water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, water-in-oil emulsion or water-in-oil microemulsion, the oil phases of said dispersions, emulsions or microemulsions comprising a volatile oil whose boiling point, or the upper end of whose boiling point range, is 200°C or less, into a gas stream with a residence time of 8 to 120 seconds and an outlet temperature of 70° to less than 100°C; and

(b) collecting resultant blend of polymer particles containing 12% or less volatiles, based on the weight of the spray-dried polymer as measured by determining the weight loss on drying the polymer at 105°C for 30 minutes.

15. A process as claimed in Claim 16, wherein the conditions of said spray-drying are as defined in any one of Claims 2-4.

16. A process as claimed in Claim 14 or Claim 15, wherein said volatile oil is as defined in any one of Claims 5-7.

17. A process as claimed in any one of Claims 14-16, wherein said first water-soluble or water-swellable vinyl-addition polymer is...
polymer-containing water-in-oil dispersion, emulsion or microemulsion has a bulk viscosity that is different from the bulk viscosity of said second water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion.

18. A process as claimed in any one of Claims 14-17, wherein either (1) said first water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion, or (2) said second water-soluble or water-swellable vinyl-addition polymer-containing water-in-oil dispersion, emulsion or microemulsion, or (3) both, is comprised of a cationic vinyl-addition polymer.

19. A process as claimed in any one of Claims 14-18, wherein the vinyl-addition polymer contained in said vinyl-addition polymer-containing water-in-oil dispersions, emulsions or microemulsions has not been formed in the presence of a crosslinking agent.

20. A process as claimed in any one of Claims 14-19 wherein said vinyl-addition polymer is selected from the vinyl-addition polymers defined in any one of Claims 10-13.

21. A process as claimed in Claim 20, wherein either said first water-in-oil microemulsion or said second water-in-oil microemulsion is comprised of Mannich poly(alk)acrylamide, quaternized Mannich poly(alk)acrylamide, or mixtures thereof.

22. A process as claimed in any preceding claim, which further comprises the step of agglomerating said polymer particles or blend of polymer particles collected in step (b).

23. A process as claimed in any preceding claim, wherein a water-in-oil emulsion or water-in-oil microemulsion is spray-dried.

Patentansprüche

1. Verfahren zur Erzeugung von im Wesentlichen trockenen wasserlöslichen oder wasserquellfähigen Vinyladditionspolymerpartikeln durch Sprühtrocknen, umfassend die folgenden Schritte:


   (b) Sammeln der resultierenden Polymerpartikel, welche 12 % oder weniger fluchtiger Bestandteile enthalten, bezogen auf das Gewicht des sprühgetrockneten Polymers, gemessen durch die Bestimmung des Gewichtsverlusts beim Trocknen des Polymers bei 105 °C für 30 Minuten.

2. Verfahren gemäß Anspruch 1, wobei die Austrittstemperatur von 75 °C bis 90 °C ist.

3. Verfahren gemäß Anspruch 1 oder 2, wobei die Verweilzeit 90 Sekunden oder kürzer ist.


5. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei der Siedepunkt oder das obere Ende des Siedepunktbereichs des flüchtigen Öls im Bereich von 70 °C bis 190 °C ist.

6. Verfahren gemäß Anspruch 5, wobei der Bereich von 130 °C bis 185 °C ist.


8. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Vinyladditionspolymer enthaltende Wasser-in-Öl-Dispersion, -Emulsion oder -Mikroemulsion aus einem Polymer besteht, welches Seitengruppen aufweist,
die ausgewählt sind aus Amid, tertiärem Aminomethyl, quaternisiertem tertiärem Aminomethyl, Hydroxyl, Glyoxal, Sulfonat, Sulfonatsalz, Carbonsäure, Carbonsäuresalz, Hydroxamsäure und Hydroxamsäuresalzgruppen, oder einem Polymer, welches periodische Einheiten aufweist, die ausgewählt sind aus Dialkylaminoalkyl(alk)acrylat, Dialkylaminoalkyl(alk)acrylatalsalz und quaternisierten Dialkylaminoalkyl(alk)acrylatgruppen.

9. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Vinyladditions polymer enthaltende Wasser-in-Öl-Dispersion, -Emulsion oder - Mikroemulsion aus einem Polymer besteht, welches periodische Einheiten aufweist, die ausgewählt sind aus Acrylamid, Dialkylaminoalkyl(alk)acrylat, Dialkylaminoalkyl(alk)acrylatalsalz, quaternisiertem Dialkylaminoalkyl(alk)acrylat, Acrylsäure und Acrylsäuresalz.

10. Verfahren gemäß Anspruch 9, wobei das wasserlösliche Polymer verzweigt ist.

11. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Vinyladditions polymer enthaltende Wasser-in-Öl-Dispersion, -Emulsion oder - Mikroemulsion aus einem Polymer besteht, das ausgewählt ist aus Mannich-Poly(alk)acrylamid, quaternisiertem Mannich-Poly(alk)acrylamid, hydroxamiertem Polyacrylamid, verestertem (Meth)acrylsäurepolymer, verestertem (Meth)acrylsäurecopolymer und hydrolysiertem Polyacrylamid ausgewählt ist.


14. Verfahren zur Erzeugung einer im Wesentlichen trockenen Mischung von wasserlöslichen oder wasserquellfähigen Vinyladditio nspolymerpartikeln durch Sprühtrocknen, umfassend die folgenden Schritte:


(b) Sammeln einer resultierenden Mischung von Polymerpartikel, welche 12 % oder weniger flüchtige Bestandteile enthalten, bezogen auf das Gewicht des sprühgetrockneten Polymers, gemessen durch Bestimmung des Gewichtsverlusts beim Trocknen des Polymers bei 105 °C für 30 Minuten gemessen.

15. Verfahren gemäß Anspruch 14, wobei die Bedingungen des Sprühtrocknens, wie in einem der Ansprüche 2 bis 4 definiert sind.

16. Verfahren gemäß Anspruch 14 oder 15, wobei das flüchtige Öl, wie in einem der Ansprüche 5 bis 7 definiert ist.


18. Verfahren nach einem der Ansprüche 14 bis 17, wobei entweder (1) die erste wasserlösliche oder wasserquellfähige Vinyladditions polymer enthaltende Wasser-in-Öl-Dispersion, -Emulsion oder - Mikroemulsion oder (2) die zweite wasserlösliche oder wasserquellfähige Vinyladditions polymer enthaltende Wasser-in-Öl-Dispersion, -Emulsion oder - Mikroemulsion oder (3) beide aus einem kationischen Vinyladditions polymer bestehen.

19. Verfahren nach einem der Ansprüche 14 bis 18, wobei das Vinyladditions polymer, welches in den Vinyladditions polymer enthaltenden Wasser-in-Öl-Dispersionen, -Emulsionen oder - Mikroemulsionen enthalten ist, nicht in der
Gegenwart eines Vernetzungsmittels gebildet wurde.

20. Verfahren nach einem der Ansprüche 14 bis 19, wobei das Vinyladditionspolymer ausgewählt ist aus den Vinyladditionspolymeren, welche in einem der Ansprüche 10 bis 13 definiert sind.


22. Verfahren gemäß einem der vorhergehenden Ansprüche, welcher des Weiteren den Schritt des Agglomerierens der Polymerpartikel oder Mischung von Polymerpartikeln, welche in Schritt (b) gesammelt wurden, umfasst.


Revendications

1. Procédé de production par séchage par atomisation, de particules de polymère d'addition de groupes vinyle soluble dans l'eau ou gonflable dans l'eau à peu près sèches, comprenant les étapes consistant :

   (a) à sécher par atomisation une dispersion eau-dans-huile, une émulsion eau-dans-huile ou une micro-émulsion eau-dans-huile contenant ledit polymère d'addition de groupes vinyle dans un courant gazeux selon un temps de séjour de 8 à 120 secondes et à une température de sortie de 70 à moins de 100 °C, la phase huileuse de ladite dispersion, émulsion ou micro-émulsion comprenant une huile volatile dont le point d'ébullition ou l'extrémité supérieure de la plage de point d'ébullition, est de 200 °C ou moins ; et

   (b) on récupère les particules de polymère résultante contenant 12 % ou moins de substances volatiles par rapport au poids du polymère séché par atomisation d'après mesure par détermination de la perte de poids par séchage du polymère à 105 °C pendant 30 minutes.

2. Procédé selon la revendication 1, dans lequel ladite température de sortie est de 75° à 90 °C.

3. Procédé selon la revendication 1 ou 2, dans lequel ledit temps de séjour est de 90 secondes ou moins.

4. Procédé selon la revendication 3, dans lequel ledit temps de séjour est de 10 à 60 secondes.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel ledit point d'ébullition ou ladite extrémité supérieure de la plage de point d'ébullition de ladite huile volatile, est dans la plage de 70 à 190 °C.

6. Procédé selon la revendication 5, dans lequel ladite plage est de 130 à 185 °C.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite huile volatile est un mélange d'hydrocarbures synthétiques de type isoparaffine ayant une plage de point d'ébullition de 160 à 177 °C.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite dispersion, émulsion ou micro-émulsion eau-dans-huile contenant le polymère d'addition de groupes vinyle, comprend un polymère comportant des groupes latéraux choisis parmi les groupes amide, amine, glyoxal, sulfitonate, sel de sulfonate, acide carboxylique, sel d'acide carboxylique, acide oxamique et sel d'acide oxamique, ou un polymère comportant des motifs répétés choisis parmi les groupes (alk)acrylate de dialkylaminoalkyle, sel d'(alk)acrylate de dialkylaminoalkyle et (alk)acrylate de dialkylaminoalkyle quaternarisés.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel ladite dispersion, émulsion ou micro-émulsion eau-dans-huile contenant le polymère d'addition de groupes vinyle, comprend un polymère comportant des motifs répétés choisis parmi les groupes acrylamide, (alk)acrylate de dialkylaminoalkyle, sel d'(alk)acrylate de dialkylaminoalkyle, (alk)acrylate de dialkylaminoalkyle quaternarisés, acide acrylique et sel d'acide acrylique.

10. Procédé selon la revendication 9, dans lequel ledit polymère soluble dans l'eau est ramifié.
11. Procédé selon l’une quelconque des revendications précédentes, dans lequel ladite dispersion, émulsion ou micro-émulsion eau-dans-huile contenant le polymère d’addition de groupes vinyle comprend un polymère choisi parmi un poly(alk) acrylamide de Mannich, un poly(alk)acrylamide de Mannich quaternarisé, un polyacrylamide à groupes hydroxamate, un polymère d’acide (méth)acrylique estérisé, un copolymère d’acide (méth)acrylique estérisé et un polyacrylamide hydrolysé.

12. Procédé selon l’une quelconque des revendications précédentes, dans lequel la phase huileuse de ladite dispersion, émulsion ou micro-émulsion comprend une huile volatile récupérée à partir d’un procédé de séchage par atomisation d’une dispersion, émulsion ou micro-émulsion eau-dans-huile contenant un polymère.

13. Procédé selon l’une quelconque des revendications précédentes, dans lequel ladite dispersion, émulsion ou micro-émulsion eau-dans-huile contenant le polymère d’addition de groupes vinyle contient 2 % ou moins d’un tensioactif en poids par rapport au poids total.

14. Procédé de production par séchage par atomisation d’un mélange à peu près sec de particules de polymère d’addition de groupes vinyle soluble dans l’eau ou gonflable dans l’eau, comprenant les étapes consistant :

(a) à sécher par atomisation un mélange comprenant (i) une première dispersion eau-dans-huile, une première émulsion eau-dans-huile ou une première micro-émulsion eau-dans-huile contenant un polymère d’addition de groupes vinyle soluble dans l’eau ou gonflable dans l’eau, et (ii) une deuxième dispersion eau-dans-huile, une deuxième émulsion eau-dans-huile ou une deuxième micro-émulsion eau-dans-huile contenant un polymère d’addition de groupes vinyle soluble dans l’eau ou gonflable dans l’eau, les phases huileuses desdites dispersions, desdites émulsions ou desdites micro-émulsions comprenant une huile volatile dont le point d’ébullition ou la limite supérieure de la plage de point d’ébullition est de 200 °C ou moins, dans un courant de gaz selon un temps de séjour de 8 à 120 secondes et à une température de sortie de 70 à moins de 100 °C ; et

(b) on récupère le mélange résultant de particules de polymère contenant 12 % ou moins de substances volatiles par rapport au poids du polymère séché par atomisation d’après mesure par détermination de la perte de poids par séchage du polymère à 105 °C pendant 30 minutes.

15. Procédé selon la revendication 16, dans lequel les conditions dudit séchage par atomisation sont telles que définies dans l’une quelconque des revendications 2 à 4.

16. Procédé selon la revendication 14 ou la revendication 15, dans lequel ladite huile volatile est telle que définie dans l’une quelconque des revendications 5 à 7.

17. Procédé selon l’une quelconque des revendications 14 à 16, dans lequel ladite première dispersion, ladite première émulsion ou ladite première micro-émulsion eau-dans-huile contenant un polymère d’addition de groupes vinyle soluble dans l’eau ou gonflable dans l’eau, a une viscosité apparente qui est différente de la viscosité apparente de ladite deuxième dispersion, ladite deuxième émulsion ou ladite deuxième micro-émulsion eau-dans-huile contenant un polymère d’addition de groupes vinyle soluble dans l’eau ou gonflable dans l’eau.

18. Procédé selon l’une quelconque des revendications 14 à 17, dans lequel (1) ladite première dispersion, ladite première émulsion ou ladite première micro-émulsion eau-dans-huile contenant un polymère d’addition de groupes vinyle soluble dans l’eau ou gonflable dans l’eau, ou (2) ladite deuxième dispersion, ladite deuxième émulsion ou ladite deuxième micro-émulsion eau-dans-huile contenant un polymère d’addition de groupes vinyle soluble dans l’eau ou gonflable dans l’eau, ou (3) les deux, comprennent un polymère cationique d’addition de groupes vinyle.

19. Procédé selon l’une quelconque des revendications 14 à 18, dans lequel le polymère d’addition de groupes vinyle contenu dans lesdites dispersions, desdites émulsions ou desdites micro-émulsions eau-dans-huile contenant un polymère d’addition de groupes vinyle, n’a pas été formé en présence d’un agent de réticulation.

20. Procédé selon l’une quelconque des revendications 14 à 19, dans lequel ledit polymère d’addition de groupes vinyle est choisi parmi les polymères d’addition de groupe vinyle définis dans l’une quelconque des revendications 10 à 13.

21. Procédé selon la revendication 20, dans lequel ladite première micro-émulsion eau-dans-huile ou ladite deuxième micro-émulsion eau-dans-huile comprend un poly(alk)acrylamide de Mannich ou un poly(alk)acrylamide de Mannich quaternarisé, un polyacrylamide à groupes hydroxamate, un polymère d’acide (méth)acrylique estérisé, un copolymère d’acide (méth)acrylique estérisé et un polyacrylamide hydrolysé.
nich quaternarisé, ou des mélanges de ceux-ci.

22. Procédé selon l'une quelconque des revendications précédentes, comprenant en outre l'étape d'agglomération desdites particules de polymère ou dudit mélange de particules de polymère récupérés dans l'étape (b).

23. Procédé selon l'une quelconque des revendications précédentes, dans lequel on sèche par atomisation une émulsion eau-dans-huile ou une micro-émulsion eau-dans-huile.