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(71) Applicant *(for all designated States except US)*: **BASF Aktiengesellschaft** [DE/DE]; 67056 Ludwigshafen (DE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **HERFERT, Norbert** [DE/DE]; Obergasse 59a, 63674 Altenstadt (DE). **MIATUDILA, Ma-Ikay Kikama** [CD/US]; 105 Price Point Drive, Monroe, Nc 28110 (US). **MITCHELL, Michael A.** [US/US]; 8805 Sweetwater Pl., Waxhaw, NC 28173 (US).

(74) Common Representative: **BASF Aktiengesellschaft**; 67056 Ludwigshafen (DE).

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(54) Title: POLYAMINE-COATED SUPERABSORBENT POLYMERS

(57) Abstract: Superabsorbent polymer particles having superior absorption capacity and permeability are disclosed. A method of producing the superabsorbent polymer particles by applying a polyamine coating to the particles also is disclosed.

POLYAMINE-COATED SUPERABSORBENT POLYMERS

FIELD OF THE INVENTION

The present invention relates to polyamine-coated superabsorbent polymer particles having an improved relationship between fluid absorbance and fluid permeability, and to methods of manufacturing the coated superabsorbent polymer particles. More particularly, the present invention relates to polyamine-coated particles prepared from base superabsorbent polymer particles having an increased amount of extractable materials. The polyamine-coated particles exhibit an excellent gel bed permeability essentially without adversely affecting absorption properties. The present invention also relates to the use of the polyamine-coated superabsorbent polymer particles in articles, such as diapers, catamenial devices, and wound dressings.

BACKGROUND OF THE INVENTION

Water-absorbing resins are widely used in sanitary goods, hygienic goods, wiping cloths, water-retaining agents, dehydrating agents, sludge coagulants, disposable towels and bath mats, disposable door mats, thickening agents, disposable litter mats for pets, condensation-preventing agents, and release control agents for various chemicals. Water-absorbing resins are available in a variety of chemical forms, including substituted and unsubsti-

tuted natural and synthetic polymers, such as hydrolysis products of starch acrylonitrile graft polymers, carboxymethylcellulose, crosslinked polyacrylates, sulfonated polystyrenes, hydrolyzed polyacrylamides, polyvinyl alcohols, polyethylene oxides, polyvinylpyrrolidones, and polyacrylonitriles. The most commonly used SAP for absorbing electrolyte-containing aqueous fluids, such as urine, is neutralized polyacrylic acid, i.e., containing about 25% up to 100%, neutralized carboxyl groups.

Such water-absorbing resins are termed "superabsorbent polymers," or SAPs, and typically are lightly crosslinked hydrophilic polymers. SAPs are generally discussed in Goldman et al. U.S. Patent Nos. 5,669,894 and 5,599,335, each incorporated herein by reference. SAPs can differ in their chemical identity, but all SAPs are capable of absorbing and retaining amounts of aqueous fluids equivalent to many times their own weight, even under moderate pressure. For example, SAPs can absorb one hundred times their own weight, or more, of distilled water. The ability to absorb aqueous fluids under a confining pressure is an important requirement for an SAP used in a hygienic article, such as a diaper.

As used herein, the terms "base polymer particles," "surface-crosslinked SAP particles," and "SAP particles" refer to superabsorbent polymer particles in the dry state, i.e., particles containing from no water up to an amount of water less than the

weight of the particles. "Base polymer particles" are SAP particles prior to a surface-crosslinking process. "Surface-crosslinked SAP particles" are base polymer particles that have been subjected to a surface-crosslinking process, as described more fully hereafter. The term "particles" refers to granules, fibers, flakes, spheres, powders, platelets, and other shapes and forms known to persons skilled in the art of superabsorbent polymers. The terms "SAP gel" and "SAP hydrogel" refer to a superabsorbent polymer in the hydrated state, i.e., particles that have absorbed at least their weight in water, and typically several times their weight in water. The term "coated SAP particles" and "coated surface-crosslinked polymer particles" refer to particles of the present invention, i.e., SAP particles having a polyamine coating comprising a polyamine and a surface crosslinking agent.

The terms "surface treated" and "surface crosslinked" refer to an SAP, i.e., base polymer, particle having its molecular chains present in the vicinity of the particle surface crosslinked by a compound applied to the surface of the particle. The term "surface crosslinking" means that the level of functional crosslinks in the vicinity of the surface of the base polymer particle generally is higher than the level of functional crosslinks in the interior of the base polymer particle. As used herein, "surface" describes the outer-facing boundaries of the particle. For porous SAP particles,

exposed internal surface also are included in the definition of surface.

The term "polyamine coating" refers to a coating on the surface of an SAP particle, wherein the coating comprises (a) a polymer containing at least two, and typically a plurality, of primary, and/or secondary, and/or tertiary, and/or quaternary nitrogen atoms, (b) water, (c) an optional cosolvent, and (d) an optional crosslinking agent. At least a portion of the water and optional cosolvent typically evaporate from the coating during the step of applying the coating to the SAP particles. The cosolvent is capable of transforming the polyamine-coated SAP surface from hydrophilic to hydrophobic.

The term "increased amount of extractable materials" refers to SAP particles having an amount of extractable materials that is greater than the amount present in conventional SAP particles, as determined by the method set forth below, e.g., greater than 3%, by weight. Typically, the increased amount of extractable materials is greater than 3%, and up to about 15%, by weight, of the SAP particles.

SAP particles can differ in ease and cost of manufacture, chemical identity, physical properties, rate of water absorption, and degree of water absorption and retention, thus making the ideal water-absorbent resin a difficult composition to design. For example, the hydrolysis products of starch-acrylonitrile graft polymers have a compara-

tively high ability to absorb water, but require a cumbersome process for production and have the disadvantages of low heat resistance and decay or decomposition due to the presence of starch. Conversely, other water-absorbent polymers are easily and cheaply manufactured and are not subject to decomposition, but do not absorb liquids as well as the starch-acrylonitrile graft polymers.

Therefore, extensive research and development has been directed to providing a method of increasing the fluid absorption properties of stable, easy-to-manufacture SAP particles to match the superior fluid absorption properties of difficult-to-manufacture particles. Likewise, it would be advantageous to further increase the fluid absorption properties of already-superior SAP particles.

This is a difficult goal to achieve because improving one desirable property of an SAP particle often adversely affects another desirable property of the SAP particle. For example, absorptivity and gel permeability are conflicting properties. Therefore, a balanced relation between absorptivity and gel permeability is desired in order to provide sufficient liquid absorption, liquid transport, and dryness of the diaper and the skin when using SAP particles in a diaper.

In this regard, not only is the ability of the SAP particles to retain a liquid under subsequent pressure an important property, but absorption of a liquid against a simultaneously acting pres-

sure, i.e., during liquid absorption, also is important. This is the case in practice when a child or adult sits or lies on a sanitary article, or when shear forces are acting on the sanitary article, e.g., leg movements. This absorption property is referred to as absorption under load.

The current trend in the hygiene sector, e.g., in diaper design, is toward ever thinner core constructions having a reduced cellulose fiber content and an increased SAP content. This is an especially important trend in baby diapers and adult incontinence products. As diaper cores become thinner, the SAP particles must possess properties that historically have been supplied by fluff pulp. For example, fluid intake by a diaper core is enhanced by a higher ratio of fluff to SAP. Also, the integrity of the core is better when a higher ratio of fibrous fluff to SAP is utilized.

This trend has substantially changed the performance profile required of SAPs. Whereas SAP development initially was focused on very high absorption and swellability, it subsequently was determined that an ability of SAP particles to transmit and distribute a fluid both into the particle and through a bed of SAP particles also is of major importance. Conventional SAPs undergo great surface swelling when wetted with a fluid, such that transport of the fluid into the particle interior is substantially compromised or completely prevented. Historically, a substantial amount of cellulose

fibers have been included in a diaper core to quickly absorb the fluid for eventual distribution to the SAP particles, and to physically separate SAP particles in order to prevent fluid transport blockage.

An increased amount of SAP particles per unit area in a hygiene article must not cause the swollen polymer particles to form a barrier layer to absorption of a subsequent fluid insult. Therefore, an SAP having good permeability properties ensures optimal utilization of the entire hygiene article. This prevents the phenomenon of gel blocking, which in the extreme case causes the hygiene article to leak. Fluid transmission and distribution, therefore, is of maximum importance with respect to the initial absorption of body fluids.

However, because the absorption properties and permeability properties of SAP particles are conflicting, it is difficult to improve one of these properties without adversely affecting the other property. Investigators have researched various methods of improving the amount of fluid absorbed and retained by SAP particles, especially under load, and the rate at which the fluid is absorbed. One preferred method of improving the absorption and retention properties of SAP particles is to surface treat the SAP particles.

The surface treatment of SAP particles with crosslinking agents having two or more functional groups capable of reacting with pendant carboxylate groups on the polymer comprising the SAP

particle is disclosed in numerous patents. Surface treatment improves absorbency and gel rigidity to increase fluid flowability and prevent SAP particle agglomeration, and improves gel strength.

Surface-crosslinked SAP particles, in general, exhibit higher liquid absorption and retention values than SAP particles having a comparable level of internal crosslinks, but lacking surface crosslinks. Internal crosslinks arise from polymerization of the monomers comprising the SAP particles, and are present in the polymer backbone. It has been theorized that surface crosslinking increases the resistance of SAP particles to deformation, thus reducing the degree of contact between surfaces of neighboring SAP particles when the resulting hydrogel is deformed under an external pressure. The degree to which absorption and retention values are enhanced by surface crosslinking is related to the relative amount and distribution of internal and surface crosslinks, and to the particular surface crosslinking agent and method of surface crosslinking.

The present invention is directed to surface-crosslinked SAP particles that are coated with a polyamine, water, an optional cosolvent, and an optional crosslinking agent. The coated SAP particles have an increased amount of extractables, and the coated SAP particles demonstrate an excellent bed permeability (GBP) while retaining the fluid

absorbency properties (e.g., centrifuge retention capacity (CRC)) of the SAP particles.

SUMMARY OF THE INVENTION

The present invention is directed to SAP particles having a polyamine coating and an increased amount of extractable materials. More particularly, the present invention is directed to surface-crosslinked SAP particles having a coating comprising a polyamine, with an optional cosolvent and/or an optional crosslinking agent, hereafter referred to as a "polyamine coating." The present invention also is directed to a method of preparing the polyamine-coated SAP particles.

One aspect of the present invention is to provide SAP particles having an excellent gel bed permeability, a high absorbance under load, a good gel strength, and a high centrifuge retention capacity, that also demonstrate an excellent ability to absorb and retain electrolyte-containing fluids, such as saline, blood, urine, and menses.

Another aspect of the present invention is to provide polyamine-coated, surface-crosslinked SAP particles. Polyamine coating and surface crosslinking of the SAP particles can be performed simultaneously or sequentially.

Still another aspect of the present invention is to prepare coated SAP particles of the present invention by applying an aqueous polyamine solution, optional cosolvent, and optional crosslinking

agent, individually or in admixture, to the surfaces of surface-crosslinked SAP particles at a temperature of about 25°C up to 200°C, and mixing for about 5 to about 90 minutes.

Yet another aspect of the present invention is to provide polyamine-coated, surface-crosslinked SAP particles having improved absorbent properties, i.e., having an improved gel bed permeability compared to identical SAP particles lacking a polyamine coating.

Another aspect of the present invention is to provide polyamine-coated, surface-crosslinked SAP particles having an excellent permeability (e.g., gel bed permeability), while retaining a high centrifuge retention capacity (CRC) and absorbance under load (AUL).

Still another aspect of the present invention is to provide absorbent hygiene articles, such as diapers, having a core comprising coated SAP particles of the present invention. The diaper cores typically contain greater than 50%, by weight, of the present polyamine-coating SAP particles.

Another aspect of the present invention is to provide absorbent hygiene articles having a core containing a relatively high concentration of polyamine-coated SAP particles which provide improved permeability essentially without a decrease in absorbent properties.

These and other aspects and advantages of the present invention will become apparent from the

following detailed description of the preferred embodiments.

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a plot of gel bed permeability (0.3 GBP) at constant centrifuge retention capacity (CRC) versus extractables (wt%) and degree of neutralization (DN); and

Fig. 2 is a plot showing contours of 0.3 GBP at constant CRC versus extractables (wt%) and DN (mole %).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to surface-crosslinked SAP particles coated with a polyamine, water, an optional cosolvent, and an optional crosslinking agent. The SAP particles contain an increased amount of extractable materials, i.e., at least 3%, by weight.

SAPs for use in personal care products to absorb body fluids are well known. SAP particles typically are polymers of unsaturated carboxylic acids or derivatives thereof. These polymers are rendered water insoluble, but water swellable, by crosslinking the polymer with a di- or polyfunctional internal crosslinking agent. These internally crosslinked polymers are at least partially neutralized and contain pendant anionic carboxyl groups on the polymer backbone that enable the polymer to ab-

sorb aqueous fluids, such as body fluids. Typically, the SAP particles are subjected to a post-treatment to crosslink the pendant anionic carboxy groups on the surface of the particle.

SAPs are manufactured by known polymerization techniques, preferably by polymerization in aqueous solution by gel polymerization. The products of this polymerization process are aqueous polymer gels, i.e., SAP hydrogels, that are reduced in size to small particles by mechanical forces, then dried using drying procedures and apparatus known in the art. The drying process is followed by pulverization of the resulting SAP particles to the desired particle size.

To improve the fluid absorption profile, SAP particles are optimized with respect to one or more of absorption capacity, absorption rate, acquisition time, gel strength, and/or permeability. Optimization allows a reduction in the amount of cellulosic fiber in a hygienic article, which results in a thinner article. However, it is difficult to impossible to maximize all of these absorption profile properties simultaneously.

The present invention is directed to overcoming problems encountered in improving the absorption profile of SAP particles because improving one property often is detrimental to a second property. The present polyamine-coated SAP particles maintain the conflicting properties of a high centrifuge

retention capacity (CRC) and an excellent gel bed permeability (GBP).

In order to use an increased amount of SAP particles, and a decreased amount of cellulose, in personal care products, it is important to maintain a high liquid permeability. In particular, the permeability of an SAP particle hydrogel layer formed by swelling in the presence of a body fluid is very important to overcome the problem of leakage from the product. A lack of permeability directly impacts the ability of SAP particle hydrogel layers to acquire and distribute body fluids.

Polyamines are known to adhere to cellulose (i.e., fluff), and polyamine-coated SAPs have some improved permeability, as measured in the bulk, for a lower capacity SAP. Coating of SAP particles with uncrosslinked polyamines improves adhesion to cellulose fibers because of the high flexibility of polyamine molecules. Preferably, covalent bonding of the polyamine to the SAP particles is avoided because the degree of SAP particle crosslinking is increased and the absorptive capacity of the particles is reduced. Moreover, covalent bonding of polyamine to the SAP particle surface may occur at a temperature greater than 150°C, which adversely affects the color of the SAP particles, and, ultimately, consumer acceptance of the hygiene article.

The addition of a cationic compound, e.g., a polyamine, to improve permeability of SAP parti-

cles has been disclosed. WO 03/043670 discloses a polyamine coating on an SAP particle wherein the polyamine molecules are covalently crosslinked to one another. WO 95/22356 and U.S. Patent No. 5,849,405 disclose an absorbent material comprising a mixture of an SAP and an absorbent property modification polymer (e.g., a cationic polymer) that is reactive with at least one component included in urine (e.g., phosphate ion, sulfate ion, or carbonate ion). WO 97/12575 also discloses the addition of a polycationic compound without further crosslinking.

Other patents disclosing incorporation of polyamine-coated superabsorbents in fibrous matrices, e.g., U.S. Patent No. 5,641,561, U.S. Patent No. 5,382,610, EP 0 493 011, and WO 97/39780, relate to an absorbent material having improved structural stability in the dry and wet states. The material comprises water-insoluble hydrogel-forming SAP particles, a polycationic polymer bonded to the absorbent particles at the surface thereof, and glue microfibers that act as an adhesive between SAP particles and the carrier layer. The carrier layer can be a woven or nonwoven material, and the polycationic polymer can be a polyamine, a polyimine, or a mixture thereof. U.S. Patent No. 5,324,561 discloses an SAP which is directly crosslinked to amine-epichlorohydrin adducts (e.g., KYMENE® products).

In accordance with the present invention, surface-crosslinked SAP particles that are coated with a polyamine, optional cosolvent, and optional crosslinking agent, are disclosed. The present SAP particles comprise a base polymer capable of absorbing several times its weight in water. The base polymer can be a homopolymer or a copolymer. The identity of the base polymer is not limited as long as the polymer is an anionic polymer, i.e., contains pendant acid moieties, and is capable of swelling and absorbing at least ten times its weight in water, when in a neutralized form. Preferred base polymers are crosslinked polymers having acid groups that are at least partially in the form of a salt, generally an alkali metal or ammonium salt.

Therefore, the base polymer has at least about 25% of the pendant acid moieties, i.e., carboxylic acid moieties, present in a neutralized form. Preferably, the base polymer has about 50 mol% and up to about 100 mol%, and more preferably about 65 up to about 80 mol%, of the pendant acid moieties present in a neutralized form. In accordance with the present invention, the base polymer has a degree of neutralization (DN) of greater than 25 to about 100.

The base polymer of the SAP particles is a lightly crosslinked polymer capable of absorbing several times its own weight in water and/or saline. SAP particles can be made by any conventional process for preparing superabsorbent polymers and are

well known to those skilled in the art. One process for preparing SAP particles is a solution polymerization method described in U.S. Patent Nos. 4,076,663; 4,286,082; 4,654,039; and 5,145,906, each incorporated herein by reference. Another process is an inverse suspension polymerization method described in U.S. Patent Nos. 4,340,706; 4,497,930; 4,666,975; 4,507,438; and 4,683,274, each incorporated herein by reference.

SAP particles useful in the present invention are prepared from one or more monoethylenically unsaturated compound having at least one acid moiety, such as carboxyl, carboxylic acid anhydride, carboxylic acid salt, sulfonic acid, sulfonic acid salt, sulfuric acid, sulfuric acid salt, phosphoric acid, phosphoric acid salt, phosphonic acid, or phosphonic acid salt. SAP particles useful in the present invention preferably are prepared from one or more monoethylenically unsaturated, water-soluble carboxyl or carboxylic acid anhydride containing monomer, and the alkali metal and ammonium salts thereof, wherein these monomers preferably comprise 50 to 99.9 mole percent of the base polymer.

The base polymer of the SAP particles preferably is a lightly crosslinked acrylic resin, such as lightly crosslinked polyacrylic acid. The lightly crosslinked base polymer typically is prepared by polymerizing an acidic monomer containing an acyl moiety, e.g., acrylic acid, or a moiety capable of providing an acid group, i.e., acrylo-

nitrile, in the presence of an internal crosslinking agent, i.e., a polyfunctional organic compound. The base polymer can contain other copolymerizable units, i.e., other monoethylenically unsaturated comonomers, well known in the art, as long as the base polymer is substantially, i.e., at least 10%, and preferably at least 25%, acidic monomer units, e.g., (meth)acrylic acid. To achieve the full advantage of the present invention, the base polymer contains at least 50%, and more preferably, at least 75%, and up to 100%, acidic monomer units. The other copolymerizable units, for example, can help improve the hydrophilicity of the polymer.

Ethylenically unsaturated carboxylic acid and carboxylic acid anhydride monomers useful in the base polymer include acrylic acid, methacrylic acid, ethacrylic acid, α-chloroacrylic acid, α-cyanoacrylic acid, β-methylacrylic acid (crotonic acid), α-phenylacrylic acid, β-acryloxypropionic acid, sorbic acid, α-chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, β-stearylacrylic acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene, and maleic anhydride.

Ethylenically unsaturated sulfonic and phosphonic acid monomers include aliphatic or aromatic vinyl sulfonic acids, such as vinylsulfonic acid, allylsulfonic acid, vinyl toluene sulfonic acid, styrene sulfonic acid, acrylic and methacrylic sulfonic acids, such as sulfoethyl acrylate, sulfo-

ethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-methacryloxypropyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid, vinylphosphonic acid, allylphosphonic acid, and mixtures thereof.

Preferred, but nonlimiting, monomers include acrylic acid, methacrylic acid, maleic acid, fumaric acid, maleic anhydride, and the sodium, potassium, and ammonium salts thereof. An especially preferred monomer is acrylic acid.

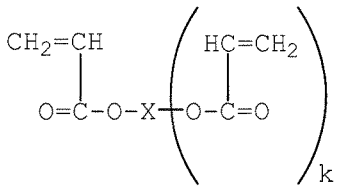
The base polymer can contain additional monoethylenically unsaturated monomers that do not bear a pendant acid group, but are copolymerizable with monomers bearing acid groups. Such compounds include, for example, the amides and nitriles of monoethylenically unsaturated carboxylic acids, for example, acrylamide, methacrylamide, acrylonitrile, and methacrylonitrile. Examples of other suitable comonomers include, but are not limited to, vinyl esters of saturated C_{1-4} carboxylic acids, such as vinyl formate, vinyl acetate, and vinyl propionate; alkyl vinyl ethers having at least two carbon atoms in the alkyl group, for example, ethyl vinyl ether and butyl vinyl ether; esters of monoethylenically unsaturated C_{3-18} alcohols and acrylic acid, methacrylic acid, or maleic acid; monoesters of maleic acid, for example, methyl hydrogen maleate; acrylic and methacrylic esters of alkoxylated monohydric saturated alcohols, for example, alcohols having 10 to 25 carbon atoms reacted with 2 to 200 moles of

ethylene oxide and/or propylene oxide per mole of alcohol; and monoacrylic esters and monomethacrylic esters of polyethylene glycol or polypropylene glycol, the molar masses (M_n) of the polyalkylene glycols being up to about 2,000, for example. Further suitable comonomers include, but are not limited to, styrene and alkyl-substituted styrenes, such as ethylstyrene and tert-butylstyrene, and 2-hydroxyethyl acrylate.

Polymerization of the acidic monomers, and any copolymerizable monomers, most commonly is performed by free radical processes in the presence of a polyfunctional organic compound. The base polymers are internally crosslinked to a sufficient extent such that the base polymer is water insoluble. Internal crosslinking renders the base polymer substantially water insoluble, and, in part, serves to determine the absorption capacity of the base polymer. For use in absorption applications, a base polymer is lightly crosslinked, i.e., has a crosslinking density of less than about 20%, preferably less than about 10%, and most preferably about 0.01% to about 7%.

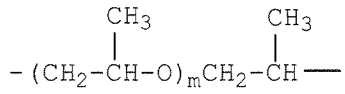
An internal crosslinking agent most preferably is used in an amount of less than about 7 wt%, and typically about 0.1 wt% to about 5 wt%, based on the total weight of monomers. Examples of crosslinking polyvinyl monomers include, but are not limited to, polyacrylic (or polymethacrylic) acid esters represented by the following formula (I), and

bisacrylamides represented by the following formula (II):



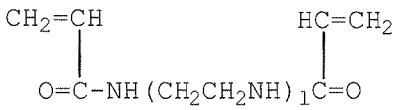
(I)

wherein X is ethylene, propylene, trimethylene, cyclohexyl, hexamethylene, 2-hydroxypropylene, $-(CH_2CH_2O)_nCH_2CH_2-$, or



,

n and m are each an integer 5 to 40, and k is 1 or 2;



(II)

,

wherein l is 2 or 3.

The compounds of formula (I) are prepared by reacting polyols, such as ethylene glycol, propylene glycol, trimethylolpropane, 1,6-hexanediol, glycerin, pentaerythritol, polyethylene glycol, or polypropylene glycol, with acrylic acid or

methacrylic acid. The compounds of formula (II) are obtained by reacting polyalkylene polyamines, such as diethylenetriamine and triethylenetetramine, with acrylic acid.

Specific internal crosslinking agents include, but are not limited to, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, 1,3-butylene glycol diacrylate, 1,3-butylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, ethoxylated bisphenol A diacrylate, ethoxylated bisphenol A dimethacrylate, ethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, polyethylene glycol diacrylate, polyethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, dipentaerythritol pentaacrylate, pentaerythritol tetraacrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, tris(2-hydroxyethyl)-isocyanurate triacrylate, ethoxylated trimethylolpropane triacrylate (ETMPTA), e.g., ETMPTA ethyoxylated with 15 moles of ethylene oxide (EO) on average, tris(2-hydroxyethyl)isocyanurate trimethyacrylate, divinyl esters of a polycarboxylic acid, diallyl esters of a polycarboxylic acid, triallyl terephthalate, diallyl maleate, diallyl fumarate, hexamethylenebismaleimide, trivinyl trimellitate, divinyl adipate, di-

allyl succinate, a divinyl ether of ethylene glycol, cyclopentadiene diacrylate, a tetraallyl ammonium halide, divinyl benzene, divinyl ether, diallyl phthalate, or mixtures thereof. Especially preferred internal crosslinking agents are N,N'-methylenebisacrylamide, N,N'-methylenebismethacrylamide, ethylene glycol dimethacrylate, and trimethylolpropane triacrylate.

The base polymer can be any internally crosslinked polymer having pendant acid moieties that acts as an SAP in its neutralized form. Examples of base polymers include, but are not limited to, polyacrylic acid, hydrolyzed starch-acrylonitrile graft copolymers, starch-acrylic acid graft copolymers, saponified vinyl acetate-acrylic ester copolymers, hydrolyzed acrylonitrile copolymers, hydrolyzed acrylamide copolymers, ethylene-maleic anhydride copolymers, isobutylene-maleic anhydride copolymers, poly(vinylsulfonic acid), poly(vinylphosphonic acid), poly(vinylphosphoric acid), poly(vinylsulfuric acid), sulfonated polystyrene, poly(aspartic acid), poly(lactic acid), and mixtures thereof. The preferred base polymer is a homopolymer or copolymer of acrylic acid or methacrylic acid.

The free radical polymerization is initiated by an initiator or by electron beams acting on a polymerizable aqueous mixture. Polymerization also can be initiated in the absence of such initia-

tors by the action of high energy radiation in the presence of photoinitiators.

Useful polymerization initiators include, but are not limited to, compounds that decompose into free radicals under polymerization conditions, for example, peroxides, hydroperoxides, persulfates, azo compounds, and redox catalysts. Water-soluble initiators are preferred. In some cases, mixtures of different polymerization initiators are used, for example, mixtures of hydrogen peroxide and sodium peroxodisulfate or potassium peroxodisulfate. Mixtures of hydrogen peroxide and sodium peroxodisulfate can be in any proportion.

Examples of suitable organic peroxides include, but are not limited to, acetylacetone peroxide, methyl ethyl ketone peroxide, tert-butyl hydroperoxide, cumeme hydroperoxide, tert-amyl perpivalate, tert-butyl perpivalate, tert-butyl perneohexanoate, tert-butyl perisobutyrate, tert-butyl per-2-ethylhexanoate, tert-butyl perisononanoate, tert-butyl permaleate, tert-butyl perbenzoate, di(2-ethylhexyl) peroxydicarbonate, dicyclohexyl peroxydicarbonate, di(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, diacetyl peroxydicarbonate, an allyl perester, cumyl peroxyneodecanoate, tert-butyl per-3,5,5-trimethylhexanoate, acetylcyclohexylsulfonyl peroxide, dilauryl peroxide, dibenzoyl peroxide, and tert-amyl perneodecanoate. Particularly suitable polymerization initiators are water-soluble azo initiators,

e.g., 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethylene)isobutyramidine dihydrochloride, 2-(carbamoylazo-isobutyronitrile, 2,2'-azobis[2-(2'-imidazolin-2-yl)propane] dihydrochloride, and 4,4'-azobis(4-cyanovaleric acid). The polymerization initiators are used, for example, in amounts of 0.01% to 5%, and preferably 0.05% to 2.0%, by weight, based on the monomers to be polymerized.

Polymerization initiators also include redox catalysts. In redox catalysts, the oxidizing compound comprises at least one of the above-specified per compounds, and the reducing component comprises, for example, ascorbic acid, glucose, sorbose, ammonium or alkali metal bisulfite, sulfite, thiosulfate, hyposulfite, pyrosulfite, or sulfide, or a metal salt, such as iron (II) ions or sodium hydroxymethylsulfoxylate. The reducing component of the redox catalyst preferably is ascorbic acid or sodium sulfite. Based on the amount of monomers used in the polymerization, about 3×10^{-6} to about 1 mol% of the reducing component of the redox catalyst system can be used, and about 0.001 to about 5.0 mol% of the oxidizing component of the redox catalyst can be used, for example.

When polymerization is initiated using high energy radiation, the initiator typically comprises a photoinitiator. Photoinitiators include, for example, α-splitters, H-abstracting systems, and azides. Examples of such initiators include, but

are not limited to, benzophenone derivatives, such as Michler's ketone; phenanthrene derivatives; fluorene derivatives; anthraquinone derivatives; thioxanthone derivatives; coumarin derivatives; benzoin ethers and derivatives thereof; azo compounds, such as the above-mentioned free-radical formers, substituted hexaarylbisimidazoles, acylphosphine oxides; or mixtures thereof.

Examples of azides include, but are not limited to, 2-(N,N-dimethylamino)ethyl 4-azidocinnamate, 2-(N,N-dimethylamino)ethyl 4-azidonaphthyl ketone, 2-(N,N-dimethylamino)ethyl 4-azidobenzoate, 5-azido-1-naphthyl 2'-(N,N-dimethylamino)ethyl sulfone, N-(4-sulfonylazidophenyl)maleimide, N-acetyl-4-sulfonylazidoaniline, 4-sulfonyl-azidoaniline, 4-azidoaniline, 4-azidophenacyl bromide, p-azidobenzoic acid, 2,6-bis(p-azidobenzylidene)cyclohexanone, and 2,6-bis(p-azidobenzylidene)-4-methylcyclohexanone. Photoinitiators customarily are used, if at all, in amounts of about 0.01% to about 5%, by weight of the monomers to be polymerized.

The base polymer is partially neutralized. As previously stated, the degree of neutralization preferably is about 25 to less than 100 mol%, more preferably about 50 to about 80 mol%. For example, the degree of neutralization can be 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95 to less than 100 mol%. The degree of polymerization even more preferably is about 55 to about 75 wt%, and

most preferably about 60 to about 70 mol%, based on monomers containing acid groups.

Useful neutralizing agents for the base polymer include alkali metal bases, ammonia, and/or amines. Preferably, the neutralizing agent comprises aqueous sodium hydroxide, aqueous potassium hydroxide, or lithium hydroxide. However, neutralization also can be achieved using sodium carbonate, sodium bicarbonate, potassium carbonate, or potassium bicarbonate, or other carbonates or bicarbonates, as a solid or as a solution. Primary, secondary, and/or tertiary amines can be used to neutralize the base polymer.

Neutralization of the base polymer can be performed before, during, or after the polymerization in a suitable apparatus for this purpose. The neutralization is performed, for example, directly in a kneader used for polymerization of the monomers.

In accordance with the present invention, polymerization of an aqueous monomer solution, i.e., gel polymerization, is preferred. In this method, a 10% to 70%, by weight, aqueous solution of the monomers, including the internal crosslinking agent, is neutralized in the presence of a free radical initiator. The solution polymerization is performed at 0°C to 150°C, preferably at 10°C to 100°C, and at atmospheric, superatmospheric, or reduced pressure. The polymerization also can be conducted under a

protective gas atmosphere, preferably under nitrogen.

In accordance with an important feature of the present invention, the weight amount of extractable materials in the base polymer is greater than the amount typically present in SAPs. In particular, the amount of extractable materials in the base polymer is at least 3%, by weight, and can be up to about 15%, by weight, e.g., 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15%, by weight. Preferably, the amount of extractable materials in the base polymer is about 4% to about 12%, and more preferably about 5% to about 9%, by weight.

The amount of extractable materials in an SAP typically is maintained as low as possible because extractables adversely effect the absorption properties of the SAP. In particular, an increased amount of extractable materials can adversely affect gel strength and can contribute to gel blocking. Contrary to accepted practices in the preparation of SAPs, the extractable materials in the present base polymer is at an increased level, and, surprisingly, after coating with a polyamine and curing at a temperature at 150°C or below, an improved SAP permeability is achieved (e.g., an improved GBP), without adversely affecting absorption, as determined by centrifuge retention capacity (CRC). Prior to the present invention, maintaining a high SAP permeability and a high SAP absorption property was difficult, and required a high temperature, i.e., greater

than 150°C, treatment. Such high temperature treatments can adversely affect the color of the SAP particles, and in turn, consumer acceptance of products incorporating the SAP particles.

The amount of extractable material in the base polymer can be increased by (a) increasing the amount of initiators utilized in the polymerization reaction, (b) adding a chain transfer agent into the polymerization reaction, (c) adding a linear, low molecular weight polymer to the base polymer hydrogel, (d) reducing the amount of internal crosslinking agent utilized in the polymerization reaction, (e) any combination of two or three of (a), (b), (c), and (d), or (f) all four of (a), (b), (c), and (d).

In particular, when the amount of extractable material is increased solely by using a higher amount of initiator, i.e., method (a) alone, the initiator utilized in the polymerization is at least 0.02%, by weight, based on the monomer to be polymerized, in order to provide at least 3 wt% extractable in the base polymer. To achieve an amount of extractable materials in the range of at least 3 to about 15 wt%, the initiator is used in an amount of about 0.033%, by weight, or greater, based on the monomers to be polymerized. If method (a) is practiced in conjunction with method (b) and/or method (c) and/or method (d), the amount of initiator can be lowered to achieve an amount of extractable material of at least 3 wt%. In such a case, the amount

of initiator can be readily determined by persons skilled in the art.

In particular, the initiator concentration depends on the type of initiator selected for the polymerization reaction. In a standard polymerization reaction, 0.011 wt% of each redox initiator component is used. To increase the amount of extractable material in the base polymer greater than 0.02 wt% active hydrogen peroxide and 0.02 wt% ascorbic acid can be used as the redox initiator components. For example, in a DN=60% polymerization reaction, 0.011 wt% hydrogen peroxide and 0.011 wt% ascorbic acid provided a base polymer having a one-hour extractable content of 2.5 wt%, whereas using 0.033 wt% hydrogen peroxide and 0.033 wt% ascorbic acid provided a base polymer having a one-hour extractable content of 3.5 wt%. In addition, blends of different types of initiators can be used, e.g., UV initiators, redox initiators, and thermal initiators.

When the amount of extractable material is increased solely by introducing a chain transfer agent into the polymerization reaction, i.e., method (b) alone, the chain transfer agent typically is added to the polymerization reaction in an amount of about 0.01% to about 1%, by weight, based on the monomer to be polymerized, to achieve at least 3% to about 15%, by weight, extractable materials in the base polymer. However, the amount of chain transfer agent may vary outside these amounts depending on

the identity of the chain transfer agent, for example, if a solvent, such as N,N-dimethylaniline, 1-propanol, triethylamine, or tripropylamine, is used as the chain transfer agent. If method (b) is practiced in conjunction with method (a) and/or method (c) and/or method (d), the amount of chain transfer agent can be lowered to achieve an amount of extractable material of at least 3 wt%. In such a case, the amount of chain transfer agent can be readily determined by persons skilled in the art. Chain transfer agents are known in the polymer art, and include, for example, mercaptans or polymercaptans, e.g., n-octyl mercaptan, n-dodecyl mercaptan, butyl or methyl mercaptopropionate, mercaptopropionic acid, ethylene dithiol, 3-mercapto-1,2-propanediol, or thiolactic acid; hypophosphorous acid and salts thereof, e.g., sodium hypophosphite; and formic acid and salts thereof.

When the amount of extractable material is increased solely by introducing a linear, low molecular weight polymer into the base polymer, i.e., method (c) alone, the extractable materials present in the base polymer can be determined, then a sufficient amount of the linear polymer is added to the base polymer hydrogel to provide a base polymer having the desired amount of extractable material from at least 3% to about 15%, by weight. If method (c) is practiced in conjunction with method (a) and/or method (b) and/or method (d), the amount of

low molecular weight polymer to be added to the base polymer can be determined as above.

The linear polymer added to increase the amount of extractable material in the base polymer particles typically has a weight average molecular weight (M_w) of about 500 to about 100,000, and preferably about 750 to about 75,000. To achieve the full advantage of the present invention, the linear polymer has an M_w of about 1000 to about 60,000. The linear polymer is prepared from monomers that provide an SAP, but the monomers are polymerized in the absence of an internal crosslinking agent. Therefore, the linear polymer comprises one or more of the acid-containing monomers discussed above, and preferably comprises acrylic acid. A preferred linear, low molecular weight polymer is polyacrylic acid, sodium polyacrylate, or a mixture thereof.

When the amount of extractable material is increased solely by reducing the amount of internal crosslinking agent used in the polymerization reaction, i.e., method (d) alone, the internal crosslinking agent is used in an amount of about 0.01% to about 0.2%, by weight, based on the weight of monomers used in the polymerization reaction, to achieve an amount of extractable material greater than 3% to about 15%, by weight of the base polymer. If method (d) is practiced in combination with method (a) and/or method (b) and/or method (c), the amount of internal crosslinking agent can be increased to achieve an amount of extractable material of at

least 3%, by weight. In such a case, the amount of internal crosslinking agent can be readily determined by persons skilled in the art.

After polymerization, the resulting hydrogel of the base polymer is dried, and the dry base polymer particles are ground and classified. The base polymer particles then are surface crosslinked and coated with a polyamine. It should be understood that the polyamine coating process step and surface crosslinking process step are different, even if performed simultaneously, and impart different properties to the surfaces of the base polymer particles. In one embodiment, the base polymer particles can be surface crosslinked, then coated with a polyamine. Alternatively, surface crosslinking is performed after forming a polyamine coating on the base polymer particles. Preferably, the surface crosslinking step and polyamine coating step are performed simultaneously.

In one embodiment, a polyamine coating is added to surface-crosslinked SAP particles after the surface-crosslinking step. In this embodiment of applying a polyamine coating to the base polymer particles, a surface-crosslinking agent is applied to the surfaces of the base polymer particles. Then, the resulting polymer particles are heated for a sufficient time and at a sufficient temperature to surface crosslink the base polymer particles. Next, a coating solution containing a polyamine dissolved in water and an optional cosolvent, and further con-

taining an optional crosslinking agent, is applied to the surfaces of the surface-crosslinked SAP particles. The polyamine coating is applied to the surface-crosslinked SAP particles having a temperature of about 25°C to about 150°C, and preferably about 50°C to about 150°C. After applying the polyamine coating to the surface-crosslinked SAP particles, the coated SAP particles are mixed for about 5 to about 90 minutes to form a uniform polyamine coating on the surface-crosslinked polymer particles and provide SAP particles of the present invention. The polyamine coating is hydrophilic in the absence of an optional cosolvent, and is hydrophobic in the presence of an optional cosolvent.

The order of applying the polyamine and surface crosslinking agent to the surfaces of the base polymer particles is not critical. Therefore, in other embodiments, the polyamine coating is applied to the base polymer particles prior to surface crosslinking. In still other embodiments, the polyamine coating and the surface crosslinking agent are applied to the base polymer particles simultaneously, followed by heating to surface crosslink and provide a polyamine coating on the base polymer particles.

In the preferred embodiment of applying a polyamine coating to the base polymer particles, a coating solution containing a polyamine dissolved in a solvent is applied to the surfaces of the base polymer particles. Next, coating solutions contain-

ing a surface crosslinking agent and/or an optional crosslinking agent for the polyamine are applied to the surfaces of the SAP particles. Then, the coated base polymer particles are heated for a sufficient time and at a sufficient temperature to at least partially evaporate the solvents of the coating solutions, surface crosslink the base polymer particles, and form a polyamine coating on the base polymer particles to provide coated SAP particles of the present invention.

In the surface crosslinking process, a multifunctional compound capable of reacting with the functional groups of the base polymer is applied to the surface of the base polymer particles, preferably using an aqueous solution. The aqueous solution also can contain water-miscible organic solvents, like an alcohol, such as methanol, ethanol, or i-propanol; a polyol, like ethylene glycol or propylene glycol; or acetone.

A solution of a surface crosslinking agent is applied to the base polymer particles in an amount to wet predominantly only the outer surfaces of the base polymer particles, either before or after application of the polyamine. Surface crosslinking and drying of the base polymer particles then is performed, preferably by heating at least the wetted surfaces of the base polymer particles.

Typically, the base polymer particles are surface treated with a solution of a surface crosslinking agent containing about 0.01% to about 4%, by

weight, surface crosslinking agent, and preferably about 0.4% to about 2%, by weight, surface crosslinking agent in a suitable solvent. The solution can be applied as a fine spray onto the surfaces of freely tumbling base polymer particles at a ratio of about 1:0.01 to about 1:0.5 parts by weight base polymer particles to solution of surface crosslinking agent. The surface crosslinking agent, if present at all, is present in an amount of 0.001% to about 5%, by weight of the base polymer particles, and preferably 0.001% to about 0.5% by weight. To achieve the full advantage of the present invention, the surface crosslinking agent is present in an amount of about 0.001% to about 0.1%, by weight of the base polymer particles.

Surface crosslinking and drying of the base polymer particles are achieved by heating the surface-treated base polymer particles at a suitable temperature, e.g., about 70°C to about 200°C, and preferably about 105°C to about 180°C. Suitable surface crosslinking agents are capable of reacting with acid moieties and crosslinking polymers at the surfaces of the base polymer particles.

Nonlimiting examples of suitable surface crosslinking agents include, but are not limited to, an alkylene carbonate, such as ethylene carbonate or propylene carbonate; a polyaziridine, such as 2,2-bishydroxymethyl butanol tris[3-(1-aziridine propionate] or bis-N-aziridinomethane; a haloepoxy, such as epichlorohydrin; a polyisocyanate, such as 2,4-

toluene diisocyanate; a di- or polyglycidyl compound, such as diglycidyl phosphonates, ethylene glycol diglycidyl ether, or bischlorohydrin ethers of polyalkylene glycols; alkoxysilyl compounds; polyols such as ethylene glycol, 1,2-propanediol, 1,4-butanediol, glycerol, methyltriglycol, polyethylene glycols having an average molecular weight M_w of 200-10,000, di- and polyglycerol, pentaerythritol, sorbitol, the ethoxylates of these polyols and their esters with carboxylic acids or carbonic acid, such as ethylene carbonate or propylene carbonate; carbonic acid derivatives, such as urea, thiourea, guanidine, dicyandiamide, 2-oxazolidinone and its derivatives, bisoxazoline, polyoxazolines, di- and polyisocyanates; di- and poly-N-methylol compounds, such as methylenebis(N-methylolmethacrylamide) or melamine-formaldehyde resins; compounds having two or more blocked isocyanate groups, such as trimethylhexamethylene diisocyanate blocked with 2,2,3,6-tetramethylpiperidin-4-one; and other surface crosslinking agents known to persons skilled in the art.

A solution of the surface crosslinking agent is applied to the surfaces of the base polymer particles before or after a solution containing the polyamine is applied to the surfaces of the base polymer particles. The polyamine also can be applied to the base polymer particles after the surface crosslinking step has been completed.

The components of the polyamine coating solution can be applied to the SAP particles in any order, from one, two, or three solutions. In particular, the cosolvent and optional crosslinking agent can be applied to the SAP particles independent of the polyamine and independent of each other. Alternatively, the polyamine, optional cosolvent, and optional crosslinking agent can be applied from a single solution.

A solution containing the polyamine comprises about 5% to about 50%, by weight, of a polyamine in a suitable solvent. Typically, a sufficient amount of a solvent is present to allow the polyamine to be readily and homogeneously applied to the surfaces of the base polymer particles. The solvent for the polyamine solution can be, but is not limited to, water, an alcohol, or a glycol, such as methanol, ethanol, ethylene glycol, or propylene glycol, and mixtures thereof.

The amount of polyamine applied to the surfaces of the base polymer particles is sufficient to coat the base polymer particle surfaces. Accordingly, the amount of polyamine applied to the surfaces of the base polymer particles is about 0.1% to about 2%, and preferably about 0.2% to about 1%, of the weight of the base polymer particle. To achieve the full advantage of the present invention, the polyamine is present on the base polymer particle surfaces in an amount of about 0.2% to about 0.5%, by weight of the base polymer particle.

A polyamine can form an ionic bond with a base or surface-crosslinked polymer and retains adhesive forces to the polymer after the polymer absorbs a fluid and swells. Preferably, an excessive amount of covalent bonds are not formed between the polyamine and the polymer, and the polyamine polymer interactions are intermolecular, such as electrostatic, hydrogen bonding, and van der Waals interactions. Therefore, the presence of a polyamine on the polymer particles does not adversely influence the absorption profile of the polymer particles.

A polyamine useful in the present invention has at least two, and preferably a plurality, of nitrogen atoms per molecule. The polyamine typically has a weight average molecular weight (M_w) of about 5,000 to about 1,000,000, and preferably about 20,000 to about 600,000. To achieve the full advantage of the present invention, the polyamine has an M_w of about 100,000 to about 400,000.

In general, useful polyamine polymers have (a) primary amine groups, (b) secondary amine groups, (c) tertiary amine groups, (d) quaternary ammonium groups, or (e) mixtures thereof. Examples of polyamines include, but are not limited to, a polyvinylamine, a polyallylamine, a polyethyleneimine, a polyalkyleneamine, a polyazetidine, a polyvinylguanidine, a poly(DADMAC), i.e., a poly(diallyl dimethyl ammonium chloride), a cationic polyacrylamide, a polyamine functionalized polyacrylate, and mixtures thereof.

Homopolymers and copolymers of vinylamine also can be used, for example, copolymers of vinylformamide and comonomers, which are converted to vinylamine copolymers. The comonomers can be any monomer capable of copolymerizing with vinylformamide. Nonlimiting examples of such monomers include, but are not limited to, acrylamide, methacrylamide, methacrylonitrile, vinylacetate, vinylpropionate, styrene, ethylene, propylene, N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, monomers containing a sulfonate or phosphonate group, vinylglycol, acrylamido(methacrylamido)-alkylene trialkyl ammonium salt, diallyl dialkylammonium salt, C_{1-4}alkyl vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, isopropyl vinyl ether, n-propyl vinyl ether, t-butyl vinyl ether, N-substituted alkyl (meth)acrylamides substituted by a C_{1-4}alkyl group as, for example, N-methylacrylamide, N-isopropylacrylamide, and N,N-dimethylacrylamide, C_{1-20}alkyl(meth)acrylic acid esters such as methyl methacrylate, ethyl methacrylate, propyl acrylate, butyl acrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, 2-methylbutyl acrylate, 3-methylbutyl acrylate, 3-pentyl acrylate, neopentyl acrylate, 2-methylpentyl acrylate, hexyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, phenyl acrylate, heptyl acrylate, benzyl acrylate, tolyl acrylate,

octyl acrylate, 2-octyl acrylate, nonyl acrylate, and octyl methacrylate.

Specific copolymers of polyvinylamine include, but are not limited to, copolymers of N-vinylformamide and vinyl acetate, vinyl propionate, a C_{1-4}alkyl vinyl ether, a (meth)acrylic acid ester, acrylonitrile, acrylamide, and vinylpyrrolidone.

A polyamine coating is hydrophilic as applied to the base or surface-crosslinked polymer particles. The polyamine coating can be rendered hydrophobic by including a cosolvent in the polyamine coating process. The optional cosolvent contains at least one, and often two or three, hydroxy groups. Useful cosolvents include, but are not limited to, alcohols, diols, triols, and mixtures thereof, for example, methanol, ethanol, propyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, oligomers of ethylene glycol, oligomers of propylene glycol, glycerin, monoalkyl ethers of propylene glycol, and similar hydroxy-containing solvents. An oligomer of ethylene glycol or propylene glycol contains two to four ethylene oxide or propylene oxide monomer units.

In accordance with the present invention, the number of covalent bonds that form between the polyamine and the base or surface-crosslinked SAP particles is extremely low, if present at all. However, for some polyamines, a polyamine coating can impart a tack to the SAP particles, which could lead to agglomeration or aggregation of polyamine-

coated polymer particles. To overcome this potential problem, a crosslinking agent for the polyamine coating solution can be used.

Crosslinking of the polyamine coating is different from surface crosslinking. The crosslinking agent for the polyamine coating forms crosslinks between the nitrogen atoms of the polyamine. The surface crosslinking agent forms crosslinks with carboxyl groups of the base polymer. In some embodiments, the surface crosslinking agent is applied to the base polymer and reacted prior to application of the polyamine coating. However, it should be understood that the crosslinking agent for the polyamine coating in some embodiments may react with the nitrogen atoms of the polyamine and a small number of carboxyl groups of the base polymer.

The crosslinking agent for the polyamine coating can be organic or inorganic in nature. An organic crosslinking agent reacts with nitrogen atoms of the polyamine to form covalent bonds with the polyamine nitrogen atoms. An inorganic crosslinking agent forms ionic crosslinks via the nitrogen atoms of the polyamine coating. The crosslinking agents can be used individually or in admixture, e.g., a mixture of inorganic crosslinking agents, a mixture of organic crosslinking agents, or a mixture of inorganic and organic crosslinking agents.

In one embodiment, the crosslinking agent is a solution containing a salt having (a) a polyvalent metal cation, i.e., a metal cation having a

valence of two, three, or four, (b) a polyvalent anion, i.e., an anion having a valence of two or greater, or (c) both a polyvalent cation and a polyvalent anion, is applied to the surfaces of the polymer particles. In this embodiment, the salt is applied to the polymer particles independently from the polyamine in order to avoid a premature crosslinking reaction. The salt can be applied to the polymer particles prior to or after the polyamine is added to the surface of the polymer particles.

The polyvalent metal cation and polyvalent anion are capable of interacting, e.g., forming ionic crosslinks, with the nitrogen atoms of the polyamine. As a result, a tackless polyamine coating is formed on the surface of the polymer particles to provide coated SAP particles of the present invention.

In accordance with the present invention, a salt applied to surfaces of the polymer particles has a sufficient water solubility such that polyvalent metal cations and/or polyvalent anions are available to interact with the nitrogen atoms of the polyamine. Accordingly, a useful salt has a water solubility of at least 0.01 g of salt per 100 ml of water, and preferably at least 0.02 g per 100 ml of water.

A polyvalent metal cation of the salt has a valence of +2, +3, or +4, and can be, but is not limited to, Mg^{2+}, Ca^{2+}, Al^{3+}, Sc^{3+}, Ti^{4+}, Mn^{2+}, $Fe^{2+/3+}$, Co^{2+}, Ni^{2+}, $Cu^{+/2+}$, Zn^{2+}, Y^{3+}, Zr^{4+}, La^{3+}, Ce^{4+}, Hf^{4+}, Au^{3+},

and mixtures thereof. Preferred cations are Mg^{2+}, Ca^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+}, La^{3+}, and mixtures thereof, and particularly preferred cations are Al^{3+}, Ti^{4+}, Zr^{4+}, and mixtures thereof. The anion of a salt having a polyvalent cation is not limited, as long as the salt has sufficient solubility in water. Examples of anions include, but are not limited to, chloride, bromide, and nitrate.

A polyvalent anion of the salt has a valence of -2, -3, or -4. The polyvalent anion can be inorganic or organic in chemical structure. The identity of the polyvalent anion is not limited as long as the anion is capable of interacting with the nitrogen atoms of the polyamine.

Examples of polyvalent inorganic anions include, but are not limited to, sulfate, phosphate, hydrogen diphosphate, and borate. Examples of polyvalent organic anions include, but are not limited to, water-soluble anions of polycarboxylic acids. In particular, the anion can be an anion of a di- or tri-carboxylic acid, such as oxalic acid, tartaric acid, lactic acid, malic acid, citric acid, aspartic acid, malonic acid, and similar water-soluble polycarboxylic acids optionally containing a hydroxy and/or an amino group. Additional useful polyvalent anions include polycarboxylic amino compounds, for example, polyacrylic acid, ethylenediaminetetraacetic acid (EDTA), ethylenebis(oxyethylenenitrile)-tetraacetic acid (EGTA), diethylenetriaminopenta-

acetic acid (DTPA), N-hydroxyethylethylenediamine-triacetic acid (HEDTA), and mixtures thereof.

In addition, a salt containing a polyvalent metal cation and a polyvalent anion can be used, provided the salt has sufficient water solubility to be dissolved in a solvent for a homogeneous application to surface-crosslinked SAP particles.

The salt can be present in a coating solution together with an optional organic crosslinking agent. The salt typically is present in the coating solution in an amount of about 0.5% to 20%, by weight, for example. The amount of salt present in a coating solution, and the amount applied to the surface-crosslinked polymer particles, is related to the identity of the salt, its solubility in the solvent of the coating solution, the identity of the polyamine applied to the surface-crosslinked polymer particles, and the amount of polyamine applied to the surface-crosslinked polymer particles. In general, the amount of salt applied to the surface-crosslinked polymer particles is sufficient to form a tackless, monolithic polyamine coating and provide coated SAP particles of the present invention.

In another embodiment, an organic crosslinking agent can be used in conjunction with the polyamine. In still another embodiment, an organic crosslinking agent is applied to the surface crosslinked polymer particles, followed by the polyamine solution. The optional cosolvent can be applied to

the surface-crosslinked polymer particles with the organic crosslinking agent, with the polyamine, with both, or alone, either before or after application of the organic crosslinking agent or the polyamine. In either case, the SAP particles then are maintained at a sufficient temperature for a sufficient time to form crosslinks between the polyamine and the crosslinking agent.

In the organic crosslinking process, a multifunctional compound capable of reacting with the amino groups of the polyamine is applied to the surface of the surface-crosslinked polymer particles. The organic crosslinking agent can be the same or different from the surface crosslinking agent. However, as discussed above, the surface crosslinking agent and the crosslinking agent for the polyamine can be applied to the base polymer particles during different process steps and the SAP particles are maintained at different temperatures, i.e., the surface crosslinking process may utilize a higher temperature to effect a reaction with the carboxy groups of the base polymer (i.e., about 70°C to about 200°C) than the polyamine crosslinking process, which can utilize a lower temperature for crosslinking through the nitrogen atoms of the polyamine (i.e., about a 25°C to about 200°C). If the surface crosslinking agent and polyamine crosslinking agent are applied to the base polymer particles in the same process step, a temperature is selected such that surface crosslinking and

polyamine crosslinking are both effected (e.g., about 70°C to about 200°C).

The organic crosslinking process typically utilizes an aqueous solution of the crosslinking agent. The aqueous solution also can contain water-miscible organic solvents, like an alcohol, such as methanol, ethanol, or i-propanol; a polyol, like ethylene glycol or propylene glycol; or acetone.

A solution of an organic crosslinking agent is applied to the polymer particles during or after application of the polyamine in an amount to wet predominantly only the outer surfaces of the polymer particles. Crosslinking and drying of the coated polymer particles then are achieved by maintaining at least the wetted surfaces of the polymer particles at a suitable temperature, e.g., about 25°C to about 200°C, preferably about 75°C to about 150°C, and more preferably about 80°C to about 150°C, for about 5 to about 90 minutes to allow the crosslinking agent to react with the nitrogen atoms of the polyamine.

Typically, the polymer particles are treated with a solution of an organic crosslinking agent containing about 0.5% to about 20%, by weight, crosslinking agent, and preferably about 3% to about 15%, by weight, crosslinking agent in a suitable solvent. The organic crosslinking agent, if present at all, is present in an amount of 0.001% to about 0.5%, by weight of the polymer particles, and preferably 0.001% to about 0.3% by weight. To achieve

the full advantage of the present invention, the organic crosslinking agent is present in an amount of about 0.001% to about 0.1%, by weight of the polymer particles.

Nonlimiting examples of suitable organic crosslinking agents include, but are not limited to, an alkylene carbonate, such as ethylene carbonate or propylene carbonate; a polyaziridine, such as 2,2-bishydroxymethyl butanol tris[3-(1-aziridine propionate] or bis-N-aziridinomethane; a haloepoxy, such as epichlorohydrin; a polyisocyanate, such as 2,4-toluene diisocyanate; a di- or polyglycidyl compound, such as diglycidyl phosphonates, ethylene glycol diglycidyl ether, or bischlorohydrin ethers of polyalkylene glycols; alkoxysilyl compounds; carbonic acid derivatives, such as urea, thiourea, guanidine, dicyandiamide, 2-oxazolidinone and its derivatives, bisoxazoline, polyoxazolines, di- and polyisocyanates; di- and poly-N-methylol compounds, such as methylenebis(N-methylolmethacrylamide) or melamine-formaldehyde resins; compounds having two or more blocked isocyanate groups, such as trimethylhexamethylene diisocyanate blocked with 2,2,3,6-tetramethylpiperidin-4-one; multifunctional aldehydes, multifunctional ketones, multifunctional acetals, multifunctional ketals, and other organic crosslinking agents known to persons skilled in the art. The organic crosslinking agent can be used alone or in combination.

A solution of the organic crosslinking agent is applied to the surfaces of the polymer particles simultaneously with, or before or after, a solution containing the polyamine is applied to the surfaces of the polymer particles.

In accordance with the present invention, the polyamine, and optional inorganic and/or organic crosslinking agent, are applied to the base or surface-crosslinked polymer particles in a manner such that each is uniformly distributed on the surfaces of the polymer particles. In addition to the crosslinking agent, other optional ingredients can be applied to the base or surface-crosslinked SAP particles in conjunction with the polyamine. Such optional ingredients include, but are not limited to, clay and silica, for example, to impart anticaking properties to the polyamine-coated SAP particles. A clay or silica also can be added to the polyamine-coated SAP particles after application and curing of the polyamine coating.

Any known method for applying a liquid to a solid can be used to apply the polyamine coating to the polymer particles, preferably by dispersing a coating solution into fine droplets, for example, by use of a pressurized nozzle or a rotating disc. Uniform coating of the polymer particles can be achieved in a high intensity mechanical mixer or a fluidized mixer, which suspends the base polymer particles in a turbulent gas stream. Methods for the dispersion of a liquid onto the surfaces of base

polymer particles are known in the art, see, for example, U.S. Patent No. 4,734,478, incorporated herein by reference.

Methods of coating the base polymer particles include applying the polyamine and optional crosslinking agent simultaneously. When an inorganic salt is used as a crosslinking agent, the polyamine and salt preferably are applied via two separate nozzles to avoid an interaction before application to the surfaces of the base or surface-crosslinked polymer particles. A preferred method of coating the base or surface-crosslinked polymer particles is a sequential addition of the components. A more preferred method is application of the polyamine first, followed by an application of the optional crosslinking agent.

The resulting polyamine coated polymer particles then are maintained at about 25°C to about 150°C for sufficient time, e.g., about 5 to about 60 minutes. In some embodiments, the polyamine coating is applied to surface-crosslinked SAP particles that have not completely cooled after the surface-crosslinking process. Accordingly, the polyamine-coating step utilizes the latent heat of the surface-crosslinked SAP particles. If necessary, external heat can be applied to maintain a desired particle temperature up to about 150°C and cure the polyamine coating. The temperature of the polyamine-coated SAP particles is maintained at about 150°C or less to avoid, or at least minimize, reactions that form

covalent bonds between the polyamine coating and the carboxyl groups of the base polymer.

After application of the polyamine, water, optional solvent, and optional crosslinking agent to the base or surface-crosslinked SAP particles, the coated SAP particles are mixed at about 25°C to about 150°C, e.g., 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145 or 150°C, for about 5 to about 90 minutes in a paddle mixer, for example, such as those available from Ruberg-Mischtechnik AG, Nieheim, Germany and Nara Machining Co., Ltd., Frechen, Germany. Other suitable mixers include Patterson-Kelly mixers, DRAIS turbulence mixers, Lödige mixers, Schugi mixers, screw mixers, and pan mixers. After mixing, a polyamine coated SAP of the present invention results, i.e., a surface-cross-linked SAP particle having an optionally crosslinked polyamine coating, wherein covalent bonds between the polyamine and the carboxyl groups of the base polymer are minimized.

The polyamine-coated SAP particles of the present invention have excellent absorption properties, permeability, and gel integrity. In particular, the present SAP particles have a centrifuge retention capacity of at least 25 g/g. The present SAP particles further exhibit a gel bed permeability (0.3 psi) of at least 3, more preferably at least 4, 5, 6, or 7, and most preferably at least 8, 9, or 10 Darcies. The present invention, therefore, provides

polyamine-coated SAP particles having excellent absorbency and fluid permeability.

The present invention also provides polyamine-coated SAP particles that have a hydrophobic surface when a cosolvent is applied as a component of the coating solution, which reduces SAP particle agglomeration attributed to the viscous, tacky nature of polyamines. The present invention also provides polyamine-coated SAP particles having a hydrophilic surface when an inorganic or organic crosslinking agent is applied as a component of the coating solution, and the SAP particles are maintained at a relatively low temperature, i.e., about 25°C to about 150°C, for about 5 to about 90 minutes.

In accordance with the present invention, a polyamine is applied to base or surface-crosslinked SAP particles in a manner such that the polyamine and any optional crosslinking agent are uniformly distributed on the surfaces of the surface-crosslinked SAP particles. The resulting coated SAP particles then are maintained at about 25°C to about 150°C, for sufficient time, e.g., about 5 to about 90, and preferably about 10 to about 60 minutes, to crosslink the polyamine coating, while minimizing covalent crosslinks between the polyamine coating and the carboxyl groups of the base polymer.

To demonstrate the unexpected advantages provided by the coated SAP particles of the present invention, polyamine-coated SAP particles were pre-

pared and tested for extractable material (1 hour), centrifuge retention capacity (CRC, g/g), absorbency under load (AUL 0.9 psi, g/g), free swell gel bed permeability (GBP, Darcies), and gel bed permeability (GBP 0.3 psi, Darcies). These tests were performed using the following procedures.

Centrifuge Retention Capacity (CRC)

This test determines the free swelling capacity of a hydrogel-forming polymer. The resultant retention capacity is stated as grams of liquid retained per gram weight of the sample (g/g). In this method, 0.2000 ± 0.0050 g of dry SAP particles of size fraction 106 to 850 µm are inserted into a teabag. A heat-sealable teabag material, such as that available from Dexter Corporation (having a place of business in Windsor Locks, Connecticut, U.S.A.) as model designation 1234T heat-sealable filter paper works well for most applications. The bag is formed by folding a 5-inch by 3-inch sample of the bag material in half and heat sealing two of the open edges to form a 2.5-inch by 3-inch rectangular pouch. The heat seals should be about 0.25 inches inside the edge of the material. After the sample is placed in the pouch, the remaining open edge of the pouch also is heat sealed. Empty bags also can be made to serve as controls. The teabag is placed in saline solution (i.e., 0.9 wt% aqueous sodium chloride) for 30 minutes (at least 0.831 (liter) saline solution/1 g polymer), making sure

that the bags are held down until they are completely wetted. Then, the teabag is centrifuged for three minutes at 250 G. The absorbed quantity of saline solution is determined by measuring the weight of the teabag. The amount of solution retained by the superabsorbent polymer sample, taking into account the solution retained by the bag itself, is the centrifuge retention capacity (CRC) of the superabsorbent polymer, expressed as grams of fluid per gram of superabsorbent polymer. More particularly, the retention capacity is determined by the following equation:

$$\frac{\text{sample bag after centrifuge-empty bag after centrifuge-dry sample weight}}{\text{dry sample weight}}$$

Free-Swell Gel Bed Permeability (GBD, Darcies)

This procedure is disclosed in U.S. Patent Publication No. 2005/0256757, incorporated herein by reference.

Gel Bed Permeability (GBP 0.3 psi, Darcies)

This procedure is disclosed in U.S. Patent Publication No. 2005/0256757, incorporated herein by reference, except the method is modified by using a 100 gram weight to provide 0.3 psi.

Absorbency Under Load (AUL)

This procedure is disclosed in WO 00/62825, pages 22-23, incorporated herein by reference, using a 317 gram weight for an AUL (0.90 psi).

Extractable Material (1 hour)

SAP particles (0.4g) have a particle size to 150-850 µm are stirred into 75 ml of a 0.9%, by weight, sodium chloride solution in a vessel. The vessel is sealed and the mixture is stirred for one hour. The test sample is filtered through a Whatman 41 ashless filter paper (or equivalent) and an amount of extractable material is determined by an acid-base titration of the filtrate for carboxyl groups, i.e., titration to pH 10 with 0.1 N NaOH, then to pH 2.7 with 0.1 N HCl.

Example 1

In a glass beaker, glacial acrylic acid (26 weight parts) was combined with 0.078 weight parts of pentaerythritol triallyl ether, 0.069 weight parts of KYMENE® 736 (available from Hercules, Inc., Wilmington, DE), and 73.3 weight parts of deionized water. The solution was purged with nitrogen for 30 minutes, while simultaneously cooling to 10°C. Then 0.20 weight parts of a 1 wt% hydrogen peroxide solution and 0.29 weight parts of a 1 wt% ascorbic acid solution were added to initiate polymerization. The mixture was allowed to polymerize

for 16 hours. The resulting hydrogel was processed with a meat grinder and divided into four batches. Each batch then was extruded with 50% sodium hydroxide solution to provide base polymer particles having the following four different degrees of neutralization (DN):

Degree of Neutralization (DN)	Weight Parts Hydrogel	Weight Parts 50% sodium hydroxide
60	1	0.173
65	1	0.188
70	1	0.202
75	1	0.217

Each hydrogel then was separately treated with 0.04 weight parts of a 6.5 wt% aqueous sodium bisulfite solution. The resulting hydrogels were dried on trays in a forced air oven at 150°C for 1 hour. The dried polymers were ground into particles and classified into a particle size range of 150 to 850 microns. The resulting polymer particles were treated with 7.1 weight parts of a solution containing 65% LUPAMIN® 9095, 17.5% water, and 17.5% propylene glycol, each by weight. LUPAMIN® 9095, available from BASF Corporation, Florham Park, NJ, contains 5% to 10%, by weight, of a linear polyvinylamine having a molecular weight (M_w) of about 340,000. The treated polymer particles then were further coated with 6.9 weight parts of a solution containing 2.1% ethylene glycol diglycidyl ether (EGDGE), 18.15% water, 18.15% propylene glycol, and 61.6% aqueous aluminum sulfate solution (27% $Al_2(SO_4)_3$), each by

weight. The coated polymer particles then were dried and cured at 150°C for 45 minutes.

	DN60	DN65	DN70	DN75
Base Polymer Particles				
CRC (g/g)	30.8	31.3	31.6	32.1
1 hr Ext. (%)	2.97	3.41	3.32	3.31
Coated Polymer Particles				
CRC (g/g)	22.8	23.6	24.2	25.3
0.3GBP (Da)	13.8	10.3	8.2	6.9
FSGBP (Da)	322.2	309.8	295.5	231.1
0.9AUL (g/g)	16.9	17.0	18.6	19.1

Example 2

The procedure of Example 1 was repeated, except for a reduction of the amount of water to 71.1 weight parts and the addition of 3.7 weight parts of a linear sodium (polyacrylate) (PSA) solution in the gel polymerization step. The PSA solution was a blend of 15 weight parts M_w=1,200 (45 wt% aqueous PSA solution), 15 weight parts M_w=8,000 (45 wt% aqueous PSA solution), 20 weight parts M_w=15,000 (35 wt% aqueous PSA solution), 15 weight parts M_w=30,000 (40 wt% aqueous PSA solution). M_w is the weight average molecular weight of the PSA in each solution. The resulting hydrogel was processed, dried, classified, and coated as described in Example 1.

	DN60	DN65	DN70	DN75
Base Polymer Particles				
CRC (g/g)	26.0	28.4	29.7	29.7
1 hr Ext. (%)	5.92	5.94	6.04	6.10
Coated Polymer Particles				
CRC (g/g)	21.3	22.4	23.3	23.8
0.3GBP (Da)	18.8	13.9	12.3	9.7
FSGBP (Da)	260.9	236.9	232.2	200.8
0.9AUL (g/g)	17.0	17.1	17.1	17.0

The table in Example 2 shows that the addition of a linear PSA increased the extractable content, while maintaining the CRC and 0.9 AUL values and improving the 0.3GBP values. Therefore, increasing the amount of extractable materials maintained the absorption properties of the SAP particles while improving the permeability of the particles. Contrary to conventional thinking in the art, increasing the amount of extractable materials in the SAP provided particles having an excellent relationship between absorption (i.e., CRC) and permeability (i.e., 0.3GBP). This result is important in the art because improving either the absorption or permeability properties of SAP particles typically adversely affects the other property.

Example 3

The procedure of Example 1 was repeated, except the hydrogel drying time was reduced to 45 minutes. The hydrogel was neutralized only to DN60.

Example 4

The procedure of Example 1 was repeated, except for a reduction of the amount of water to 71.1 weight parts and the addition of 3.7 weight parts of linear PSA solution in the gel polymerization. The PSA solution was a blend of 15 parts M_w=1,200 (45 wt% aqueous PSA solution), 15 weight parts M_w=8,000 (45 wt% aqueous PSA solution), 20 weight parts M_w=15,000 (35 wt% aqueous PSA solution), 15 weight parts M_w=30,000 (40 wt% aqueous PSA solution). The resulting hydrogel was processed to DN60, dried at 150°C for 45 minutes, classified, and coated as described in Example 1.

Example 5

The procedure of Example 1 was repeated, except for a reduction of the amount of water to 69.0 weight parts and the addition of 7.3 weight parts of a linear PSA solution in the gel polymerization. The PSA solution was a blend of 15 weight parts M_w=1,200 (45 wt% aqueous PSA solution), 15 weight parts M_w=8,000 (45 wt% aqueous PSA solution), 20 weight parts M_w=15,000 (35 wt% aqueous PSA solution), 15 weight parts M_w=30,000 (40 wt% aqueous PSA solution). The resulting hydrogel was processed to DN60, dried to 150°C for 45 minute, classified, and coated as described in Example 1.

	Example 3	Example 4	Example 5
Base Polymer Particles (DN60)			
CRC (g/g)	30.0	28.7	27.9
1 hr Ext. (%)	1.53	6.68	10.30
Coated Polymer Particles (DN60)			
CRC (g/g)	25.1	24.1	23.2
0.3GBP (Da)	9.2	17.1	18.0

The preceding table shows that the amount of extractable material in the base polymer particles of Examples 4 and 5 were substantially greater than the base polymer particles of Example 3. The preceding table also shows that the polyamine coated SAP particles maintained absorption properties (i.e., CRC) at increased extractable material levels, and that the polyamine-coated particles of Examples 4 and 5, each containing an increased amount of extractable material, demonstrated substantially improved permeability (i.e., 0.3GBP) over the coated particles of Example 3.

Example 6

The procedure of Example 1 was repeated, except for the addition of varying amounts of sodium hypophosphite (SHP) as a chain transfer agent (i.e., 0.10, 0.20, and 0.30 wt%, based on acrylic acid monomer). Also, the pentaerythritol triallyl ether level was reduced to 0.065 weight parts for each polymerization. The resulting hydrogel was processed to DN65, dried to 150°C for 60 minutes, classified, and coated as described in Example 1.

SHP (wt%)	0	0.1	0.15	0.2	0.3
Base Polymer Particles (DN65)					
CRC (g/g)	31.8	31.6	32.4	32.6	34.8
1 hr Ext. (%)	0.7	4.5	8.1	12.4	11.9
Coated Polymer Particles (DN65)					
CRC (g/g)	24.8	24.0	23.2	23.7	24.3
0.3GBP (Da)	9.1	15.8	14.1	13.0	10.4
FSGBP (Da)	303.0	275.7	267.8	221.9	256.6
0.9AUL (g/g)	18.3	18.1	17.4	16.8	16.8

In another set of experiments, the base polymer was coated as in Example 1, but cured at 120°C for 45 minutes:

SHP (wt%)	0	0.1	0.15	0.2	0.3
Base Polymer Particles (DN65)					
CRC (g/g)	31.8	31.6	32.4	32.6	34.8
1 hr Ext. (%)	0.7	4.5	8.1	12.4	11.9
Coated Polymer Particles (DN65)					
CRC (g/g)	24.4	24.1	23.4	23.3	23.9
0.3GBP (Da)	8.0	14.9	13.3	15.4	13.2
FSGBP (Da)	278.9	339.8	281.3	272.4	265.7
0.9AUL (g/g)	17.5	18.1	17.4	16.3	16.0

The above tables show that including a chain transfer agent increases the amount of extractables in the base polymer particles, while retaining an excellent absorption-permeability relationship, as discussed above in Examples 1-5. The tables also show that the polyamine-coated SAP particles can be cured at a temperature below 150°C, without adversely affecting the properties of the polyamine-coated SAP particles. Curing polyamine-coated SAP particles at a temperature below 150°C also provides benefits, such as an improved SAP

particle color. The ability to provide SAP particles having a good absorption-permeability relationship using a low temperature cure also is unexpected. Using conventional SAP manufacturing and processing steps, e.g., a low amount of extractable materials, required a high curing temperature to achieve good absorption and permeability properties. This temperature can be substantially reduced by utilizing a combination of a polyamine coating and an increased amount of extractable material as disclosed herein.

Example 7

The procedure of Example 1 was repeated, except for the addition of varying amounts of 0.15 wt% sodium hypophosphite (SHP) solution, as a chain transfer agent. In addition, the pentaerythritol triallyl ether level was lowered to 0.065 weight parts for each polymerization. The resulting hydrogel was processed to DN60, dried at 150°C for 60 minutes, classified, and coated as described in Example 1. The coated polymer particles then were cured at 150°C for 45 minutes or at 120°C for 45 minutes.

Cure Temp. (°C)	120	150
Base Polymer Particles (DN60)		
CRC (g/g)	31.2	
1 hr Ext. (%)	7.5	
Coated Polymer Particles (DN60)		
CRC (g/g)	22.2	23.0
0.3GBP (Da)	17.8	18.9
FSGBP (Da)	258.6	277.7
0.9AUL (g/g)	17.2	18.8

The data in the above table shows that the polyamine-coated SAP particles can be cured at a temperature less than 150°C without an adverse effect on absorbance, e.g., CRC and 0.9 AUL, or permeability, e.g., 0.3GBP and FSGBP.

The advantages of the present invention also are illustrated in Figures 1 and 2. Figure 1 is a plot of 0.3 GBP, in Darcies, at a constant CRC, in relation both to extractables (wt%) and mole % DN. Figure 2 is a plot showing the contours of 0.3 GBP at constant CRC in relation to weight percent of extractables and mole % DN.

In particular, Figures 1 and 2 are plots of 0.3 GBP vs. extractables (wt%) and mole % DN for polyamine coated SAP particles having a CRC of 24±1 g/g. Figures 1 and 2 show that at a given CRC, the 0.3GBP performance improves as the degree of neutralization decreases. It also is demonstrated that as the weight percent extractable material in the base polymer increases, the 0.3GBP at a given CRC increases. The figures also demonstrate a ridge of maxima. However, the 0.3GBP at very high ex-

tractable levels (e.g., 13 wt%) is still superior to the 0.3GBP of polymer particles having a lower amount of extractable material at a given degree of neutralization.

Therefore, it has been found that a one-hour extractable content of a base polymer above 3 wt% provides unexpected results with respect to maintaining absorbency and improving permeability. In preferred embodiments, the weight percent of extractable material in the polyamine-coated SAP particles is greater than 3 wt% up to about 15 wt%, and most preferably between about 5 wt% to about 9 wt%. The extractable content of the polyamine-coated SAP particles can be increased by one or more of an added linear polymer, over initiation, decreased internal crosslinking agent, or, preferably, by the addition of a chain transfer agent.

Examples 1 through 7 show that polyamine-coated SAP particles of the present invention demonstrate excellent permeability (0.3GBP and FSGBP), and absorbency is maintained (CRC and 0.9 AUL), in addition to a reduced agglomeration of particles when the SAP particle surface is rendered hydrophobic by incorporating a cosolvent in the coating process.

The balanced properties of absorbance and permeability demonstrated by the present polyamine-coated SAP particles is attributed to the relatively high amount of extractable material in the SAP particles and to the relatively low temperature at

which the SAP particles can be maintained after application of the polyamine to the surfaces of the SAP particles. The low curing temperature also helps maintain an excellent gel integrity, which is adversely affected by a high temperature cure of the polyamine coating.

The polyamine-coated SAP particles of the present invention are useful as absorbents for water and other aqueous fluids, and particularly can be used as an absorbent component in hygiene articles, such as diapers, tampons, and sanitary napkins. The present polyamine-coated SAP particles also can be used in the following applications, for example: storage, packaging, transportation as a packaging material for water-sensitive articles, for example, flower transportation, and shock protection; food sector for transportation of fish and fresh meat, and the absorption of water and blood in fresh fish and meat packs; water treatment, waste treatment and water removal; cleaning; and agricultural industry in irrigation, retention of meltwater and dew precipitates, and as a composting additive.

Additional applications for the present polyamine-coated SAP particles include medical uses (wound plaster, water-absorbent material for burn dressings or for other weeping wounds, rapid dressings for injuries, rapid uptake of body fluid exudates for later analytical and diagnostic purposes), cosmetics, carrier material for pharmaceuticals and medicaments, rheumatic plaster, ultrasound gel,

cooling gel, thickeners for oil/water or water/oil emulsions, textile (gloves, sportswear, moisture regulation in textiles, shoe inserts, synthetic fabrics), hydrophilicization of hydrophobic surfaces, chemical process industry applications (catalyst for organic reactions, immobilization of large functional molecules (enzymes), heat storage media, filtration aids, hydrophilic component in polymer laminates, dispersants, liquefiers), and building construction (sealing materials, systems or films that self-seal in the presence of moisture, and fine-pore formers in sintered building materials or ceramics).

The present invention also provides for use of the polyamine-coated SAP particles in an absorption core of hygienic articles. The hygienic articles exhibit improved acquisition rates. Hygiene articles include, but are not limited to, incontinence pads and incontinence briefs for adults, diapers for infants, catamenial devices, bandages, and similar articles useful for absorbing body fluids.

Hygiene articles, like diapers, comprise (a) a liquid pervious topsheet; (b) a liquid impervious backsheet; (c) a core positioned between (a) and (b) and comprising about 10% to 100%, and preferably about 50% to about 100%, by weight of the present polyamine-coated SAP particles, and 0% to 90% by weight of hydrophilic fiber material; (d) optionally a tissue layer positioned directly above

and below said core (c); and (e) optionally an acquisition layer positioned between (a) and (c).

Obviously, many modifications and variations of the invention as hereinbefore set forth can be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated by the appended claims.

WHAT IS CLAIMED IS:

1. A superabsorbent polymer particle comprising a base polymer having an amount of extractable material greater than 3%, by weight, and having a surface coating comprising a polyamine.

2. The superabsorbent polymer particle of claim 1 wherein the base particle is surface crosslinked.

3. The superabsorbent polymer particle of claim 1 wherein the amount of extractable material is greater than 3%, and up to about 15%, by weight.

4. The superabsorbent polymer particle of claim 1 wherein the amount of extractable material is about 4% to about 12%, by weight.

5. The superabsorbent polymer particle of claim 1 wherein the amount of extractable material is about 5% to about 10%, by weight.

6. The superabsorbent polymer particle of claim 1 wherein the base polymer has a degree of neutralization of about 25 to about 100.

7. The superabsorbent polymer particle of claim 1 wherein the base polymer has a degree of neutralization of about 60 to about 70.

8. The superabsorbent polymer particle of claim 1 wherein the base polymer comprises acrylic acid, methacrylic acid, or a mixture thereof.

9. The superabsorbent polymer particles of claim 1 wherein the surface coating comprises a polyamine, an optional cosolvent, an optional cross-linking agent, and water.

10. The superabsorbent polymer particle of claim 1 wherein the polyamine is present on surfaces of the base polymer in an amount of about 0.1% to about 2%, by weight of the particle.

11. The superabsorbent polymer particle of claim 1 wherein the polyamine has one or more of primary amino groups, secondary amino groups, tertiary amino groups, and quaternary ammonium groups.

12. The superabsorbent polymer particle of claim 1 wherein the polyamine has a weight average molecular weight of about 5,000 to about 1,000,000.

13. The superabsorbent polymer particle of claim 1 wherein the polyamine is a homopolymer or a copolymer selected from the group consisting of a polyvinylamine, a polyethyleneimine, a polyallylamine, a polyalkyleneamine, a polyazetidine, a polyvinylguanidine, a poly(DADMAC), a cationic polyacrylamide, a polyamine functionalized polyacrylate, and mixtures thereof.

14. The superabsorbent polymer particles of claim 9 wherein the crosslinking agent comprises a salt having (a) a polyvalent metal cation of valence +2, +3, or +4, (b) a polyvalent anion of valence -2, -3, or -4, or (c) a polyvalent cation and a polyvalent anion.

15. The superabsorbent polymer particles of claim 14 wherein the polyvalent metal cation is selected from the group consisting of Mg^{2+}, Ca^{2+}, Al^{3+}, Sc^{3+}, Ti^{4+}, Mn^{2+}, $Fe^{2+/3+}$, Co^{2+}, Ni^{2+}, $Cu^{+/2+}$, Zn^{2+}, Y^{3+}, Zr^{4+}, La^{3+}, Ce^{4+}, Hf^{4+}, Au^{3+}, and mixtures thereof.

16. The superabsorbent polymer particles of claim 14 wherein the polyvalent anion is selected from the group consisting of sulfate, phosphate, hydrogen phosphate, borate, an anion of a polycarboxylic acid, and mixtures thereof.

17. The superabsorbent polymer particles of claim 9 wherein the crosslinking agent comprises a multifunctional organic component capable of reacting with amino groups of the polyamine.

18. The superabsorbent polymer particles of claim 17 wherein the crosslinking agent is selected from the group consisting of an alkylene carbonate, a polyaziridine, a haloepoxy, a polyisocyanate, a di- or polyglycidyl compound, a alkoxysilyl compound, urea, thiourea, guanidine, dicyandiamide, 2-oxazolidinone or a derivative thereof, bisoxazoline, a polyoxazoline, di- and polyisocyanate, di- and poly-N-methylol compounds, or a compound having two or more blocked isocyanate groups, a multifunctional aldehyde, a multifunctional ketone, a multifunctional acetal, a multifunction ketal, and mixtures thereof.

19. The superabsorbent polymer particles of claim 9 wherein the cosolvent comprises an alcohol, a diol, a triol, or a mixture thereof.

20. The superabsorbent polymer particles of claim 19 wherein the cosolvent comprises methanol, ethanol, propyl alcohol, isopropyl alcohol, ethylene glycol, propylene glycol, an oligomer of ethylene glycol, an oligomer of propylene glycol, glycerin, a monoalkyl ether of propylene glycol, and mixtures thereof.

21. The superabsorbent polymer particles of claim 1 wherein the base polymer comprises a polyacrylic acid.

22. The superabsorbent polymer particles of claim 21 wherein the polyamine comprises a polyvinylamine homopolymer or copolymer.

23. The superabsorbent polymer particles of claim 21 wherein the particles are surface cross-linked.

24. A method preparing the superabsorbent polymer particle of claim 2 comprising:

(a) providing a base polymer particle having an amount of extractable material greater than 3%, by weight;

(b) applying a surface crosslinking agent to the surfaces of the base polymer particle;

(c) heating the coated base polymer resulting from steps (b) at a sufficient temperature and for a sufficient time to provide a surface crosslinked polymer particle;

(d) applying a composition comprising a polyamine, an optional cosolvent, and an optional crosslinking agent to surfaces of the base polymer particle;

(e) heating the coated base polymer resulting from step (d) at a sufficient temperature and for a sufficient time to provide a cured polyamine coating on the polymer particle.

25. The method of claim 24 wherein heating step (c) is performed at about 70°C to about 200°C for about 5 to about 90 minutes.

26. The method of claim 24 wherein heating step (e) is performed at about 25°C to about 200°C for about 5 to about 90 minutes.

27. The method of claim 24 wherein steps (b) and (c) are performed prior to steps (d) and (e).

28. The method of claim 24 wherein steps (b) and (c) are performed after steps (d) and (e).

29. The method of claim 24 wherein steps (b) and (d) are performed prior to steps (c) and (e), and steps (c) and (e) are performed simultaneously at a temperature of about 70°C to about 200°C.

30. The method of claim 29 wherein the base polymer having an amount of extractable material greater than 3%, by weight, is prepared by:

(a) adding a linear polymer having a weight average molecular weight of about 500 to about 100,000 to a hydrogel of the base polymer;

(b) adding a chain transfer agent to a monomer mixture used in a gel polymerization that provides the base polymer,

(c) increasing the amount of initiator in a monomer mixture used in a gel polymerization that provides the base polymer,

(d) decreasing the amount of internal crosslinking agent in a monomer mixture used in a gel polymerization that provides the base polymer,

(e) any combination of two, three, or four of (a), (b), (c), and (d).

31. The method of claim 30 wherein linear polymer comprises a polyacrylic sodium polyacrylate, or a mixture thereof.

32. The method of claim 30 wherein the chain transfer agent comprises a mercaptan, a polymercaptan, hypophosphorous acid, a hypophosphorous acid salt, formic acid, a salt of formic acid, or a mixture thereof.

33. A method preparing superabsorbent polymer particles comprising:

(a) providing surface-crosslinked superabsorbent polymer particles having an amount of extractable material greater than 3%, by weight;

(b) applying a composition comprising a polyamine, an optional cosolvent, and an optional crosslinking agent to surfaces of the surface-crosslinked polymer particles;

(c) maintaining the coated surface-crosslinked polymer particles of step (b) at about 25°C to about 150°C for a sufficient time to provide a cured polyamine coating on the surface-crosslinked polymer particles.

34. The method of claim 33 wherein step (b) and step (c) are performed simultaneously.

35. A hygiene article, comprising:

(a) a liquid pervious topsheet;

(b) a liquid impervious backsheet;

(c) a core positioned between (a) and (b), said core comprising about 10% to 100% by weight of the superabsorbent polymer particles of claim 1 and 0% to about 90% by weight of hydrophilic fiber material;

(d) optionally a tissue layer positioned directed above and below said core (c); and

(e) optionally an acquisition layer positioned between (a) and (c).

36. The hygiene article of claim 35 selected from the group consisting of a diaper, a catamenial device, an incontinence pad, an incontinence brief, a bandage, and a burn or wound dressing.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/058172

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J3/12 C08J3/24 A61L15/60

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/082197 A (BASF AG [DE]; HERFERT NORBERT [US]; MIATUDILA MA-IKAY KIKAMA [US]; MIT) 10 August 2006 (2006-08-10) claims 1-23 page 19, line 10 - line 14	1,2,6, 8-18, 21-24, 33,35,36
A	WO 03/043670 A (BASF AG [DE]; AZAD MICHAEL M [US]; HERFERT NORBERT [US]; MITCHELL MICH) 30 May 2003 (2003-05-30) cited in the application claims 1-3,28	1
A	US 2005/013992 A1 (AZAD MICHAEL M [US] ET AL) 20 January 2005 (2005-01-20) claims 29,73	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but *cited to understand the principle or theory underlying the* invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 December 2007	02/01/2008

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Niaounakis, Michael

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/058172

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006082197 A	10-08-2006	EP 1846052 A1	24-10-2007
WO 03043670 A	30-05-2003	AU 2002352016 A1	10-06-2003
US 2005013992 A1	20-01-2005	NONE	