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(54) Title: FLEXIBLE SUPERABSORBENT BINDER POLYMER COMPOSITION

(57) Abstract: A process of making the flexible superabsorbent binder polymer composition includes preparing a preneutralized monomer solution having at least about 40mol% degree of neutralization, preparing a monomer solution including monoethylenically unsaturated monomers, one of which includes an alkyloxysilane functionality, preparing initiator system solutions and adding the solutions to the monomer solution, mixing the foregoing solutions into a polymerization solution, cooling the polymerization solution, and post neutralizing the polymer.



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FLEXIBLE SUPERABSORBENT BINDER POLYMER COMPOSITION

This application claims priority to U.S. Application Nos. 11/293,043 and 11/561,145 filed December 2, 2005 and November 17, 2006, respectively, the disclosures of which are
5 expressly incorporated herein by reference.

BACKGROUND

This invention is directed to a flexible superabsorbent binder polymer composition and a polymerization method of making the flexible superabsorbent binder polymer
10 composition.

Adhesives or binders are a necessary element of many absorbent products. While adhesives beneficially hold products together, adhesives may also have a tendency to interfere with the absorbency of fluids in absorbent products. Adhesives are typically hydrophobic and therefore are not conducive to absorbency or liquid transfer functions.
15 Furthermore, most adhesives are non-absorbent and thus serve no liquid retention function.

Hydrophilic adhesives include adhesives formulated from water-soluble polymers such as poly(vinyl alcohol), poly(vinyl methyl ether), poly(vinyl pyrrolidone), poly(ethylene oxide), or cellulose derivatives such as hydroxypropyl cellulose. Dextrans, starches, and vegetable gums have been used to provide hydrophilic adhesives. These materials provide
20 adhesion under dry conditions. However, upon exposure to aqueous fluids, these materials lose bonding capability because they are substantially soluble in aqueous fluids.

A known approach for making hydrophilic adhesives more functional upon exposure to aqueous fluid is to crosslink water-soluble polymers. As a result of crosslinking, the material becomes swellable and no longer soluble in aqueous fluid. However, since
25 crosslinked polymers are thermosets, they are difficult to apply to substrates or to establish

intimate contact with surfaces because the crosslinked polymers are solid materials and have little or no ability to flow. Usually, crosslinked polymers are hard, rigid, and brittle. These polymers do not have flexibility that many absorbent products need for end uses of the polymers.

5 Most existing binders have little or no absorbency. What is therefore needed is a binder polymer that also acts as an absorbent adding additional absorbency to the application. Herein, the binder polymer having these characteristics is referred to as a flexible superabsorbent binder polymer composition, which may be referred to as flexible absorbent binder or FAB herein, for use in a hydrophilic flexible binder or coating that has
10 latent crosslinking capability. Such a superabsorbent polymer composition could be easily applied, like a water-soluble polymer, since the hydrophilic polymer solution would be capable of flow prior to crosslinking. Latent crosslinking capability would also provide a simple means of crosslinking the polymer after the polymer has established intimate contact with substrates or has formed a desired final shape or form.

15 Soerens et al., in U.S. Pat. No. 6,737,491, describes an absorbent binder composition including a monoethylenically unsaturated polymer and an acrylate or methacrylate ester that contains an alkoxysilane functionality that is particularly suitable for use in manufacturing absorbent articles. Also described in Soerens et al. is a method of making the absorbent binder composition that includes the steps of preparing a monomer solution,
20 adding the monomer solution to an initiator system, and activating a polymerization initiator within the initiator system reported as an alcohol-based, water-soluble binder composition.

One of the issues in preparing water-soluble polymers is the amount of the residual monoethylenically unsaturated monomer content remaining in the polymer. For applications

in personal hygiene, it is required that the amount of residual monoethylenically unsaturated monomer content of the superabsorbent polymer composition be less than about 1000ppm. In addition, it is desirous for the flexible superabsorbent binder composition to have a solids content of at least 24% by weight.

5 In addition to the foregoing, another aspect of the existing flexible absorbent binder composition is that a relatively dilute polymer solution must be used so that the solution does not begin to crosslink, wherein crosslinking is known as gelling. Since the solution is generally used by applying the solution to a substrate and then drying the solution to form the crosslinked, absorbent coating, the cost of drying a dilute solution may be more costly
10 than desirous.

 In the case of using alkoxysilane as a crosslinking agent, gelling can be explained, without this invention being limited, by the following theory. As a function of the statistical probability, the alkoxysilane functional units on two polymer chains “find” each other in solution to allow condensation and formation of a crosslink. One approach is to keep this
15 probability low by using a polymer concentration of about 20% by weight. Another approach is to reduce the probability of gellation by reducing the amount of alkoxysilane functionality incorporated into the polymer. For example, a simple approximation suggests that incorporating half as much alkoxysilane into the polymer should allow the polymer concentration to be doubled. Thus, a 40% polymer solution with half the alkoxysilane
20 incorporation should have the same stability as a 20% solution of flexible superabsorbent binder polymer composition. However, the 40% solution requires much less energy, and cost, to dry the solution into an absorbent coating.

What is therefore needed is a hydrophilic polymer that has latent crosslinking capability and can be produced at an attractive cost. Such polymers could be easily applied, like a water-soluble polymer, since the hydrophilic polymer would be capable of flow prior to crosslinking. Latent crosslinking capability would also provide a simple means of crosslinking the polymer after the polymer has established intimate contact with substrates or has formed a desired final shape or form. There is also a need or desire for such a polymer which has a suitable level of flexibility.

In addition, there is a need within the field of absorbent products for flexible absorbent binders, adhesives, or coatings from a polymer solution, wherein the superabsorbent polymer composition has a residual monoethylenically unsaturated monomer of less than about 1,000ppm, such as less than about 700ppm. It is an objective of the present invention to increase the solids content of the polymer solution to at least about 24% by weight, and such as at least about 30% by weight. Another objective of the present invention is to have a viscosity after 16 hours (from the completion of polymerization) of the superabsorbent polymer composition of less than about 10,000cps, such as in the range of from about 500cps to about 5,000cps.

The color and viscosity stability of a flexible superabsorbent binder polymer composition, as well as the performance of the coated substrate, may also require improvement. In order to achieve such an improvement, an alternative method of making the flexible superabsorbent binder polymer composition is desired.

Furthermore, there is a need within the field of absorbent products for such flexible absorbent binders, adhesives, or coatings that can be prepared by post-application, moisture-induced crosslinking of superabsorbent polymers.

SUMMARY

In response to the needs in the field of superabsorbent polymers, a new flexible superabsorbent binder polymer composition, useful as a flexible binder, adhesive, or coating material, is the subject matter of this application. The new flexible superabsorbent binder polymer composition has binder and absorbency characteristics. The superabsorbent polymer composition includes a binder polymer that has the capability of post-application, moisture-induced crosslinking, and a residual monoethylenically unsaturated monomer content of less than about 1,000ppm. This capability provides for absorbent products having greater use in hygiene products.

The flexible superabsorbent binder polymer composition is formed by the reaction of a monomer solution including at least 15% by mass monoethylenically unsaturated monomer, an acrylate or methacrylate ester that contains an alkoxysilane functionality; a copolymerizable hydrophilic glycol containing an ester monomer; and an initiator system, wherein the flexible superabsorbent binder polymer composition has a residual monoethylenically unsaturated monomer content of less than about 1,000ppm.

In another aspect, the flexible superabsorbent binder polymer composition may be made from monomers that are at least 15% by mass monoethylenically unsaturated monomer, an initiator system; an acrylate or methacrylate ester that contains an alkoxysilane functionality; and a plasticizer, wherein said superabsorbent polymer has a weight average molecular weight of from about 100,000 to about 650,000 g/mol, and the superabsorbent polymer composition has a viscosity after 16 hours of less than about 10,000 cps and a residual monoethylenically unsaturated monomer content of less than about 1,000ppm. Furthermore, in another aspect, the flexible superabsorbent binder polymer composition has a solids content of at least 24% by weight.

In still another aspect, the flexible superabsorbent binder polymer composition is made by a process including the steps of a) preparing an initiator system; b) preparing a monomer solution including monoethylenically unsaturated monomers, one of which includes an alkyloxysilane functionality; c) mixing the initiator system and the monomer solution to form a polymerization solution; d) polymerizing the solution; (e) optionally neutralizing the polymer of step d); the dry polymer of which has a residual monoethylenically unsaturated monomer content of less than about 1,000ppm.

In still another aspect, the flexible superabsorbent binder polymer composition is made in water by a process including the steps of a) preparing a aqueous monomer solution including a plasticizer, a component of a redox initiator system, thermal initiator, a crosslinking monomer that contains an alkoxysilane functionality, a chain transfer agent; monoethylenically unsaturated monomer, including acid groups that are neutralized to at least 25 mol%; b) initiating the monomer solution mixture of step a) to polymerize said monomer solution mixture of a) to at least 50% degree of neutralization; c) adding a second monomer solution comprising; monoethylenically unsaturated monomer, including acid groups that are neutralized to at least 25 mol% and optionally the remaining elements of step a) to the polymerization solution of step b); d) polymerizing the solution of step c); and e) optionally neutralizing the polymer of step d) to form a flexible superabsorbent binder polymer composition having a average molecular weight of from about 100,000 to about 650,000g/moles, a viscosity after 16 hours of less than about 10,000 cps, and a residual monoethylenically unsaturated monomer content of less than about 1,000ppm.

In still another aspect, a polymerization method was discovered that resulted in a suitable flexible superabsorbent binder polymer composition with improved viscosity

stability and performance characteristics. In the polymerization method as set forth herein, a flexible superabsorbent binder polymer composition may be made in water by a process including the steps of a) preparing a preneutralized monomer solution; b) adding a mixture of low molecular weight polyolefinic glycols having a molecular weight from about 200 to about 10,000, and an ethylenically unsaturated monomer containing a trialkoxysilane functional group to the preneutralized monomer solution; c) preparing at least 2 initiator system solutions; d) adding monomer solution mixture of step b) and the initiator system solutions of step c) to water wherein the mixture reacts to form a polymer; e) optionally adding the at least 2 initiator solutions of step c) beyond monomer solution addition at an accelerated flow rate; f) cooling the polymer; and g) post-neutralizing the cooled polymer of step f) to increase the neutralization of the polymer to at least about 60mol%.

With the foregoing in mind, it is a feature and advantage of the invention to provide a method of making the flexible binder polymer solution and coating composition.

DEFINITIONS

It should be noted that, when employed in the present disclosure, the terms “comprises,” “comprising,” and other derivatives from the root term “comprise” are intended to be open-ended terms that specify the presence of any stated features, elements, integers, steps, or components, and are not intended to preclude the presence or addition of one or more other features, elements, integers, steps, components, or groups thereof.

The term “absorbent article” generally refers to a device that can absorb and contain fluids. For example, personal care absorbent articles refer to devices that are placed against or near the skin to absorb and contain the various fluids discharged from the body. The term “disposable” is used herein to describe absorbent articles that are not intended to be laundered or otherwise restored or reused as an absorbent article after a single use.

Examples of such disposable absorbent articles include, but are not limited to, personal care absorbent articles, health/medical absorbent articles, and household/industrial absorbent articles.

The term “binder” includes materials that are capable of attaching themselves to a substrate or are capable of attaching other substances to a substrate.

The term “knife over roll coating” refers to a process in which a knife is positioned, with a specified gap, above a substrate that is moving beneath the knife on a moving roll. In this manner, the knife spreads a specified thickness of coating material onto the substrate.

The term “monomer(s)” as used herein includes monomers, oligomers, polymers, mixtures of monomers, and any other reactive chemical species that is capable of co-polymerization with monoethylenically unsaturated carboxylic, sulphonic, or phosphoric acid or salts thereof.

The terms “nonwoven” and “nonwoven web” refer to materials and webs or materials having a structure of individual fibers or filaments that are interlaid, but not in an identifiable manner as in a knitted fabric. The terms “fiber” and “filament” are used interchangeably. Nonwoven fabrics or webs have been formed from many processes such as, for example, melt blowing processes, spun bonding processes, air laying processes, and bonded carded web processes. The basis weight of nonwoven fabrics is usually expressed in ounces of material per square yard (osy) or grams per square meter (gsm), and the fiber diameters are usually expressed in microns. (Note that to convert from osy to gsm, multiply osy by 33.91.)

The term “polymers” includes, but is not limited to, homopolymers, copolymers, such as for example, block, graft, random, and alternating copolymers, terpolymers, etc., and

blends and modifications thereof. Furthermore, unless otherwise specifically limited, the term “polymer” shall include all possible configurational isomers of the material. These configurations include, but are not limited to, isotactic, syndiotactic, and atactic symmetries.

The term “roll printing” or “roll coating” refers to a process in which the application of a deposited material, generally as a paste, onto a substrate is carried out by transferring the deposited material from a roll onto the substrate in a more or less uniform layer using one or more rolls, which may be engraved, and a pool cylinder. A doctor blade is used to scrape any excess deposited material from the rolls or substrate. The doctor blade may be flat or have a patterned edge such as slots or ridges.

The term “solution,” when used in the phrase “flexible superabsorbent binder polymer solution,” and derivatives thereof, refers to a polymer solution that has not yet been substantially crosslinked (i.e., a precursor) but will result in the flexible superabsorbent binder polymer composition once crosslinking occurs.

The term “spontaneous crosslinking” refers to crosslinking, which occurs without radiation, catalysis, or any other inducement other than the specified temperature of not more than about 150 °C, such as not more than about 120 °C, or not more than about 100 °C.

The term “superabsorbent” refers to a water-swellable, water-insoluble organic or inorganic material capable, under the most favorable conditions, of absorbing at least about 10 times its weight or at least about 15 times its weight in an aqueous solution containing 0.9 weight percent sodium chloride. The superabsorbent materials can be natural, synthetic, and modified natural polymers and materials. In addition, the superabsorbent materials can be inorganic materials, such as silica gels, or organic compounds such as cross-linked polymers.

DETAILED DESCRIPTION

The present invention is directed to a flexible superabsorbent binder polymer composition having the capability of post-application, moisture-induced crosslinking. The present invention also includes a method of making and applying such a flexible superabsorbent binder polymer composition. The flexible superabsorbent binder polymer composition may be used in absorbent binder composition that can provide fluid retention properties in addition to adhesive properties. Thus, the flexible superabsorbent binder polymer composition is particularly suitable for use in forming absorbent products. Flexible superabsorbent binder polymer composition may be referred to herein as composition or as superabsorbent polymer composition.

More specifically, the flexible superabsorbent binder polymer composition is the reaction product of at least 15% by mass monoethylenically unsaturated carboxylic, sulphonic or phosphoric acid or salts thereof, an acrylate or methacrylate ester that contains an alkoxy silane functionality which, upon exposure to water, forms a silanol functional group which condenses to form a crosslinked polymer, a copolymerizable hydrophilic glycol containing ester monomer; and/or, a plasticizer. The flexible superabsorbent binder polymer composition may be made by a polymerization process including the steps of a) preparing a preneutralized monomer solution; b) adding a mixture of low molecular weight polyolefinic glycols having a molecular weight from about 200 to about 10,000, and an ethylenically unsaturated monomer containing a trialkoxy silane functional group to the preneutralized monomer solution; c) preparing at least 2 initiator system solutions; d) adding the monomer solution mixture of step b) and the initiator system solutions of step c) separately wherein the mixture reacts to form a polymer; e) optionally adding the at least 2 initiator solutions of

step c) beyond monomer solution addition at an accelerated flow rate than that used in step d); f) cooling the polymer; and g) post-neutralizing the cooled polymer of step f) to increase the neutralization of the polymer to at least about 60mol%.

Suitable monomers that may be included to make a suitable superabsorbent polymer solution include carboxyl group-containing monomers: for example monoethylenically unsaturated mono or poly-carboxylic acids, such as (meth)acrylic acid (meaning acrylic acid or methacrylic acid; similar notations are used hereinafter), maleic acid, fumaric acid, crotonic acid, sorbic acid, itaconic acid, and cinnamic acid; carboxylic acid anhydride group-containing monomers: for example monoethylenically unsaturated polycarboxylic acid anhydrides (such as maleic anhydride); carboxylic acid salt-containing monomers: for example water-soluble salts (alkali metal salts, ammonium salts, amine salts, and the like) of monoethylenically unsaturated mono- or poly-carboxylic acids (such as sodium (meth)acrylate, trimethylamine (meth)acrylate, triethanolamine (meth)acrylate), sodium maleate, methylamine maleate; sulfonic acid group-containing monomers: for example aliphatic or aromatic vinyl sulfonic acids (such as vinylsulfonic acid, allyl sulfonic acid, vinyltoluenesulfonic acid, styrene sulfonic acid), (meth)acrylic sulfonic acids [such as sulfopropyl (meth)acrylate, 2-hydroxy-3-(meth)acryloxy propyl sulfonic acid]; sulfonic acid salt group-containing monomers: for example alkali metal salts, ammonium salts, amine salts of sulfonic acid group containing monomers as mentioned above; and/or amide group-containing monomers: vinylformamide, (meth)acrylamide, N-alkyl (meth)acrylamides (such as N-methylacrylamide, N-hexylacrylamide), N,N-dialkyl (meth)acryl amides (such as N,N-dimethylacrylamide, N,N-di-n-propylacrylamide), N-hydroxyalkyl (meth)acrylamides [such as N-methylol (meth)acrylamide, N-hydroxyethyl (meth)acrylamide], N,N-

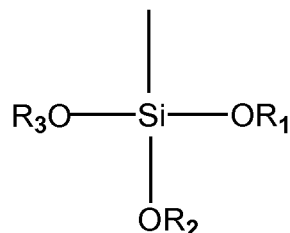
dihydroxyalkyl (meth)acrylamides [such as N,N-dihydroxyethyl (meth)acrylamide], vinyl lactams (such as N-vinylpyrrolidone).

The amount of monoethylenically unsaturated carboxylic, sulphonic, or phosphoric acid or salts thereof relative to the weight of the flexible superabsorbent binder polymer composition may range from about 15% to about 99.9% by weight. In some aspects, the levels of monoethylenically unsaturated carboxylic, sulphonic, or phosphoric acid or salts thereof may be between about 25% and about 99.9% by weight of the flexible superabsorbent binder polymer composition, such as between about 25% and about 90% by weight of the flexible superabsorbent binder polymer composition, or between about 30% and about 80% by weight of the flexible superabsorbent binder polymer composition; or between about 50% and about 70% by weight of the flexible superabsorbent binder polymer composition for some intended uses.

The acid groups are initially neutralized to the extent of at least about 40 mol%, that is, the acid groups are preferably present as sodium, potassium, or ammonium salts. It is preferred to obtain polymers obtained by polymerization of acrylic acid or methacrylic acid, the carboxyl groups of which are neutralized to the extent of about 60 mol%, in the presence of internal crosslinking agents. The neutralization can be accomplished by neutralizing the monomer solution before mixture up to at least 40mol%, and post neutralization of the polymer so that the polymer has at least 60mol% neutralization.

Organic monomers capable of co-polymerization with monoethylenically unsaturated carboxylic, sulphonic, or phosphoric acid or salts thereof, which monomers contain a trialkoxysilane functional group or a moiety that reacts with water to form a silanol

group, are useful in the practice of this invention. The trialkoxysilane functional group has the following structure:



5 wherein R₁, R₂, and R₃ are alkyl groups independently having from 1 to 6 carbon atoms.

Ethylenically unsaturated monomers containing a trialkoxysilane functional group are appropriate for this invention and are desired. Desired ethylenically unsaturated monomers include acrylates and methacrylates, such as acrylate or methacrylate esters that contain an alkoxy silane functionality. A particularly desirable ethylenically unsaturated

10 monomer containing a trialkoxysilane functional group is methacryloxypropyl trimethoxy silane, commercially available from Dow Corning[®] (having a place of business in Midland, Michigan, U.S.A), under the trade designation Z-6030 Silane and from Degussa (a business having offices in Parsippany, New Jersey, U.S.A.), under the trade name DYNASYLAN[®] MEMO. Other suitable ethylenically unsaturated monomers containing a trialkoxysilane

15 functional group include, but are not limited to, methacryloxyethyl trimethoxy silane, methacryloxypropyl triethoxy silane, methacryloxypropyl tripropoxy silane, acryloxypropylmethyl dimethoxy silane, 3-acryloxypropyl trimethoxy silane, 3-methacryloxypropylmethyl diethoxy silane, 3-methacryloxypropylmethyl dimethoxy silane, and 3-methacryloxypropyl tris(methoxyethoxy)silane. However, it is contemplated

20 that a wide range of vinyl and acrylic monomers having trialkoxysilane functional groups or a moiety that reacts easily with water to form a silanol group, such as a chlorosilane or an

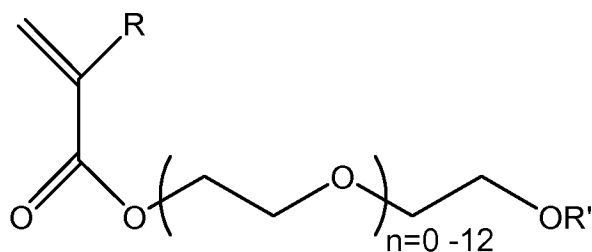
acetoxysilane, provide the desired effects and are effective monomers for copolymerization in accordance with the present invention.

Whereas most superabsorbent polymers require addition of an internal crosslinker to reinforce the polymer, the flexible superabsorbent binder polymer composition of the present invention does not require the addition of a crosslinking agent because the organic monomers including the trialkoxysilane functional act as an internal crosslinker. The internal crosslinker allows the superabsorbent binder polymer composition to be formed by coating the water-soluble precursor polymer onto the substrate and then removing the water to activate the latent crosslinker.

In addition to monomers capable of co-polymerization that contain a trialkoxysilane functional group, it is also feasible to use a monomer capable of co-polymerization that can subsequently be reacted with a compound containing a trialkoxysilane functional group, or a moiety that reacts with water to form a silanol group can also be used. Such a monomer may contain, but is not limited to, an amine or an alcohol. An amine group incorporated into the co-polymer may subsequently be reacted with, for example, but not limited to, (3-chloropropyl)trimethoxysilane. An alcohol group incorporated into the co-polymer may subsequently be reacted with, for example, but not limited to, tetramethoxysilane.

The amount of organic monomer having trialkoxysilane functional groups or silanol-forming functional groups relative to the weight of the polymeric binder composition may range from about 0.1% to about 15% by weight. Suitably, the amount of monomer should exceed 0.1% by weight in order provide sufficient crosslinking upon exposure to moisture. In some aspects, the monomer addition levels are between about 0.1% and about 20% by weight of the flexible superabsorbent binder polymer composition, such as, between about

0.5% and about 10% by weight of the flexible superabsorbent binder polymer composition; or between about 0.5% and about 5% by weight of the flexible superabsorbent binder polymer composition for some intended uses. The flexible superabsorbent binder polymer composition can include a copolymerizable hydrophilic glycol containing an ester monomer, for example a long chain, hydrophilic monoethylenically unsaturated esters, such as poly(ethylene glycol) methacrylate having from 1 to 13 ethylene glycol units. The hydrophilic monoethylenically unsaturated esters have the following structure:



R=H or CH₃

10 R' = H, alkyl, phenyl

The amount of monoethylenically unsaturated hydrophilic esters relative to the weight of the polymeric binder composition thereof may range from 0 to about 75% by weight of monomer to the weight of the flexible superabsorbent binder polymer composition. In some aspects, the monomer addition levels are between about 10% and about 60% by weight of the flexible superabsorbent binder polymer composition; such as between about 20% and about 50% by weight of the flexible superabsorbent binder polymer composition; or between about 30% and about 40% by weight of the flexible superabsorbent binder polymer composition for some intended uses.

In some aspects, the flexible superabsorbent binder polymer composition may also include a hydrophilic plasticizer. Suitable hydrophilic plasticizers that may be used include, but are not limited to, a polyhydroxy organic compounds such as glycerin, and a low molecular weight polyolefinic glycols such as polyethylene glycol (PEG) of molecular weight range from about 200 to about 10,000.

The amount of plasticizer relative to the weight of the flexible superabsorbent binder polymer composition thereof may range from 0 to about 75% by weight of plasticizer to the weight of the flexible superabsorbent binder polymer composition. In some aspects, the plasticizer addition levels are from about 10% to about 60% by weight of the flexible superabsorbent binder polymer composition; such as from about 10% to about 40% by weight of the flexible superabsorbent binder polymer composition for some intended uses.

In some aspects, the flexible superabsorbent binder polymer composition of the present invention may be made from monomers that include at least 15% by weight monoethylenically unsaturated monomer selected from carboxylic acid, carboxylic acid salts, sulphonic acid, sulphonic acid salts, phosphoric acid, or phosphoric acid salts; an initiator system; and an acrylate or methacrylate ester that contains a group readily transformed into a silanol functionality by subsequent reaction with water, wherein the said resulting flexible superabsorbent binder polymer composition has an average molecular weight of from about 100,000 to about 650,000g/mol, such as about 100,000 to about 300,000g/mol, and the superabsorbent polymer composition has a viscosity of less than about 10,000cps and a residual monoethylenically unsaturated monomer content of less than about 1,000ppm.

One advantage of the flexible superabsorbent binder polymer composition of the present invention is that it provides a water-soluble ionic polymer capable of sufficient spontaneous crosslinking within about 10 minutes, such as less than about 5 minutes, or less than about 1 minute, at a web temperature not more than about 150 °C, to provide the

5 flexible absorbent binder layer with an absorbent capacity of at least one (1) gram of fluid per gram of flexible superabsorbent binder polymer composition, such as at least three (3) grams of fluid per gram of flexible superabsorbent binder polymer composition, using the Centrifuge Retention Capacity Test (described below).

The crosslinking at web temperatures not more than about 150 °C, such as not more

10 than about 120 °C, or not more than about 100 °C, permits the flexible superabsorbent binder polymer composition to be applied to one or more substrate layers, and then crosslinked, without degrading or damaging the substrate. Significant crosslinking occurs within about 10 minutes, such as within about 8 minutes, or within about six minutes, to provide an efficient, commercially feasible, cost-effective crosslinking process. The crosslinking may

15 then continue until a flexible superabsorbent binder polymer composition having the desired absorbent capacity is obtained. The ionic polymer may bear a positive charge, a negative charge, or a combination of both, and should have an ionic unit content of about 15mol% or greater. The ionic polymer may include a variety of monomer units described below.

The superabsorbent polymer composition may be prepared by mixing an initiator

20 system with a monomer solution, at a suitable temperature, for thermal initiators to generate free radicals, for example, at temperatures between about 50 °C and about 90 °C. Lower temperatures can be used for redox initiator systems or redox initiator system solutions. An initiator system solution may be prepared by dissolving an initiator in a solvent. Initiators

are used to start the polymerization of a monomer. The action of an initiator is similar to that of a catalyst, except that the initiator is generally consumed in the reaction. Possible solvents include, but are not limited to, water and alcohols such as ethanol. A variety of initiators may be useful in the practice of this invention. The polymerization initiator system
5 may be activated using a variety of methods including, but not limited to, thermal energy, radiation, redox chemical reactions, thermal initiators, and other methods known in the art.

One suitable class of initiators is organic peroxides and azo compounds, with benzoyl peroxide and azobisisobutyronitrile (AIBN), as examples. Examples of suitable initiators include t-amylperoxypivalate; 2,2'-Azobis(2,4'-dimethylvaleronitrile) (V65B),
10 sodium persulfate (NaPS); and 2,2'-azobis-2-amidinopropanedihydrochloride (ABAH).

Suitable amounts of initiators depend upon the particular initiator. Examples include, but are not limited to at least about 0.003mol/mol of t-amylperoxypivalate; at least about 0.01mol/mol of 2,2'-Azobis(2,4'-dimethylvaleronitrile); at least about 200ppm of sodium persulfate; and at least about 200ppm of 2,2'-azobis-2-amidinopropanedihydrochloride.

15 Compounds containing an O—O, S—S, or N = N bond may be used as thermal initiators. Compounds containing O—O bonds; i.e., peroxides, are commonly used as initiators for polymerization. Examples of peroxide initiators include: alkyl, dialkyl, diaryl and arylalkyl peroxides such as cumyl peroxide, t-butyl peroxide, di-t-butyl peroxide, dicumyl peroxide, cumyl butyl peroxide, 1,1-di-t-butyl peroxy-3,5,5-trimethylcyclohexane,
20 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexyne-3 and bis(a-t-butyl peroxyisopropylbenzene); acyl peroxides such as acetyl peroxides and benzoyl peroxides; hydroperoxides such as cumyl hydroperoxide, t-butyl hydroperoxide, p-methane hydroperoxide, pinane hydroperoxide and cumene hydroperoxide; peresters or peroxyesters

such as t-butyl peroxy pivalate, t-amyl peroxy pivalate, t-butyl peroctoate, t-butyl perbenzoate, 2,5-dimethylhexyl-2,5-di(perbenzoate) and t-butyl di(perphthalate); alkylsulfonyl peroxides; dialkyl peroxy monocarbonates; dialkyl peroxy dicarbonates; sodium persulfate, 2,2'-Azobis(2,4'-dimethylvaleronitrile), 2,2'-azobis-2-

5 amidinopropanedihydrochloride, diperoxy ketals; ketone peroxides such as cyclohexanone peroxide and methyl ethyl ketone peroxide. In one particular aspect of the present invention, an organic initiator, t-amyl peroxy pivalate (TAPP), which decomposes very fast to form a stable ethyl ($\text{CH}_3\text{CH}_2\bullet$) free radical, was utilized to reduce the residual monoethylenically unsaturated monomer significantly.

10 A redox initiator system where free radicals are generated by oxidation-reduction reactions without the application of heat can be used for the polymerization of the monomer solution to make the flexible superabsorbent binder polymer composition. In this method, polymerization is started by adding either one of oxidizing or reducing components of the initiator system to the rest of the solution mixture of monomers and other components of the
15 redox initiator system. Suitable oxidizing components of the redox initiator system include, but are not limited to, hydrogen peroxide, alkali metal persulfates, ammonium persulfate, alkali hydroperoxides, peresters, diacryl peroxides, silver salts, and combinations thereof.

Suitable reducing components of the initiator system include, but are not limited to, ascorbic acid, alkali metal sulfites, alkali metal bisulfites, ammonium sulfite, ammonium
20 bisulfite, alkali metal hydrogen sulfites, ferrous metal salts such as ferrous sulfates, sugars, aldehydes, primary and secondary alcohols, and combinations thereof. A combination of redox and thermal initiators can also be used. A redox initiator system that comprises hydrogen peroxide, ferrous sulfate, and ascorbic acid coupled with thermal initiator sodium

persulfate (NaPS) was found to be able to reduce residual monoethylenically unsaturated monomer significantly in aqueous polymerization of the present invention while yielding weight average molecular weight of superabsorbent polymer in the target range of about 100,000 to about 650,000 g/mol, such as about 1,000,000 to about 300,000 g/mol.

5 In addition, it has been found that a redox initiator system comprising a mole ratio of oxidizing agent to reducing agent from about 6:1 to about 2:1, a mole ratio of 4:1, and a mole ratio of 2:1 were found to result in a reduction of residual monoethylenically unsaturated monomer significantly in the aqueous polymerization of the present invention.

 A chain transfer agent that can limit the polymer chain growth during the
10 polymerization and thereby can control the molecular weight and viscosity of flexible binder polymer solution may additionally be used in the polymerization solution. Suitable chain transfer agents include, but are not limited to, alcohols such as isopropyl alcohol, organic acids such as formic acid, inorganic acids such as hypophosphorus acid, organic amines such as triethylamine, and combinations thereof. In one aspect, hypophosphorus acid was
15 found to be an effective chain transfer agent for the flexible superabsorbent binder polymer composition.

 The amount of chain transfer agent relative to the weight of monoethylenically unsaturated carboxylic, sulphonic, or phosphoric acid or salts monomers may range from 0.1 to about 20% by weight of the chain transfer agent to the weight of the monomers. In some
20 aspects, the chain transfer agent addition levels are between about 5% and about 15% by weight of the monomer such as between about 2% and about 10% by weight of the monomer, or between about 0.5% and about 1% by weight of the monomer to obtain desired

molecular weight and viscosity levels of the flexible superabsorbent binder polymer composition for some intended uses.

The method to make the flexible superabsorbent polymer composition of the present invention may further include a transition metal salt. Examples of some suitable transition
5 metals for the transition metal salt include, but are not limited to, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, silver, and the like. For instance, a transition metal salt may be combined with the flexible superabsorbent binder polymer compositions before, during, and/or after its formation. For instance, some transition metal salts that may be used in the present invention include, but are not limited
10 to, halides, such as iron chloride, copper chloride, sulfates, nitrates, acetates, oxalates, carbonates, and so forth. Iron sulfate may be used in the present invention.

The flexible superabsorbent binder polymer composition of the present invention may be applied to a substrate, such as for the purpose of adhering various components of an absorbent product to one another during the manufacturing process of absorbent products.
15 Alternatively, the superabsorbent polymer composition may be applied to a substrate as a coating by itself, thereby serving as an absorbency additive. The flexible superabsorbent binder polymer composition may be applied to the substrate using any suitable application process, including knife over roll coating, or roll coating, either in a continuous coverage or a patterned coverage. Printing applications are other suitable application techniques,
20 including gravure printing, screen, and jet printing. The flexible superabsorbent binder polymer composition may also be applied to the substrate using a spray application.

In some aspects of the present invention, a new source of crosslinking having silanol functionality may be added to the superabsorbent binder polymer composition just before the concentrated solution is applied to a substrate. The added source of silanol crosslinking functionality may in effect “activate” the solution for gelation as it is being applied to the substrate. Potential sources of silanol (Si-OH) functionality include, but are not limited to: silica nano particles, such as SNOWTEX® ST-40 (available from Nissan Chemical – America Corporation, a business having offices located in Houston, Texas, U.S.A.); silica aerosol particles, such as SYLOID® silica (available from Grace Davison, a division of W.R. Grace & Co., having a place of business in Columbia, Maryland, U.S.A.); clays with Si-OH surface, such as Kaolin, bentonite, or attapulgite; and zeolites. In addition, soluble sources of silanol can be added, such as silicates, or in the form of monomeric silanes that are readily hydrolyzed to silanols, such as, but not limited to, alkoxysilanes; for example, tetraethoxy silane (TEOS).

The source of silanol can be added in any suitable manner to provide sufficient mixing with the flexible superabsorbent binder polymer composition solution prior to coating onto the substrate. For example, two separate, metered, feed streams of the flexible superabsorbent binder polymer solution and silanol source may be combined at a Y-juncture with a down-stream static mixer in the flow line to provide mixing.

Suitable ranges may be any that provide for a stable solution at a polymer concentration greater than 25%. Alkoxysilane functionality is incorporated into a base flexible binder polymer solution at an acrylate to silane mole ratio of 170:1. Flexible superabsorbent binder polymer composition with 75%, 50% and 25% of base flexible binder

polymer solution incorporation have been prepared. (Mole ratios of acrylate to silane in these polymers are 227:1, 340:1, and 680:1.)

Table 1 below shows the absorbent capacity data, based on the Centrifuge Retention Capacity Test (described below):

5 Table 1

Polymer composition	CRC g/g
Standard FAB: acrylate : Si-OH ratio 56:1	14.2
50% reduced alkoxysilane: acrylate to Si-OH ratio 112:1	21.4
50% reduced alkoxysilane: with kaolin added to reduce acrylate to Si-OH ratio to 20:1	15.1
50% reduced alkoxysilane: with syloid silica added to reduce acrylate to Si-OH ratio to 20:1	14.6
50% reduced alkoxysilane: with tetraethoxy silane added to reduce acrylate to Si-OH ratio to 20:1	17.1

As demonstrated in Table 1, reducing the alkoxysilane incorporation increased the Centrifuge Retention Capacity (CRC) due to lower crosslink density, compared to a base flexible superabsorbent binder polymer composition. Addition of sources of silanol, even to levels greater than a base flexible superabsorbent binder polymer composition, provides a higher CRC than a base flexible superabsorbent binder polymer composition, even with higher crosslinking potential. Once the flexible superabsorbent binder polymer composition is applied to the substrate, crosslinking can be moisture-induced by hydrolysis and condensation of alkoxysilanes. Activation by this method can take place during solvent

10

removal or after solvent removal by exposure to air at ambient humidity. Solvent may be removed from the substrate either by evaporating the solvent or by any other suitable technique. Heat or radiation may be applied to increase the rate of the process. Recovery of the solvent is a part of the process, and methods for this are widely known to those skilled in the art.

In addition, modifying agents such as compatible polymers, plasticizers, colorants, and preservatives may be incorporated in the flexible superabsorbent binder polymer composition of the present invention.

In some aspects of the present invention, the flexible superabsorbent binder polymer composition of the present invention may be prepared in an aqueous solution by the process comprising the steps of a) preparing a aqueous monomer solution including a plasticizer, a component of a redox initiator system, thermal initiator, a crosslinking monomer that contains an alkoxysilane functionality, a chain transfer agent; monoethylenically unsaturated monomer, including acid groups that are neutralized to at least 25 mol%; b) initiating the monomer solution mixture of step a) to polymerize said monomer solution mixture of a) to at least 50% degree of neutralization; c) adding a second monomer solution comprising monoethylenically unsaturated monomer, including acid groups that are neutralized to at least 25 mol% and optionally the remaining elements of step a) to the polymerization solution of step b); d) polymerizing the solution of step c); and e) optionally neutralizing the polymer of step d) to form a flexible superabsorbent binder polymer composition having an average molecular weight of from about 100,000 to about 650,000 g/mole, and the composition has a viscosity after 16 hours of less than about 10,000 cps and a residual monoethylenically unsaturated monomer content of less than about 1000ppm. Furthermore,

the flexible superabsorbent binder polymer composition may have a solids content of at least about 24% by weight.

In other aspects of the present invention, the flexible superabsorbent binder polymer composition of the present invention may be prepared in an aqueous solution by the process including the steps of: a) preparing an initiator system solution; b) preparing a monomer solution including monoethylenically unsaturated monomers, one of which includes an alkyloxysilane functionality; c) mixing the initiator system and the monomer solution to form a polymerization solution; d) heating the polymerization solution to promote a reaction of the polymerization solution; e) cooling the polymerization solution; and f) neutralizing the polymer of step e) to at least about 25 mole% to form a flexible superabsorbent binder polymer composition, the dry polymer of which a residual monoethylenically unsaturated monomer content has less than about 1000 ppm. In addition, the polymer composition may have a weight average molecular weight of from about 100,000 to about 650,000 g/mole, such as from about 100,000 to about 300,000 g/mole, and/or a viscosity after 16 hours of less than about 10,000 cps. Furthermore, the flexible superabsorbent binder polymer composition may have a solids content of at least about 24% by weight.

In still other aspects of the present invention, the flexible superabsorbent binder polymer composition of the present invention may be prepared in an aqueous solution by the process including the steps of: a) preparing a monomer solution including an initiator system that includes one component of a redox initiator; a chain transfer agent; a plasticizer; a cross-linker monomer that contains an alkoxy silane functionality; and monoethylenically unsaturated monomers, one of which includes a functionality wherein the acid groups are neutralized to at least 25 mole%; b) adding another component of the redox initiator to the

monomer solution mixture of step a) to polymerize the monomer solution mixture of a); c) cooling the polymerization solution to a temperature less than 30 °C; d) adding a similar solution mixture of step a) to the polymerization solution of step c); e) adding a transition metal salt to the solution of step d); f) polymerizing the solution of step e); and g) optionally

5 neutralizing the polymer of step f) to form a flexible superabsorbent binder polymer composition having a average molecular weight of from about 100,000 to about 650,000 g/mole, such as from about 100,000 to about 300,000 g/mole, and/or the superabsorbent polymer composition having a viscosity after 16 hours of less than about 10,000 cps and/or a residual monoethylenically unsaturated monomer content of less than about 1,000 ppm.

10 Furthermore, the flexible superabsorbent binder polymer composition may have a solids content of at least about 24% by weight.

In another aspect, a flexible superabsorbent binder polymer composition may be made in water by a process including the steps of a) preparing a preneutralized monomer solution having at least about 40mol% degree of neutralization; b) adding a chain transfer

15 agent to the preneutralized monomer solution; c) adding a mixture of low molecular weight polyolefinic glycols having a molecular weight from about 200 to about 10,000, and an ethylenically unsaturated monomer containing a trialkoxysilane functional group to the preneutralized monomer solution; d) preparing at least two initiator system solutions;

e) adding monomer solutions mixture of step c) and the initiator system solutions of step d)

20 separately, but simultaneously and continuously to a pre-calculated amount of water, wherein the mixture reacts to form a polymer; f) continue adding initiator solutions beyond monomer solution addition for a fixed period of time at an accelerated flow rate than that

used in step e); g) cooling the polymer of step f); and h) post-neutralizing the cooled polymer of step g) to increase the neutralization of the polymer to at least about 60mol%.

The flexible superabsorbent binder polymer composition of the present invention can be used in the manufacture of absorbent products, thereby adding absorbent capacity to such absorbent products. Examples of such articles include training pants, diapers, diaper pants, feminine hygiene products including sanitary pads and napkins, as well as tampons and interlabial feminine hygiene products, swimwear, incontinence products, absorbent toweling, other personal care or health care garments, including medical garments, or the like. As used herein, the term "incontinence products" includes absorbent underwear for children, absorbent garments for children or young adults with special needs such as autistic children or others with bladder/bowel control problems as a result of physical disabilities, as well as absorbent garments for incontinent adults.

TEST PROCEDURES

Residual Monoethylenically Unsaturated Monomer Test

The residual monoethylenically unsaturated monomer analysis is carried out using solid film obtained from the polymer solution or superabsorbent composition. By way of example for this test description, the monoethylenically unsaturated monomer is acrylic acid. High performance liquid chromatography (HPLC) with a SPD-10Avp Shimadzu UV detector (available from Shimadzu Scientific Instruments, having a place of business in Columbia, Maryland, U.S.A) is used to determine the residual acrylic acid monomer content. To determine the residual acrylic acid monomer, about 0.5 grams of cured film is stirred in 100 ml of a 0.9% NaCl-solution for 16h using a 3.5 cm L x 0.5 cm W magnetic stirrer bar at 500 rpm speed. The mixture is filtered, and the filtrate is then passed through a

Nucleosil C8 100A reverse phase column (available from Column Engineering Incorporated, a business having offices located in Ontario, California, U.S.A.) to separate the acrylic acid monomer. The acrylic acid monomer elutes at a certain time with detection limit at about 10 ppm. The peak area of resulting elutes calculated from the chromatogram is then used to calculate the amount of residual acrylic acid monomer in the film. Initially, a calibration curve was generated by plotting the response area of pure acrylic acid elutes against its known amount (ppm). A linear curve with a correlation coefficient of greater than 0.996 was obtained.

16 Hr Extractable Test (%)

The following test methods are used to calculate the 16-hour extractable levels for the superabsorbent composition. The first test method is intended for use on carboxylic acid based superabsorbent materials. About 0.5 g of cure film obtained from the polymer solution is placed into a 250 ml conical flask containing 100 ml 0.9% NaCl solution. The mixture was stirred with a 3.5 cm L x 0.5 cm W magnetic stirrer bar at 500 rpm speed for 16 hours. The sample is then filtered using WHATMAN #3 filter paper (available from Whatman, Inc., a business having offices located in Florham Park, New Jersey, U.S.A.) and an aspirator attached to a water faucet that creates a vacuum in the filtration unit by sucking air with running water. The entire solution is filtered and special care is taken to ensure that no fluid is lost and that no solid material passes through or around the filter paper. About 50 g of the filtered solution is then taken into a 100 ml beaker. The pH of the solution is adjusted to 8.5 stepwise by using 1.0N NaOH and 0.1N HCl. The resulting solution is titrated to pH 3.9 using the Brinkman Titoprocessor (available from Brinkmann Instruments, Inc., a business having offices located in Westbury, New York, U.S.A.). The results are

calculated by weight basis, with a assumed sodium/hydrogen acrylate formula weight of 87.47. The formula weight is derived from that of 70% neutralized acrylic acid.

Centrifuge Retention Capacity (CRC) Test

As used herein, the Centrifugal Retention Capacity (CRC) is a measure of the Absorbent Capacity of the superabsorbent polymer composition retained after being subjected to centrifugation under controlled conditions. The CRC can be measured by placing a sample of the material to be tested into a water-permeable bag that will contain the sample while allowing the test solution (0.9 percent NaCl solution) to be freely absorbed by the sample. A heat-sealable tea bag material (available from Dexter Nonwovens of Windsor Locks, Conn., U.S.A., as item #11697) 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 inch inside the edge of the material. After the sample is placed in the pouch, the remaining open edge of the pouch is also heat-sealed. Empty bags are also made to be tested with the sample bags as controls. A sample size is chosen such that the teabag does not restrict the swelling of the material, generally with dimensions smaller than the sealed bag area (about 2-inch by 2.5-inch). Three sample bags are tested for each material.

The sealed bags are submerged in a pan of 0.9 percent NaCl solution. After wetting, the samples remain in the solution for 60 minutes, at which time they are removed from the solution and temporarily laid on a non-absorbent flat surface.

The wet bags are then placed into the basket of a suitable centrifuge capable of subjecting the samples to a g-force of 350. (A suitable centrifuge is a Heraeus LABOFUGE 400, Heraeus Instruments, part number 75008157, available from Heraeus Infosystems

GmbH, Hanau, Germany.) The bags are centrifuged at a target of 1600 rpm, but within the range of 1500-1900 rpm, for 3 minutes (target g-force of 350). The bags are removed and weighed. The amount of fluid absorbed and retained by the material, taking into account the fluid retained by the bag material alone, is the Centrifugal Retention Capacity of the material, expressed as grams of fluid per gram of material.

Viscosity After 16 Hours

Viscosity of the flexible binder polymer solution is measured using a Brookfield DVII+ Programmable viscometer (available from Brookfield Engineering, a business having offices located at Middleboro, Massachusetts, U.S.A.). About 200-250 ml of binder composition is taken in a 25-ounce plastic cup. The viscometer is generally zeroed initially with a desired Spindle. For binder composition, Spindle Number 3 is used. The viscosity is measured at 20 RPM and at temperature $22 \pm 1^\circ\text{C}$.

Percent Solids

About 20 ± 0.5 g of flexible superabsorbent binder polymer composition is accurately weighed (W1) into a tared (W2) hexagonal plastic weighing dish. Approximate internal diameter weighing dish is 5inch/3.5inch (Top/Base). The polymer composition-containing dish is placed in a fuming hood at room temperature for about 16-20 hours. The dish containing partially dried solid film is then placed into a laboratory oven pre-heated at 80°C for 30 minutes. The dish and its content are allowed to cool to room temperature. The dried dish with resulting solid film is then weighed together (W3). The percent solids is calculated using the following formula:

$$\% \text{ Solids} = [(W3 - W2) / (W1 - W2)] \times 100$$

Determining Retention Capacities of Coated Substrate (GRC)

FAB performance characteristics are evaluated by measuring 0.9% saline absorbing liquid retention capacities of a coated non-woven substrate. The sample for the retention capacity measurement is prepared as follows: Approximately 50 g of FAB solution is poured
5 onto a 10"x14" metal cookie dish. FAB solution is rolled out with a paint roller until the solution is evenly spread across the dish and paint roller is saturated with FAB solution. Then a 8"x12" sheet of spun-bond substrate is placed on top of FAB cookie dish. The substrate is coated with FAB saturated pain roller until it is thoroughly coated and assumes a transparent appearance. The coated substrate is then placed on a plastic screen and dried in
10 a laboratory convection oven, Lindberg/Blue M Model M01460SA-1 at 105 °C for 15 minutes. The dried coated substrate is removed from the oven after drying period and immediately cut into 1.75" circles by a circular die. The circles are immediately placed into a plastic bag to prevent absorption of ambient moisture.

The retention capacity is measured as follows. For each FAB sample, the retention
15 capacity of four coated circles is determined and averaged the results. For each determination, initial weight of the circle is recorded (W1). A glass dish is filled with 0.9% saline solution. The level of the saline solution should be approximately 4 cm high. A timer is set for 20 minutes. The coated circles are placed on the surface of the test liquid and gently manipulated to immerse, and the timer is started. The circles are removed from
20 the test liquid after 20 minutes and placed onto a polypropylene back sheet. The wet circles are placed at least half an inch apart from each other. Then another uncoated spun-bond sheet is placed on top of the coated circles. The back sheet/circle/spun-bond assembly is then placed onto the table of a suction box and covered the assembly with the plastic top

sheet. The suction box timer is set to five minutes and 15 seconds. The suction box controller and vacuum pump are then turned on. The pressure should read 14 ± 1 inches of water. This yields a net pressure of 0.5 psi. When the timer sounds, the silence button is pressed, and the plastic cover is lifted up. The back sheet/circle/spun-bond assembly is
5 carefully removed, and the upper spun-bond layer is also removed. Each circle is carefully removed and weighed individually (W2).

CALCULATION:

Gross Adjusted Retention Capacity (GRC), $\text{g/g} = (W2 - W1)/W1$

Net Adjusted Retention Capacity (NRC), $\text{g/g} = (W2 - W1)/(W1 - 0.0263)$

10 W1 = Initial weight of coated circle

W2 = Weight of wet coated circle after suction box
0.0263 = A factor for
uncoated dry circle weight

EXAMPLES

The following examples are provided to illustrate the invention and do not limit the
15 scope of the claims. Unless otherwise stated, all parts and percentages are by weight.

Comparative Example 1

A 2 L glass, jacketed reactor is initially purged with nitrogen. A circulating heater bath is equilibrated to 75 °C. In a 500 mL Erlenmeyer flask, the initiator system was prepared by dissolving benzoyl peroxide(BPO) (0.7105 g, 2.93×10^{-3} moles) in 250 mL of
20 ethanol (Mallinckrodt[®], completely denatured available from Mallinckrodt Laboratory Chemicals, a division of Mallinckrodt Baker, Inc., a business having offices located in Phillipsburg, New Jersey, U.S.A.). In a 1 L pear-shaped flask, the monomer solution is prepared by mixing acrylic acid (56 mL, 0.817 moles), di(ethylene glycol) methyl ether

methacrylate (62 mL, 0.336 moles) and 3-(trimethoxysilyl)propyl methacrylate (2.8 mL, 1.18×10^{-2}) in 565 mL of ethanol (Mallinckrodt[®], completely denatured). Nitrogen was bubbled through the dissolved initiator system for 5 minutes, and the solution was transferred to the reactor. A positive pressure of nitrogen is maintained on the reactor.

- 5 After the nitrogen was bubbled through the monomer solution for 5 minutes, a 12 inch needle connected to the inlet port of a Masterflex[®] peristaltic pump (available from Cole-Parmer Instrument Company, a business having offices located in Vernon Hills, Illinois, U.S.A.) was placed into the monomer solution. The outlet port of the Masterflex[®] pump was connected to a 12 inch needle which was inserted into the jacketed reactor. A positive
- 10 pressure of nitrogen was maintained on the monomer flask. The initiator system was heated to 75 °C with stirring by connecting the jacketed reactor to the circulating bath. When the internal temperature reached 60 °C, the monomer solution was added at a rate of about 3 g/min to the initiator system. The polymerization solution was stirred and heated at 75 °C for approximately 2 hours at which time a solution of azobisisobutyronitrile (AIBN) (0.1954
- 15 g, 1.19×10^{-3} moles) in 20 mL of ethanol is added. Stirring and heating at 75 °C was continued for an additional hour at which time a second solution of AIBN (0.1931 g, 1.18×10^{-3} moles) in 20 mL of ethanol was added to the polymerization solution. Stirring and heating at 75 °C was continued for an additional hour at which time a third solution of AIBN (0.1945 g, 1.18×10^{-3} moles) in 20 mL of ethanol was added to the polymerization solution.
- 20 Stirring and heating was continued at 75 °C for a total reaction time of about 5 hours. The reactor was cooled to 35 °C in over 30 min and the solution was drained into a 2 L plastic container.

To obtain about 70 mol% degree of neutralization for acrylic acid content of the resulting polymer solution, an aqueous solution of sodium hydroxide (6.59 sodium hydroxide pellets dissolved in 40.8 g deionized (DI) water) was slowly added to 240 g of binder solution with constant stirring. The residual acrylic acid monomer was determined on films by using the Residual Monoethylenically Unsaturated Monomer Test method disclosed herein and was found to be 51,143. The CRC was using the CRC Test method disclosed herein and was found to be 9.3g/g. The 16-hour extractables were also measured using the 16-Hr Extractables Test method disclosed herein and was found to be 15.3%.

Comparative Example 2

This comparative example was prepared using the following process. Solution No. 1 was prepared as follows. To 237 grams (3.289 moles) of acrylic acid was added to 31.5 grams polyethylene glycol (mol. wt. = 200) and 52.6 grams of sodium hydroxide in 350 grams of water (40% neutralization) and 1.5 grams of ascorbic acid. This solution was cooled in an ice bath.

Solution No. 2 was prepared as follows: 31.5 grams polyethylene glycol (mol. wt. = 200) was diluted with 200 g water, then, with rapid stirring 5ml of 3-(trimethoxysilyl)propyl methacrylate(2.7×10^{-2} moles) was added to produce a hazy solution; then 3.15 g of 30% aqueous hydrogen peroxide was added to the solution.

Solution No. 3 was prepared by dissolving 39.5 grams (0.987moles) sodium hydroxide in 300 grams of water.

Solution No. 2 was added to Solution No. 1 in an ice bath while stirring with a magnetic stir bar. A thermocouple was used to monitor the temperature and observe the reaction exotherm. The polymerization reaction began after about 5 minutes of mixing.

Once the exotherm reaction was detected, water was added gradually to keep the solution viscosity suitable for stirring. A total of 450 gram of water was added over 20 minutes. A maximum polymerization temperature of 85° C was observed about 8 minutes after mixing of the two monomer solutions. After about 20 minutes Solution No. 3 was added with stirring to bring neutralization to 70%, followed by additional water to reduce the polymer concentration to about 20%.

The resulting aqueous binder composition was cast into a film by pouring 22.6 grams of solution into a polystyrene weigh boat and allowing the water to evaporate overnight in a hood at room temperature, followed by drying a Model No. DK-63 laboratory oven (available from Scientific Products, a division of Allegiance Healthcare Corporation, a business having offices located in McGraw Park, Illinois U.S.A.) at 50° C for 50 minutes. The resulting film weighed 5.95 grams, indicating a solution concentration of about 26%.

Comparative Example 2 resulted in the following properties: CRC of 11.9g/g, residual acrylic acid monomer of 5852ppm and 16-hour extractables of 7.1%.

Example 1

A 1 L glass, jacketed reactor equipped with a thermometer and a mechanical stirrer system is initially purged with nitrogen. In a 500 mL Erlenmeyer flask, an initiator system is prepared by dissolving 2,2'-Azobis(2,4'-dimethylvaleronitrile)(V65B) (moles given in Table 2 below) in 125 mL of ethanol (Mallinckrodt®, completely denatured). In a 1 L beaker, the monomer solution is prepared by mixing acrylic acid (28 mL, 0.4085 moles), di(ethylene glycol) methyl ether methacrylate (31 mL, 0.168 moles) and 3-(trimethoxysilyl)propyl methacrylate (1.4 mL, 0.59×10^{-2}) in 283 mL of ethanol (Mallinckrodt®, completely denatured). After nitrogen was bubbled through the dissolved initiator system as well as

through the solution of monomer mixture for 5 minutes, both solutions were transferred to the reactor. A positive pressure of nitrogen was maintained on the reactor.

The reactor content was then heated to 55 °C under constant stirring at a modest speed. The reaction was continued for two hours. Then the reactor temperature was raised to 70 °C and a solution of t-amylperoxypivalate (TAPP)(moles given in Table 1) in 10 mL of ethanol was added. Stirring and heating at 70 °C was continued for two additional hours. The total polymerization time was about 4 hours. The reactor is cooled to about 35 °C over 30 min and the solution was drained into a 2 L plastic container. To obtain a 70 mol% degree of neutralization for the acrylic acid content of the resulting polymer solution, an aqueous solution of sodium hydroxide (6.59 sodium hydroxide pellets dissolved in 40.8 g deionized (DI) water) was slowly added to 240 g of binder solution with constant stirring. The results of Example 1 are shown in Table 2 below.

Table 2. Results of Example 1

Example	Initiator Package	Reaction Time (hrs)	Reaction Temperature °C	Degree of Neutralization (mol%)	CRC (g/g)	Residual Monomer (ppm)	16 hour extr. (%)
1	V65B (0.1mol/mol)	2	55	70	12.9	428	28.2
	TAPP (0.0043mol/mol)	2	70				

Examples 2-6:

Thermally decomposable initiators including sodium persulfate (NaPS), and 2,2'-azobis-2-amidinopropanedihydrochloride (ABAH) are included in addition to the redox initiator system in the amounts set forth in Table 3 below. Three solutions were prepared separately.

Solution No. 1 was prepared as follows: to 237 grams (3.289 moles) of acrylic acid was added to 31.5 grams polyethylene glycol (mol. wt. = 200) and 52.6 grams of sodium hydroxide in 350 grams of water (40% neutralization) and 1.5 grams of ascorbic acid. This solution was cooled in an ice bath.

Solution No. 2 was prepared as follows: 31.5 grams polyethylene glycol (mol. wt. = 200) was diluted with 200 g water, then, with rapid stirring 5ml of 3-(trimethoxysilyl)propyl methacrylate (2.7×10^{-2} moles) was added to produce a hazy solution; then 3.15 g of 30% aqueous hydrogen peroxide was added to this solution.

Solution No. 3 was prepared by dissolving 39.5 grams (0.987 moles) sodium hydroxide in 300 grams of water.

Solution No. 2 was added to Solution No. 1 in an ice bath while stirring with a magnetic stir bar. A thermocouple was used to monitor the temperature and observe the reaction exotherm. The polymerization reaction began after about 5 minutes of mixing. Once the exotherm reaction was detected, water was added gradually to keep the solution viscosity suitable for stirring. A total of 450 grams of water was added over 20 minutes. A maximum polymerization temperature of 75° C was observed about 8 minutes after mixing of the two monomer solutions. After about 20 minutes Solution No. 3 was added with

stirring to bring the neutralization to 70%, followed by additional water to reduce the polymer concentration to about 20%.

The resulting aqueous binder composition was cast into a film by pouring 22.6 grams of solution into a polystyrene weigh boat and allowing the water to evaporate overnight in a hood at room temperature, followed by drying a Model No. DK-63 laboratory oven at 50°C for 50 minutes. The resulting film weighed 5.95 grams, indicating a solution concentration of about 26%.

The results of Examples 2-6 are shown in Table 3 below.

Table 3: Examples 2-6

Example	H₂O₂ ppm	ASC ppm	NaPS ppm	ABAH ppm	CRC (g/g)	Residual acrylic acid monomer (ppm)	16 hr extract (%)
2	755	1199	600	600	11.9	557	22.1
3	755	1199	800	800	11.7	689	9.2
4	755	1199	400	400	10.9	697	10.2
5	755	1199	600	none	12.7	466	27.7
6	755	1199	800	none	11.2	235	29.1

The data in Table 3 shows that all of the thermal initiators decrease the residual acrylic acid monomer of the Flexible Superabsorbent Binder Polymer Composition preparations to below 1,000-ppm.

5 Examples 7-11:

An aqueous solution of NaOH was prepared to obtain approximately 40% degree of neutralization for desired amount of acrylic acid monomer by diluting 105.2 g of 50% aqueous NaOH in 1000 g of water. This solution was cooled in an ice bath. An acrylic acid/PEG200 (polyethylene glycol, mol. wt.=200) was prepared by adding 237 g of glacial acrylic acid to 63.0 g PEG200 and mixed for about 5 minutes. This mixture was added to the NaOH solution and the resulting solution was cooled in an ice bath.

Initiator systems were prepared by dissolving 1.5 g ascorbic acid in 50 g deionized (DI) water, 1.0 g NaPS in 50 g DI water, and 2.7 g of 35% H₂O₂ was diluted with 50 g DI water. The latent crosslinker solution was prepared just prior to initiation. With rapid stirring 2.5 ml of 3-(trimethoxysilyl)propyl methacrylate (MEMO) was added to 100 g DI water producing a hazy solution. When the monomer solution reached 20°C the initiation sequence began. The monomer solution was removed from the ice bath prior to initiation. No further cooling was used in the rest of the polymerization process. The hydrogen peroxide solution, the NaPS solution, the crosslinker solution, and finally the ascorbic acid solution was added to the monomer solution. A thermometer was used to monitor the temperature and observe the reaction exotherm. The polymerization reaction began almost immediately once the initiator solutions were mixed under medium pace stirring with a mechanical power-stirrer. The reaction was allowed to proceed for 25 minutes. Then 79.0 g of 50% NaOH solution was added to post-neutralize the polymer solution to a final degree of neutralization of 70%.

The cross-linker, MEMO was reduced by 50% in the above procedure. The amounts of sodium hydroxide and acrylic acid were varied to obtain various solid levels. The results are summarized in Table 4 below.

Table 4: Examples 7-11

Sample ID	Acrylic Acid (% wt TMS)	% Solids film	CRC (g/g)	Residual acrylic acid monomer (ppm)	16 hr Extr (%)	Viscosity After 16 hours (cPs)
7	13.9	24.7	17.4	619	40.7	573
8	14.8	25.7	17.2	672	40.3	571
9	16.9	29.2	18.0	617	32.4	1700
10	16.9	30.6	13.8	283	23.6	7250
11	18.2	32.9	14.2	267	34.0	4420

5

Examples 12-15:

In conjunction with Table 5 below for specific amounts of H₂O₂, Ascorbic Acid, Hypophosphorus Acid, the following is the procedure for Examples 12-15:

Into a 1-gallon plastic bucket about 626.8g water was added. To this water, 118.5 g of glacial acrylic acid was added. Then 52.8 g of 50% aqueous NaOH and 31.5 g PEG 200

were added. This solution mixture was cooled to 20 - 22°C while sparging with N₂ gas. No cooling water or ice bath was used.

Initiator solutions were prepared as follows: (1) 1.04 g ascorbic acid was dissolved in 21.3 g water;(2) 0.5 g NaPS (sodium persulfate) was dissolved in 2.9 g water; and (3)
5 1.93 g 35% H₂O₂ was weighed out.

A crosslinker solution was prepared just prior to initiation. With rapid stirring 1.4 mL of 3-(trimethoxysilyl)propyl methacrylate (MEMO) was added to 21.3 g water producing a hazy solution. When the monomer solution reached 20-22°C the initiation sequence began. To the monomer solution were added the hydrogen peroxide solution, the
10 NaPS solution, 1.16 g of 50% w/w hypophosphorous acid (chain transfer agent), the crosslinker solution, and finally the ascorbic acid solution. The solution was stirred at medium pace with a mechanical stirrer. A thermocouple was used to monitor the temperature and observe the reaction exotherm. When the reaction reached T_{max} (~50-55°C), 212.7 g water was added to the resulting polymer solution. The polymer solution
15 was allowed to cool while stirring was continued. No cooling water or ice bath was used.

When the polymer solution reached 25 - 27°C, the remaining 118.5 g glacial acrylic acid, 52.8 g 50% aq. NaOH, and 31.5 g PEG 200 were added to the solution. This solution mixture was allowed to cool to 25 - 27°C while sparging with N₂ gas. No cooling water or ice bath was used. The remaining initiator solutions were prepared by dissolving 1.04 g
20 ascorbic acid in 21.3 g water; dissolving 0.5 g NaPS (sodium persulfate) in 2.9 g water; weighing out 1.93 g 35% H₂O₂; and dissolving 1 g Fe(SO₄)₃ *7H₂O in 100 g water. Then 1.0 g of the 1% FeSO₄ solution was added to 5 g water.

The remaining crosslinker solution was prepared just prior to initiation. With rapid stirring 1.4 mL of 3-(trimethoxysilyl)propyl methacrylate (MEMO) was added to 21.3 g water producing a hazy solution. In the second initiation step, the hydrogen peroxide solution, the NaPS solution, 1.16 g of 50% w/w hypophosphorous acid, the crosslinker
5 solution, the diluted iron sulfate solution, and finally the ascorbic acid solution were added to polymer/monomer solution mixture. The polymer/monomer solution mixture was stirred with a mechanical stirrer. A thermocouple was used to monitor the temperature and observe the reaction exotherm. The resulting polymer solution was allowed to cool after it reached its maximum temperature ($T_{\max}$). No cooling water or ice bath was used. When the reaction
10 solution reached 30 °C, 78.5 g of 50% NaOH solution was added to post-neutralize the polymer solution to a final degree of neutralization of 70%. The resulting polymer solution was stirred to approximately 5 minutes after addition of NaOH.

The results are summarized in Table 5 below.

Table 5: Examples 12-15

	Step 1			Step 2				Solution Properties		Film Properties		
Sample ID	H ₂ O ₂ ppm	Asc. Acid ppm	HPA % wt AA	H ₂ O ₂ ppm	Asc. Acid ppm	HPA % wt AA	Fe ppm	Visc. cps	Mol. WtMw g/mol 10 ³	RM ppm	% Sol	CRC g/g
12	1375	766	-	1836	1020	-	12.2	5980	372305	656	30.6	14
13	1375	766	-	1836	1020	2	12.2	1334	157296	21	33.4	16.6
14	1375	766	-	1836	1020	1	13.2	1943	230894	70	31.7	11.4
15	1375	766	0.5	1375	766	0.5	6.8	1277	174922	202	34.8	13.9

TMS = Total Monomer Solution

5 Asc. A. = Ascorbic Acid

HPA = Hypo phosphorus Acid

Comparative Example 3

A flexible absorbent binder solution of this comparative example was prepared by a two-step polymerization method wherein an equal amount of the latent cross-linker, 3-(trimethoxysilyl)propyl methacrylate (MEMO), was used in the both steps of the polymerization.

Step 1

Monomer preparation was carried out as follows: Into a 100-gallon jacketed stainless steel pilot plant reactor equipped with electrical motor driven agitator, about 317 pounds (LB) of water was added by a pump. To this water, 61.3 LB of glacial acrylic acid was added. Then, 40.8 LB of 50% aqueous NaOH was added by a pump, and the mixture was stirred. The solution mixture was cooled to about 27°C.

Initiator solutions were prepared as follows: 1) 1.55 LB 35% H₂O₂ was weighed out; 2) 1.61 LB SEB (sodium erythorbate) was dissolved in 17 LB water; and 3) 0.26 LB NaPS (sodium persulfate) was dissolved in 2 LB water.

The chain transfer agent, cross-linker and plasticizer were prepared as follows: 1) 0.80 LB of 50% hypophosphorous acid was weighed out; and 2) 1.13 LB of 3-(trimethoxysilyl)propyl methacrylate (MEMO) was added to 9.0 LB PEG400, and the mixture was stirred to form a homogeneous solution.

When the monomer solution reached temperature 27°C, an oxygen stripping process sequence began. First, a vacuum on the reactor was pulled, and then the reactor was blanketed with nitrogen gas, followed by 3-5 minutes stirring before pulling vacuum again. This process was repeated three times. After the oxygen stripping process, the initiation sequence began. To the monomer solution were added the hydrogen peroxide solution, the

NaPS solution, hypophosphorous acid solution, the MEMO/PEG mixture, and finally the SEB solution. The solution was stirred, and the reaction exotherm was monitored through a digital readout. When the reaction reached $T_{\max}$ (~ 50 - 55 °C), 37 LB water was added to the resulting polymer solution. The polymer solution was allowed to cool slowly to 25 °C using cooling water while stirring was continued.

Step 2

When the polymer solution reached 25 - 27 °C, the reactor was sparged with air before adding a second monomer charge to prevent autopolymerization. While the reactor was sparging with air, 20.4 LB of the remaining 61.3 LB glacial acrylic acid was added to the reactor, followed by the addition of 13.6 LB of the remaining 40.8 LB 50% NaOH, such that the batch temperature did not exceed 35 °C. This process was repeated two more times to complete the neutralization of all remaining acrylic acid monomer. This solution mixture was allowed to cool down to 27 °C.

The remaining initiator solutions were prepared by weighing out 1.55 LB 35% H_2O_2 ; dissolving 0.26 LB NaPS (sodium persulfate) in 2 LB water; dissolving 0.0026 LB $Fe(SO_4)_3 \cdot 7H_2O$ in 5 LB deionized water; and dissolving 1.61 LB SEB (sodium erythorbate) in 17 LB water. The remaining chain transfer agent, cross-linker, and plasticizer were prepared by weighing out 0.80 LB of 50% hypophosphorous acid and dissolving 1.13 LB of 3-(trimethoxysilyl)propyl methacrylate (MEMO) in 9.0 LB PEG400.

When the temperature of the reaction mixture reached 27 °C, the oxygen stripping process began by a similar process to that described in Step 1. After the oxygen stripping process, the second polymerization was initiated. In the second polymerization step, the hydrogen peroxide solution, NaPS solution, hypophosphorous acid solution, MEMO/PEG

mixture, iron sulfate solution, and finally the SEB solution were added manually to the polymer/monomer solution mixture. The polymer/solution mixture was stirred, and the reaction isotherm was monitored through a digital readout. After the reaction reached $T_{\max}$, 37 LB water was added to the resulting polymer solution. The polymer solution was
5 allowed to cool slowly to below 30 °C using cooling water while stirring was continued. Then, to bring the final degree of neutralization of resulting flexible absorbent binder polymer solution to 77%, 23.1 LB 50% NaOH followed by 10 LB of water was added with care so that the rise in temperature did not exceed 45 °C. The polymer solution was then cooled to ~30°C again by circulating water through the jacket of the reactor. The physical
10 and performance results are given in Table 6.

Comparative Example 4

The same exact procedure as described in Comparative Example 3 above was used in the preparation of Comparative Example 4, except the crosslinker, MEMO, was added in 75%/25% proportion between Step 1 (1.70 LB MEMO) and Step 2 (0.56 LB MEMO), but
15 keeping the total amount the same as above.

Examples 16–19

The following description in Example 16 and the specific proportional amounts of all ingredients for larger volume of flexible absorbent binder polymer solutions preparation as set forth in Table 6 provide the basis for Examples 16-19.

20 Example 16

First, a pre-neutralized (about 60% degree of neutralization, DN) monomer solution was prepared by the following method. About 180 g water was added into a 1-L beaker equipped with a magnetic stirrer and a temperature probe. To the water, 59.23g of glacial

acrylic acid was added with stirring. Then, 39.5 g of 50% aq. NaOH was added slowly to the aqueous solution with a moderate speed of stirring. This aqueous solution was cooled to about 30°C in a water bath, and another aliquot of 59.25 g glacial acrylic acid was added to the aqueous solution. Then, a second aliquot of 39.5 g 50% aq. NaOH was added slowly to the aqueous solution. Then the neutralized acrylic acid solution was cooled to about 25-30 °C in a water bath.

To the pre-neutralized monomer solution, 0.3 g of 50% w/w hypophosphorous acid solution (chain transfer agent) was added.

A homogenous mixture of 17.5 g polyethylene glycol (PEG)400 and 2.1 mL of 3-(trimethoxysilyl)propyl methacrylate (MEMO) crosslinker was prepared by adding MEMO into PEG with rapid stirring. This mixture was then added to preneutralized monomer solution, and the mixture was well stirred for a few minutes.

Two initiator system solutions were prepared by dissolving 1.71 g sodium erythorbate (SEB) in 18.96 g water and by dissolving 4.56 g 35% H₂O₂ in 17.73 g water.

The polymerization was carried out as follows: Into a 1-L jacketed glass reactor, 195.6 g previously sparged water with N₂ gas was added. The temperature of this heel water was kept at 22-24°C. The slow flowing N₂ gas, the preneutralized monomer solution, and the two initiator system solutions were introduced into a reactor via three inlets in the reactor lid. Each of the two initiator system solutions were introduced into the reactor through the inlets of opposite sides of the reactor. The monomer and initiator solutions were added drop wise by three peristaltic pumps simultaneously for a predetermined period of time at predetermined dosage rates while the reaction solution water was being stirred under a slow stream of N₂ gas. The peristaltic pumps were previously calibrated for desired

flow rate of each solution. The polymerization reaction kinetics data was monitored and recorded by a data acquisition software for recording temperature change as a function of time. The preneutralized monomer solution was added over a period of time, usually between 30 minutes and 120 minutes, but typically 60 minutes. The two initiator system
5 solutions were added both during the polymerization procedure and for an additional 60 minutes beyond the monomer addition time.

The solution temperature starts to increase after 6-8 minutes of addition of reactants and continues to gradually climb. The temperature of the reaction was allowed to reach a predetermined maximum temperature, usually between 40 and 70 °C, and most typically
10 60 °C. This temperature was maintained by circulating cooling water through the reactor.

During the preneutralized monomer addition, the initiator solutions are added at a rate such that half of the solutions described above are added during the monomer addition. After the monomer feed is completed, the rate of the initiator solutions addition was altered such that the remaining half of each solution was added during a 30-minute period. Then,
15 additional SEB and H₂O₂ solutions at concentrations of SEB 1.31 g in 14.60 g water and 1.31 g 35% H₂O₂ in 5.05 g water were added for additional 30 minutes as a kill for residual monomer. The speeds of the peristaltic pumps used to dose the initiator solutions were adjusted such that appropriate feed rates were obtained.

After the completion of all initiator solutions additions, the polymerization solution
20 was stirred for additional 90 minutes. At this time, the polymerization solution starts to cool down gradually. After 90 minutes of additional stirring, the polymer solution is cooled to approximately (~) 30 °C by circulating water through the jacket of the reactor. 22.35 g of 50% NaOH solution was added to post-neutralize the superabsorbent polymer binder

solution to a final degree of neutralization of 77%. Cooling was continued during the addition of the sodium hydroxide post-neutralization such that the temperature of the reaction mixture does not exceed 45 °C. The resulting polymer solution was stirred for approximately 5-30 minutes after the addition of NaOH. The polymer solution was then

5 cooled to ~30 °C again by circulating water through the jacket of the reactor.

Table 6 includes information about the properties of the solution and the resulting flexible absorbent binder.

Table 6: Solution and Performance Characteristics of Flexible Absorbent Binder

Sample ID	Wt of FAB Solution (LB)	Solution Properties				Performance Characteristics of Flexible Absorbent Binder			
		% Solids	Visc. (cPs)	Solution Residual Acrylic Acid (ppm)	Color	Product Residual Acrylic Acid (ppm)	GRC g/g	NRC g/g	Color
Comp 3	700	33.7	467	1005	Gradually developed brownish yellow	-	9.8	13.9	Slight white
Comp 4	700	-	330	-	Slight brown	-	7.7	11.2	None
Ex 16	1.28	-	-	415	Clear, Colorless	BDL	16.2	22.6	None
Ex 17	215			482	Clear, Colorless	964	14.0	20.5	None
Ex 18	1050	33.5	585	307	Clear, Colorless	254	12.3	18.9	None
Ex 19	1450	33.7	1280	2863	Clear, Colorless	698	14.7	21.1	None

10

BDL= Below Detection Limit
 GRC= Gross Adjusted Retention Capacity
 NRC= Net Adjusted Retention Capacity

15

Claims

What is claimed is:

1. A flexible superabsorbent binder polymer composition comprising the reaction product of:

5 a monomer solution including at least 15% by mass monoethylenically unsaturated monomer selected from carboxylic acid, carboxylic acid salts, sulphonic acid, sulphonic acid salts, phosphoric acid, or phosphoric acid salts;

an acrylate or methacrylate ester that contains an alkoxysilane functionality;

a copolymerizable hydrophilic glycol containing an ester monomer,

10 an initiator system; and

a neutralizing agent wherein the unsaturated monomer is neutralized to at least 25mol%; and

wherein the flexible superabsorbent binder polymer composition has a residual monoethylenically unsaturated monomer content of less than about 1000ppm.

15

2. The flexible superabsorbent binder polymer composition of claim 1, wherein, upon exposure to water, the alkoxysilane functionality forms a silanol functional group which condenses to form a crosslinked polymer.

20 3. The flexible superabsorbent binder polymer composition of claim 1, wherein the monoethylenically unsaturated monomer comprises a carboxylic acid salt-containing monomer.

4. The flexible superabsorbent binder polymer composition of claim 1, wherein the acrylate or methacrylate ester comprises a monomer containing a trialkoxysilane functional group.

5. The flexible superabsorbent binder polymer composition of claim 4, wherein the monomer comprises at least one of methacryloxypropyl trimethoxy silane, methacryloxyethyl trimethoxy silane, methacryloxypropyl triethoxy silane, methacryloxypropyl tripropoxy silane, acryloxypropylmethyl dimethoxy silane, 3-acryloxypropyl trimethoxy silane, 3-methacryloxypropylmethyl diethoxy silane, 3-methacryloxypropylmethyl dimethoxy silane, 3-(trimethoxysilyl)propyl methacrylate, or 3-methacryloxypropyl tris(methoxyethoxy)silane.

6. The flexible superabsorbent binder polymer composition of claim 1 wherein the initiator system comprises an initiator selected from the group consisting of t-amylperoxypivalate, and 2,2'-Azobis(2,4'-dimethylvaleronitrile).

7. The flexible superabsorbent binder polymer composition of claim 1 wherein the copolymerizable hydrophilic glycol containing ester monomer is selected from the group consisting of di(ethylene glycol) methyl ether methacrylate and poly(ethylene glycol) methacrylate.

8. A process for a flexible superabsorbent binder polymer composition comprising the steps of:

- a) preparing an initiator system solution;
- b) preparing a monomer solution including monoethylenically unsaturated
5 monomers, one of which includes an alkyloxysilane functionality;
- c) mixing the initiator system and the monomer solution to form a polymerization solution;
- d) heating the polymerization solution to promote a reaction of the polymerization solution;
- 10 e) cooling the polymerization solution; and
- f) neutralizing the polymer of step e) to at least about 25 mole %;

to form an superabsorbent polymer composition, the dry polymer of which a residual monoethylenically unsaturated monomer content has less than about 1000ppm.

15 9. The process to make the flexible superabsorbent binder polymer composition of claim 8 wherein the initiator system comprises an initiator selected from t-amylperoxypivalate, or 2,2'-Azobis(2,4'-dimethylvaleronitrile).

10. A flexible superabsorbent binder polymer composition comprising the reaction product of:

at least 15% by mass monoethylenically unsaturated monomer selected from carboxylic acid, carboxylic acid salts, sulphonic acid, sulphonic acid salts, phosphoric acid,
5 or phosphoric acid salts;

a plasticizer;

an acrylate or methacrylate ester that contains an alkoxysilane functionality;

an initiator system; and

a neutralizing agent;

10 wherein the superabsorbent polymer has a residual monoethylenically unsaturated monomer content of less than about 1000ppm.

11. The flexible superabsorbent binder polymer composition of claim 10, wherein the monoethylenically unsaturated monomer comprises a carboxylic acid salt-
15 containing monomer.

12. The flexible superabsorbent binder polymer composition of claim 10 wherein the plasticizer is a polyhydroxy organic compound.

20 13. The flexible superabsorbent binder polymer composition of claim 10, wherein the plasticizer comprises between about 15% and about 40% by weight of the flexible superabsorbent binder polymer composition.

14. The flexible superabsorbent binder polymer composition of claim 10 wherein the initiator system comprises an initiator selected from sodium persulfate (NaPS); or 2,2'-azobis-2-amidinopropanedihydrochloride (ABAH).

5 15. The flexible superabsorbent binder polymer composition of claim 10 wherein said plasticizer is polyethylene glycol, said neutralizing agent is sodium hydroxide and said an acrylate or methacrylate ester that contains an alkoxysilane functionality is 3-(trimethoxysilyl)propyl methacrylate.

10 16. A flexible superabsorbent binder polymer composition comprising the reaction product of:

at least 15% by mass monoethylenically unsaturated monomer selected from carboxylic acid, carboxylic acid salts, sulphonic acid, sulphonic acid salts, phosphoric acid, or phosphoric acid salts;

15 a plasticizer;

an acrylate or methacrylate ester that contains an alkoxysilane functionality

a chain transfer agent;

an initiator system; and

neutralizing agent;

20 wherein said flexible superabsorbent binder polymer composition has an average molecular weight of from about 100,000 to about 650,000g/mole, and the superabsorbent polymer composition has a viscosity after 16 hours of less than about 10,000 cps and a residual monoethylenically unsaturated monomer content of less than about 1000ppm.

17. The flexible superabsorbent binder polymer composition of claim 16, wherein the acrylate or methacrylate ester comprises a monomer containing a trialkoxy silane functional group wherein the monomer is at least 0.1% by weight of the superabsorbent polymer composition.

18. The flexible superabsorbent binder polymer composition of claim 16 wherein the initiator system comprises an initiator selected from the group consisting of sodium persulfate (NaPS); and hydrogen peroxide.

19. The flexible superabsorbent binder polymer composition of claim 16 wherein said acrylate or methacrylate ester that contains an alkoxysilane functionality is 3-(trimethoxysilyl)propyl methacrylate.

20. The flexible superabsorbent binder polymer composition of claim 16 wherein the plasticizer is a polyhydroxy organic compound.

21. The flexible superabsorbent binder polymer composition of claim 16 wherein the plasticizer is a polyethylene glycol.

22. The flexible superabsorbent binder polymer composition of claim 16 wherein the chain transfer agent is at least one of alcohol, organic acid, inorganic acid, or organic amine.

23. The flexible superabsorbent binder polymer composition of claim 16 wherein the chain transfer agent is hypophosphorous acid.

5 24. The flexible superabsorbent binder polymer composition of claim 16 wherein said plasticizer is polyethylene glycol; said neutralizing agent is sodium hydroxide; and said acrylate or methacrylate ester that contains an alkoxysilane functionality is 3-(trimethoxysilyl)propyl methacrylate.

10 25. The flexible superabsorbent binder polymer composition of claim 16 having a solids content of at least 24% by weight.

26. The flexible superabsorbent binder polymer composition of claim 16 wherein the initiator system comprises an initiator selected from sodium persulfate (NaPS); or 2,2'-azobis-2-amidinopropanedihydrochloride (ABAH).

27. The flexible superabsorbent binder polymer composition of claim 16 wherein the superabsorbent polymer has a weight average molecular weight of from about 100,000 to about 300,000g/mole.

20 28. The flexible superabsorbent binder polymer composition of claim 16 wherein the transition metal salt is iron sulfate.

29. A process to make a flexible superabsorbent binder polymer composition comprising the steps of:

- a) preparing a monomer solution comprising a chain transfer agent; a plasticizer, a cross-linker monomer that contains an alkoxysilane functionality, monoethylenically unsaturated monomers, one of which includes an functionality wherein the acid groups are neutralized to at least 25 mole-%;
- b) initiating the monomer solution mixture of step a) to polymerize the monomer solution mixture of a) to at least 50% degree of polymerization;
- c) adding a second monomer solution to the polymerization solution of step b);
- d) polymerizing the solution of step c); and
- e) optionally neutralizing the polymer of step d);

to form an superabsorbent polymer having a average molecular weight of from about 100,000 to about 650,000g/mole, and the superabsorbent polymer composition having a viscosity after 16 hours of less than about 10,000 cps and a residual monoethylenically unsaturated monomer content of less than about 1000ppm.

30. The process to make the flexible superabsorbent binder polymer composition of claim 29 wherein said superabsorbent polymer has a weight average molecular weight of from about 100,000 to about 300,000g/mole, and the superabsorbent polymer composition has a residual monoethylenically unsaturated monomer content of less than about 500ppm and a solids content of at least about 24% by weight.

31. The superabsorbent polymer composition of claim 29 wherein the initiator system comprises an initiator selected from sodium persulfate (NaPS); or 2,2'-azobis-2-amidinopropanedihydrochloride (ABAH).

5 32. The flexible superabsorbent binder polymer composition of claim 10 further comprising a silanol functional crosslinking agent.

33. The flexible superabsorbent binder polymer composition of claim 16 further comprising a silanol functional crosslinking agent.

10 34. A process for making a flexible superabsorbent binder polymer composition comprising the steps of:

a) preparing a preneutralized monomer solution where the acidic monomer is at least partially neutralized;

15 b) adding a mixture of low molecular weight polyolefinic glycols having a molecular weight from about 200 to about 10,000, and an ethylenically unsaturated monomer containing a trialkoxysilane functional group to the preneutralized monomer solution;

c) preparing at least 2 initiator system solutions;

20 d) continuously adding the monomer solution of step b) during polymerization and the at least 2 initiator system solutions of step c) to water to form a mixture wherein the mixture reacts to form a polymer;

- e) optionally adding the at least 2 initiator system solutions of step c) at an accelerated flow rate;
- f) cooling the polymer; and
- g) post-neutralizing the cooled polymer of step f) to increase the neutralization of the polymer to at least about 60mol%.

35. The process to make the flexible superabsorbent binder polymer composition of claim 34 wherein the preneutralized monomer solution comprises acrylic acid.

36. The process to make the flexible superabsorbent binder polymer composition of claim 34 wherein the initiator system comprises an initiator selected from an oxidizing agent and a reducing agent.

37. The process to make the flexible superabsorbent binder polymer composition of claim 34 wherein the oxidizing agent is hydrogen peroxide and the reducing agent is sodium erythorbate.

38. The process to make the flexible superabsorbent binder polymer composition of claim 34 wherein the mole ratio of oxidizing agent to the reducing agent is from about 6:1 to about 2:1.

39. The process to make the flexible superabsorbent binder polymer composition of claim 34 wherein the polymerization solution is cooled in step g) to from about 20 °C to about 40 °C.

5 40. The process to make the flexible superabsorbent binder polymer composition of claim 34 wherein the ethylenically unsaturated monomer containing a trialkoxysilane functional group is methacryloxypropyl trimethoxy silane (MEMO).

41. The process to make the flexible superabsorbent binder polymer composition
10 of claim 34 wherein the low molecular weight polyolefinic glycols is a polyethylene glycol (PEG).

42. A flexible superabsorbent binder polymer composition of claim 34.

15 43. A process for making a flexible superabsorbent binder polymer composition comprising the steps of:

- a) preparing a monomer solution where the acidic monomer is at least partially neutralized;
- b) adding a chain transfer agent to the monomer solution;
- 20 c) adding a mixture of low molecular weight polyolefinic glycols having a molecular weight from about 200 to about 10,000, and an ethylenically unsaturated monomer containing a trialkoxysilane functional group to the monomer solution;

- d) preparing at least 2 initiator system solutions and adding the initiator system solutions to the monomer solution wherein the mixture reacts to form a polymer;
- e) cooling the polymer of step d); and
- 5 f) post-neutralizing the cooled polymer of step e) to increase the neutralization of the polymer to at least about 60mol%.

wherein the mole ratio of oxidizing agent to the reducing agent is from about 6:1 to about 2:1.

10 44. The process to make the flexible superabsorbent binder polymer composition of claim 43 wherein the preneutralized monomer solution comprises acrylic acid.

45. The process to make the flexible superabsorbent binder polymer composition of claim 43 wherein the initiator system comprises an initiator selected from an oxidizing
15 agent and a reducing agent.

46. The process to make the flexible superabsorbent binder polymer composition of claim 43 wherein the oxidizing agent is hydrogen peroxide and the reducing agent is sodium erythorbate.

20

47. The process to make the flexible superabsorbent binder polymer composition of claim 43 wherein the polymerization solution is cooled in step e) to from about 20°C to about 40°C.

48. The process to make the flexible superabsorbent binder polymer composition of claim 43 wherein the ethylenically unsaturated monomer containing a trialkoxysilane functional group is methacryloxypropyl trimethoxy silane (MEMO).

5

49. The process to make the flexible superabsorbent binder polymer composition of claim 43 wherein the low molecular weight polyolefinic glycols is a polyethylene glycol (PEG).

10

50. A flexible superabsorbent binder polymer composition of claim 43.

51. A process for making a flexible superabsorbent binder polymer composition comprising the steps of:

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a) preparing a preneutralized monomer solution, having at least about 40mol% degree of neutralization comprising a chain transfer agent, and a mixture of low molecular weight polyolefinic glycols having a molecular weight from about 200 to about 10,000, and an ethylenically unsaturated monomer containing a trialkoxysilane functional group;

b) preparing at least 2 initiator system solutions;

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c) continuously adding the monomer solution of step a) during polymerization and the at least 2 initiator system solutions of step b) to water to form a mixture wherein the mixture reacts to form a polymer;

- d) adding the at least 2 initiator system solutions of step b) at an accelerated flow rate;
- e) cooling the polymer of step d); and
- f) post-neutralizing the cooled polymer of step e) to increase the neutralization of the polymer to at least about 60mol%.

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52. The process to make the flexible superabsorbent binder polymer composition of claim 51 wherein the preneutralized monomer solution comprises acrylic acid.

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53. The process to make the flexible superabsorbent binder polymer composition of claim 51 wherein the initiator system comprises an initiator selected from an oxidizing agent and a reducing agent.

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54. The process to make the flexible superabsorbent binder polymer composition of claim 51 wherein the oxidizing agent is hydrogen peroxide and the reducing agent is sodium erythorbate.

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55. The process to make the flexible superabsorbent binder polymer composition of claim 51 wherein the mole ratio of oxidizing agent to the reducing agent is from about 6:1 to about 2:1.

56. The process to make the flexible superabsorbent binder polymer composition of claim 51 wherein the polymerization solution is cooled in step e) to from about 20 °C to about 40 °C.

5 57. The process to make the flexible superabsorbent binder polymer composition of claim 51 wherein the ethylenically unsaturated monomer containing a trialkoxysilane functional group is methacryloxypropyl trimethoxy silane (MEMO).

58. The process to make the flexible superabsorbent binder polymer composition
10 of claim 51 wherein the low molecular weight polyolefinic glycols is a polyethylene glycol (PEG).

59. A flexible superabsorbent binder polymer composition of claim 51.