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(71) Applicant: KIMBERLY-CLARK WORLDWIDE, INC. [US/US]; Neenah, Wisconsin 54956 (US).

(72) Inventors: MacDONALD, John, Gavin; 1472 Knollwood Terrace, Decatur, Georgia 30033 (US). DULCAMARA, Jr., Peter, B.; 480 Hawthorne Street, Neenah, Wisconsin 54956 (US). SOERENS, Dave, A.; 736 Kensington Road, Neenah, Wisconsin 54956 (US). FALK, Thomas, J.; 5638 Stonegate Road, Dallas, Texas 75209 (US).

(74) Agents: KLEMBUS, Nancy, M. et al.; 2300 Winchester Road, Neenah, WI 54956 (US).

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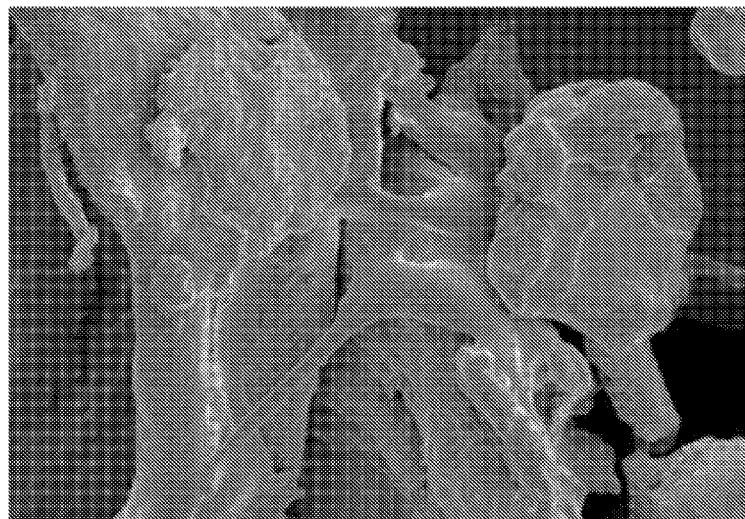


FIG. 3

(57) Abstract: A porous absorbent structure is disclosed which includes absorbent particles and a superabsorbent polymer material having less than about 1000 parts per million residual monoethylenically unsaturated monomer, the superabsorbent polymer material substantially coating the absorbent particles and connecting the particles into a porous network to form the porous absorbent structure.

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## COMPOSITION FOR FORMING A POROUS ABSORBENT STRUCTURE

### FIELD OF THE INVENTION

10 The present invention relates generally to the field of porous absorbent materials, and more specifically to porous absorbent particulate structures which may be sprayed onto a variety of surfaces.

### BACKGROUND OF THE INVENTION

15

Good hygiene is a global need, and using disposable absorbent articles is frequently an easier and more hygienic way to meet this need. The term "absorbent article" generally refers to a device which can absorb and contain fluids. For example, personal care absorbent articles refer to devices which 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.

Availability of absorbent articles can be limited in some areas due to the complex and costly manufacturing required for some absorbent articles. Necessary materials may not be locally available. Traditional disposable absorbent articles can include a topsheet, a backsheet, and an absorbent core positioned therebetween.

Alternate methods of forming disposable garments are also known. For example, garments formed by dipping and spraying are known in the art. U.S. Patent Number 6,987,210 to Giloh discloses a disposable protective undergarment that

5 may be formed by dipping a form into an elastic liquid permeable material. An absorbent pad may be attached to the dip-formed garment in the crotch area. The garment may be sprayed with adhesive so that cotton or other fibers may be attached to the interior of the garment. In another example, U.S. Patent Number 8,124,549 to Torres discloses a composition for forming a fabric by spraying the  
10 composition onto a supporting surface. The composition includes fibers, a binder and a diluent. The composition may be sprayed directly onto a person to form a shirt or dress. In some embodiments, the composition may be sprayed over a wire frame positioned on a person so that the resulting garment has a particular shape. However, the composition disclosed in Torres is not sufficiently absorbent to  
15 function as a substitute or replacement for most commonly available absorbent articles.

There remains a need for articles that are both absorbent and easily manufactured in all regions of the world which have the integrity, coverage and absorbent  
20 capacity to meet the needs of the consumer.

### SUMMARY OF THE INVENTION

25 The present invention is directed to a porous absorbent structure and a method of forming porous absorbent structures. In one embodiment, the method of forming a porous absorbent structure may include the steps of providing a superabsorbent polymer material having a viscosity of less than about 10,000 cps.  
30 Absorbent particles including, but not limited to, organic absorbent particles may be added into the superabsorbent polymer material to form a mixture. The mixture may have a ratio by weight of superabsorbent polymer material to absorbent particles that is greater than 3:1 and, in some embodiments, greater than about 3.5:1 and less than about 6:1. Certain embodiments of the invention may include  
35 absorbent particles having an average ratio of length to width of less than about 5, and preferably less than about 3. The absorbent particles may have an average

5 length of greater than about 20 microns and less than about 100 microns.

The mixture of superabsorbent polymer material and absorbent particles is sprayed onto a form, and the mixture is dried to produce a porous absorbent  
10 structure substantially conforming to the shape of the form. In some embodiment, the form may be at least a portion of a human body. The form may, however, also be a nonwoven material, a woven material, paper, a film or a combination thereof. The method of forming a porous absorbent structure may also include the step of removing the porous absorbent structure from the form.

15

In selected embodiments, the superabsorbent polymer material has less than about 1000 parts per million residual monoethylenically unsaturated monomer which may be an acrylic acid.

20 The porous absorbent structure in certain embodiments may formed by the process of providing a superabsorbent polymer material having a viscosity of less than about 10,000 cps and adding absorbent particles into the superabsorbent polymer material to form a mixture, wherein the ratio by weight of superabsorbent polymer material to absorbent particles in the mixture is greater than 3:1 and less  
25 than about 6:1. The mixture may be applied to a form and dried to produce a porous absorbent structure substantially conforming to the shape of the form.

The porous absorbent structure may include absorbent particles and a superabsorbent polymer material that substantially coats the absorbent particles  
30 and connects the absorbent particles into a porous absorbent network as shown in the figures. The ratio by weight of the superabsorbent polymer material to the absorbent particles in the porous absorbent structure may be greater than 1:1, and may be greater than 1.1:1 and in some embodiments may be less than 1.5 : 1. Such porous absorbent structures may have a Peak Stretch of at least about 10%  
35 and at least about 25% in certain embodiments. The porous absorbent structure may also have a Peak Energy of at least about 150 g/cm, and in some

5 embodiments a Peak Energy of at least about 250 g/cm.

The present invention is also suitable for use as an absorbent wiper when the

porous absorbent structure is attached to a material such as a nonwoven material.

The mixture of superabsorbent polymer material and absorbent particles may be

10 applied directly, by spraying, pouring or other application method, to a nonwoven material to increase the absorbency of the nonwoven material.

An absorbent article may be formed using an outer cover adapted to be secured to a person, the outer cover having an inner side. A porous absorbent structure

15 which includes absorbent particles and superabsorbent polymer material may be applied to the inner side of the outer cover. Alternately, a mixture of superabsorbent polymer material and absorbent particles may be sprayed onto the inner side of the outer cover, the porous absorbent structure being formed directly on the outer cover which may act as a form for the porous absorbent structure.

20

The superabsorbent polymer material in the porous absorbent structure may substantially coat the absorbent particles and connect the particles into a porous network. In selected embodiments, the ratio by weight of the superabsorbent polymer material to the absorbent particles in the porous absorbent structure is

25 greater than 0.8:1 and less than 1.4:1.

The invention will be described in greater detail below by reference to particular embodiments illustrated in the drawings.

30

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional view of an embodiment of the porous absorbent structure of the present invention;

Figure 2 is an enlarged cross-sectional view of an embodiment of the 35 porous absorbent structure of the present invention;

Figure 3 is a close up view of an embodiment of the porous absorbent

5 structure of the present invention;

Figure 4 is a view of the top surface of the porous absorbent structure of the present invention; and

Figure 5 is an enlarged view of the top surface of the porous absorbent structure of the present invention.

10

### DETAILED DESCRIPTION

Reference will now be made in detail to embodiments of the invention, one or more examples of which are illustrated in the figures. Each example is provided 15 by way of explanation of the invention, and not meant as a limitation of the invention. For example, features illustrated or described as part of one embodiment, may be used with another embodiment, to yield still a further embodiment. It is intended that the present invention include modifications and variations to the embodiments described herein.

20

The present invention is directed to porous absorbent structures and methods for forming porous absorbent structures. An embodiment of the porous absorbent structure of the present invention is pictured in Figures 1-5. Porous absorbent structures according to the present invention include absorbent particles that are 25 substantially coated with a superabsorbent polymer material or composition. The superabsorbent polymer material also connects the absorbent particles into a porous absorbent network. In such embodiments, the ratio by weight of the superabsorbent polymer material to the absorbent particles in the porous absorbent structure may be greater than 1:1 and less than about 1.5 : 1. In a 30 preferred embodiment, the weight ratio of superabsorbent polymer material to the absorbent particles in the porous absorbent structure is 1.1 : 1. As used herein, 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 35 solution containing 0.9 weight percent sodium chloride. The superabsorbent materials can be natural, synthetic, and modified natural polymers and materials.

- 5 In addition, the superabsorbent materials can be inorganic materials, such as silica gels, or organic compounds such as cross-linked polymers. The superabsorbent polymer material substantially covers the particles and binds them together. Selected embodiments of the present invention include a mixture of superabsorbent polymer material and absorbent particles which can be applied
- 10 using a commonly available low cost hand spray bottle.

The particular embodiment shown in Figures 1-5 is formed from micronized cellulose particles in a superabsorbent polymer material. The mixture may be sprayed directly onto a spill or a part of a human body and, upon drying, becomes a porous absorbent composition. Once the porous absorbent composition has absorbed the spill or exudate, it can be removed and replaced, if desired. For example, the mixture may be applied directly to a wound. When the mixture dries into a porous absorbent structure, it absorbs exudate in the wound. The porous absorbent structure retains its integrity and may be removed from the wound without damaging the surrounding tissue. The porous absorbent structure of the present invention has sufficient integrity to maintain its shape and attachment to the form onto which it was sprayed.

Alternately, the mixture may be sprayed onto a low-cost commonly available substrate that may or may not have absorbent properties. The combination may be used as an absorbent garment or article such as a wipe. After the porous absorbent material has absorbed the exudate, the porous absorbent material can be easily removed from the substrate and the substrate re-used after application of additional mixture.

30

A method for forming such a porous absorbent structure includes providing a superabsorbent polymer material which, in selected embodiments, has a viscosity that permits delivery of the superabsorbent polymer material through a commonly available low cost conventional hand sprayer or spray bottle. In some embodiments, the viscosity of the superabsorbent polymer material is less than

5 about 10,000 cP and greater than about 500 cP. In other embodiments, the viscosity of the superabsorbent polymer material is preferably less than 2,000 cP and more preferably less than 1000 cP. In some embodiments, the viscosity of the superabsorbent polymer material is greater than 500 cP, and in other embodiments greater than 650 cP. The viscosity of the superabsorbent polymer  
10 material is measured at 16 hours according to the test procedure outlined in U.S. Patent No. 7,312,286. As explained therein, the viscosity of the superabsorbent polymer material is measured using a Brookfield DVII+ Programmable viscometer which is available from Brookfield Engineering, Middleboro, Mass., U.S.A. About 200-250 ml of the superabsorbent polymer material is taken in a 25-ounce plastic  
15 cup. The viscometer is generally zeroed initially with a desired Spindle. For the superabsorbent polymer material, Spindle Number 3 is used. The viscosity is measured at 20 RPM and at temperature of 22. $\pm$ 1 degrees C.

20 A superabsorbent polymer material suitable for use in the present invention is described as a superabsorbent binder polymer solution in U.S. Patent Nos. 6,849,685 to Soerens et al., 7,312,286 to Lang et al., and U.S. 7,335,713 to Lang et al., the entirety of each of these references is herein incorporated by reference. The superabsorbent binder polymer solution described therein is capable of post-application, moisture-induced crosslinking. Whereas most superabsorbent  
25 polymers require the addition of an internal crosslinker to reinforce the polymer, the superabsorbent polymer material used in the present invention does not require the addition of a crosslinking agent because the organic monomers act as an internal crosslinker. The internal crosslinker allows the superabsorbent polymer material to be formed by coating the water-soluble precursor polymer onto the  
30 substrate and then removing the water to activate the latent crosslinker.

Soerens et al., in U.S. Patent No. 6,737,491, describes an absorbent binder composition that may be used as a superabsorbent polymer material in the present invention. The absorbent binder composition disclosed in Soerens et al. is

5 a monoethylenically unsaturated polymer and an acrylate or methacrylate ester that contains an alkoxy silane 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, adding the monomer solution to an initiator system, and

10 activating a polymerization initiator within the initiator system reported an alcohol-based, water-soluble binder composition. "Monomer(s)" as used herein includes monomers, oligomers, polymers, mixtures of monomers, oligomers and/or polymers, and any other reactive chemical species which are capable of co-polymerization with monoethylenically unsaturated carboxylic, sulphonic or

15 phosphoric acid or salts thereof. 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.

20 The superabsorbent binder polymer composition disclosed in the references noted above is the reaction product of at least 15 percent 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

25 condenses to form a crosslinked polymer, a copolymerizable hydrophilic glycol containing ester monomer; and/or, a plasticizer.

The monoethylenically unsaturated monomer is preferable acrylic acid. Other suitable monomers include carboxyl group-containing monomers: for example monoethylenically unsaturated mono or poly-carboxylic acids, such as

30 (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

35 water-soluble salts (alkali metal salts, ammonium salts, amine salts, and the like)

5 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

10 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-

15 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).

20 Suitably, the amount of monoethylenically unsaturated carboxylic, sulphonic or phosphoric acid or salts thereof relative to the weight of the superabsorbent binder polymer composition may range from about 15 percent to about 99.9 percent by weight. The acid groups are desirably neutralized to the extent of at least about 25 mol percent, that is, the acid groups are preferably present as

25 sodium, potassium or ammonium salts. The degree of neutralization is preferably at least about 50 mol percent.

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 the amount of residual

30 monoethylenically unsaturated monomer content of the superabsorbent polymer composition be less than about 1000 ppm, and more preferably less than 500 ppm, and even more preferably less than 100 ppm. U.S. Patent No. 7,312,286 discloses at least one method by which an absorbent binder composition may be manufactured so that the residual monoethylenically unsaturated monomer

35 content is at least less than 1000 parts per million. The analysis of residual

5 monoethylenically unsaturated monomer is determined according to the Residual Monoethylenically Unsaturated Monomer Test which is disclosed in U.S. Patent No. 7,312,286. More specifically, 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

10 monoethylenically unsaturated monomer is acrylic acid. High performance liquid chromatography (HPLC) with a SPD-IOAvp Shimadzu UV detector (available from Shimadzu Scientific Instruments, having a place of business in Columbia, Md., 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

15 stirred in 100 ml of a 0.9% NaCl-solution for 16 h using a 3.5 cm Lx0.5 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, Calif., U.S.A.) to separate the acrylic acid monomer. The acrylic acid monomer

20 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.

25 996 was obtained.

Absorbent particles are added to the superabsorbent polymer material to form a mixture which has not yet been substantially cross-linked, but will result in a porous absorbent structure when cross-linking occurs. As used herein, the term

30 "absorbent particles" generally refers to particles which can absorb and contain fluids.

The absorbent particles may be organic or inorganic. Suitable organic absorbent particles include but are not limited to cellulose, rice, wheat flour, teff, fava, almond

35 nut flour, kenaf and corn starch. Suitable inorganic particles include but are not

5 limited to Arizona sand, pumice, diatomaceous earth and chalk.

In selecting absorbent particles to use in the present invention, care must be taken to avoid increasing the cross-linking of the superabsorbent polymer material to a level sufficiently high so that the resulting material will be too brittle to maintain

10 integrity and function properly as an absorbent material.

The size of the absorbent particles is preferably chosen to permit the particles to add sufficient absorbency to the porous absorbent material without interfering with the delivery method of the mixture. For example, certain fibers may clog a typical

15 hand sprayer. Particles having an average ratio of length to width of less than about 5 are preferred. Even more preferred are absorbent particles having an average ratio of length to width of less than about 3. In many preferred embodiments, the absorbent particles have an average length of greater than about 20 microns and less than about 80 microns.

20

Absorbent particles may be added to the superabsorbent polymer material material (an aqueous solution of sodium polyacrylate available from Evonick Stockhausen, LLC under the designation "SR1717" or "Absorbent Binder A" which is manufactured in accordance with U.S. Patent No. 7,312,286) so that the ratio by

25 weight of superabsorbent polymer material to absorbent particles is greater than about 3:1, and in some embodiments is greater than or equal to 3.5:1. In selected embodiments the ratio by weight of superabsorbent polymer material to absorbent particles in the mixture is less than about 6:1. In certain embodiments, absorbent particles are added into the superabsorbent polymer material to form a mixture

30 wherein the ratio by weight of superabsorbent polymer material to absorbent particles in the mixture is greater than 3:1 and less than about 6:1. Ratios within these ranges enable formation of porous absorbent structures with suitable integrity and absorbency.

35 After mixing the absorbent particles until they are dispersed in the superabsorbent polymer material and the desired weight ratio has been attained, other additives

5 may be added to the mixture. For example, glycerol may be added to the mixture of superabsorbent polymer material and absorbent particles to increase the flexibility and elongation of the porous absorbent material. Other additives may be utilized to increase the flexibility and integrity of the porous absorbent material, as well as other properties. For example, some embodiments may include

10 poly(ethylene glycol) (PEG) having a molecular weight of 8000 in an amount of approximately fifteen percent (15%) by weight.

The mixture may be poured or sprayed onto a desired form. In some instances, the mixture may be applied directly onto the area where the absorbent properties 15 are needed. For example, the mixture may be sprayed directly onto a wound or onto another area of a human where absorbency is needed. In such examples, the form would be the person. Other forms useful in the present invention include paper, film, woven materials, nonwoven materials and combinations thereof. For example, the mixture may be applied to a nonwoven material to increase its 20 absorbency and thereby enable the composite material to be used as a wiper for any number of surfaces including, but not limited to, skin. "Nonwoven" or "nonwoven web" refers to materials and webs or material having a structure of individual fibers or filaments which are interlaid, but not in an identifiable manner as in a knitted fabric. Nonwoven fabrics or webs have been formed from many 25 processes such as, for example, meltblowing processes, spunbonding processes, air laying processes, and bonded carded web processes. In certain embodiments, a rigid form may be used to shape a porous absorbent structure, after which the porous absorbent structure may be removed from the form and used alone or as part of an absorbent article.

30

The absorbent capacity of the superabsorbent polymer material or composition alone should be at least one (1) gram of fluid per gram of superabsorbent polymer material, and in some embodiments at least three (3) grams of fluid per gram of superabsorbent polymer material, when measured using the Centrifuge Retention 35 Capacity Test described in U.S. Patent No. 7,312,286.

5

In selected embodiments, the retention capacity of the porous absorbent structure of the present invention is preferably greater than 10 g/g, and more preferably is greater than 12 g/g when measured using the Centrifuge Retention Capacity Test described in U.S. Patent No. 7,312,286.

10

A number of samples were formed and test values for these samples are reported in Tables 1 and 2. The superabsorbent polymer material used in each of the samples was obtained from Evonik Stockhausen, LLC (Greensboro, North Carolina, U.S.A.) under the designation "SR1717" or "Absorbent Binder A", which 15 is manufactured in accordance with U.S. Patent No. 7,312,286. Absorbent Binder A is an aqueous solution of sodium polyacrylate. Two (2) grams of each of the substances listed in the tables was added to seven (7) grams of this superabsorbent polymer material and stirred for three minutes. For the alginate sample, two (2) grams of alginate was added to seven (7) grams of Absorbent 20 Binder A. For the first sample listed in Table 1, no particles or other substance was added to superabsorbent polymer material. Each of the mixtures was poured into a commonly available round glass evaporation dish and set aside to dry for at least 20 minutes. The resulting porous absorbent structure conformed to the shape of the glass dishes.

25

In order to gauge the strength and toughness of the porous absorbent structures, a series of samples were subjected to tensile testing. An MTS Insight Electromechanical 1kN Extended Length unit was used to conduct the testing with a 100N head (Model 820-1XLTEL/0060. MTS Systems Corp., Eden Prairie, MN). 30 The samples were approximately 6cm circles or squares. The thickness of each sample was also measured using a digital caliper. Test values reported in Tables 1 and 2 include Peak Load, Peak Stretch and Peak Energy. Peak Stretch is a measure of the ductility of a material and is determined in a tensile test. It is the increase in the length of the sample measured after rupture (that is, the length of

- 5 the sample after rupture minus the original sample length) divided by original sample length. Higher elongation indicates higher ductility. Peak Energy is the energy absorbed by the sample up to the point of maximum load. For the samples reported in Tables 1 and 2, the maximum load corresponded to either failure (the energy the sample can absorb before failing) or an amount greater than 100N.
- 10 Peak Load, as reported in the tables, is the highest value reached by the sample during a test.

The superabsorbent polymer material sample listed in Table 1 showed a reasonable balance of properties but lacked the appropriate concentration of particles which is necessary to achieve the present invention. The sample which included alginate powder showed less Peak Load than desired and lacked the particles necessary to enhance the absorbency of the material.

The almond nut shell powder formed a porous absorbent structure with less integrity than other absorbent particles, but was still satisfactory. A number of samples of porous absorbent structures in Table 1 were formed with flour (wheat flour (Pillsbury® Best All-Purpose Flour available from The J.M. Smucker Co, Orrville Ohio, U.S.A.), rice flour, teff flour and garbanzo bean and fava bean flour (all available from Bob's Red Mill, Milwaukee, Oregon, U.S.A.)), and corn starch (available from Pinnacle Foods Corp., Cherry Hill, New Jersey U.S.A). All of the porous absorbent structures made with these particles demonstrated good integrity. The porous absorbent structure formed with kenaf particles demonstrated particularly good load characteristics, although peak stretch values were less than desired. However, glycerol may be added to the particles and superabsorbent polymer material when forming the porous absorbent structure to enhance the stretch and flexibility of the porous absorbent structure. Micronized cellulose was used to formed a porous absorbent structure, also reported in Table 1, that had good integrity.

5

Table 1

Sample Description	Sample Thickness (mm)	Peak Load (gF)	Peak Stretch (%)	Peak Energy (g/cm)	Particle Size (μm)
Superabsorbent polymer material	1.15	1062.0	175.2%	10843.3	n/a
Alginate	0.42	961.4	27.5	1547.4	n/a
Almond Nut Shell Powder	1.81	1932.0	10.8	1208.7	250
Cellulose	1.66	2340.1	4.6	512.0	20
Corn starch	1.46	1720.2	10.2	273.6	0.1-0.8
Fava	1.85	2096.2	9.7	1137.0	110
Kenaf	3.31	>100N load	not tested	not tested	250
Rice	1.58	1727.3	9.5	910.4	180
Wheat Flour	0.82	764.4	4.8	193.2	60
Teff	1.62	1782.5	4.0	374.8	180

Figures 1-5 are views of the porous absorbent structure formed with micronized cellulose. Figure 1 is a scanning electron micrograph image of a cross-section of the porous absorbent structure formed with micronized cellulose. Figures 2 and 3 are enlargements of portions of the cross-sectional view. As can be seen in Figures 2 and 3, the absorbent particles are substantially coated with superabsorbent polymer material, which also acts to bind the absorbent particles together. The porosity of the porous absorbent structure is created by the evaporating water, which also permits the superabsorbent polymer material to

5 effectively cross-link.

It is believed that, when the porous absorbent structure comes into contact with a fluid, the superabsorbent polymer material is the first to absorb the fluid. Although the absorbent particles may, in some embodiments, be substantially or completely 10 covered by superabsorbent polymer material, the absorbent particles still contribute to the absorptive capacity of the porous absorbent structure as they are positioned to absorb fluid from the superabsorbent polymer material.

The samples formed with the particles listed in Table 2 were formed in the same 15 manner as the samples listed in Table 1. The porous absorbent structure formed with Arizona sand (available from CR Minerals Co., Golden, Colorado, U.S.A.) and pumice (available from Charles B. Crystal Co., New York, New York, U.S.A.) demonstrated good integrity and strength. The surface of these porous absorbent structures was similar to a fine-grit sandpaper. The bentonite particles (available 20 from Acros Organics, Fair Lawn New Jersey, U.S.A) formed a material with quite high peak load values. The diatomaceous earth (available from Aldrich Chemical Company, Milwaukee Wisconsin, U.S.A.) and silica samples (Sigma-Aldrich Chemical Co. Milwaukee Wisconsin, U.S.A.) formed structures that were not able to be tested due to their lack of integrity. One possible reason for this is that these 25 particles provided too much cross-linking capability within the example.

5

Table 2

Sample Description	Sample Thickness (mm)	Peak Load (gF)	Peak Stretch (%)	Peak Energy (g/cm)	Particle Size (μm)
Arizona sand	1.14	2023.1	7.3	740.6	30
Bentonite	1.46	>100N	not tested	not tested	75
Chalk	1.62	1028.3	80.5	1722.9	30
Diatomaceous earth	1.46	Brittle	n/a	n/a	3
Pumice	1.76	>100N	37.1	957.3	35
Silica	1.81	brittle	n/a	n/a	300-600
Silica (nanoparticle)	1.50	brittle	n/a	n/a	0.014

Based on the above samples, preferred embodiments of the present invention

10 may have a Peak Energy of at least about 150 g/cm, and may preferably have a Peak Energy of at least about 500 g/cm.

The porous absorbent structure may be used in a variety of absorbent products, such as, for example, bandages, training pants, diapers, diaper pants, wipes, 15 feminine hygiene products, swimwear, incontinence products, absorbent toweling, other personal care or health care garments, including medical garments, or the like. Such absorbent products may include an outer cover adapted to be secured to a person. On an inside surface of the outer cover, the porous absorbent structure may be formed or may be applied once formed.

5

It should be appreciated by those skilled in the art that various modifications and variations may be made to features of the dispenser described herein, particularly to the mechanical and control circuitry aspects of the dispenser, without departing from the scope and spirit of the invention. It is intended that the invention include

10 all such variations.

5 **WHAT IS CLAIMED IS:**

1. A method of forming a porous absorbent structure comprising the steps of:
  - providing a superabsorbent polymer material having a viscosity of less than about 10,000 cps;
- 10 adding absorbent particles into the superabsorbent polymer material to form a mixture such that the ratio by weight of superabsorbent polymer material to absorbent particles is greater than 3:1;
  - spraying the mixture of superabsorbent polymer material and absorbent particles onto a form; and
- 15 drying the mixture to produce a porous absorbent structure substantially conforming to the shape of the form.
2. The method of claim 1 wherein the superabsorbent polymer material has less than about 1000 parts per million residual monoethylenically unsaturated monomer.
- 20 3. The method of claim 1 wherein the form is at least a portion of a human body.
4. The method of claim 1 wherein the form is selected from the group comprising:
  - 25 a nonwoven material, a woven material, paper, a film or a combination thereof.
5. The method of claim 1 further comprising the step of removing the porous absorbent structure from the form.
- 30 6. The method of claim 1 wherein the monoethylenically unsaturated monomer is acrylic acid.
7. The method of claim 1 wherein the absorbent particles are organic particles.
- 35 8. The method of claim 1 wherein the absorbent particles have an average ratio of length to width of less than about 5.

5

9. The method of claim 1 wherein the step of drying the mixture further includes drying the mixture to induce cross-linking in the superabsorbent polymer material and to produce a porous absorbent structure substantially conforming to the shape of the form.

10

10. The method of claim 1 wherein the absorbent particles have an average length of greater than 20 microns.

15

11. The method of claim 1 wherein the ratio by weight of superabsorbent polymer material to absorbent particles in the mixture is less than about 6:1.

12. The method of claim 11 wherein the ratio by weight of superabsorbent polymer material to absorbent particles in the mixture is greater than 3.5:1.

20

13. The method of claim 1 wherein the step of adding absorbent particles into the superabsorbent polymer material further includes wherein the superabsorbent polymer material substantially coats the absorbent particles.

25

14. A porous absorbent structure formed by the process comprising the steps of: providing a superabsorbent polymer material having a viscosity of less than about 10,000 cps;

adding absorbent particles into the superabsorbent polymer material to form a mixture, wherein the ratio by weight of superabsorbent polymer material to absorbent particles in the mixture is greater than 3:1 and less than about 6:1;

30

applying the mixture of superabsorbent polymer material and absorbent particles to a form; and

drying the mixture to produce a porous absorbent structure substantially conforming to the shape of the form.

35

15. The porous absorbent structure of claim 14 wherein the superabsorbent polymer material has less than about 1000 parts per million residual

5 monoethylenically unsaturated monomer.

16. The porous absorbent structure of claim 14 wherein the form is at least a portion of a human body.

10 17. The porous absorbent structure of claim 14 wherein the form is selected from the group comprising: a nonwoven material, a woven material, paper, a film or a combination thereof.

15 18. The porous absorbent structure of claim 14 further comprising the step of removing the porous absorbent structure from the form.

19. A porous absorbent structure comprising:

absorbent particles;

a superabsorbent polymer material substantially coating the absorbent

20 particles and connecting the absorbent particles into a porous absorbent network; and

wherein the ratio by weight of the superabsorbent polymer material to the absorbent particles in the porous absorbent structure is greater than 1:1 and less than 1.5 : 1.

25

20. The porous absorbent structure of claim 19 wherein the superabsorbent polymer material has less than about 1000 parts per million residual monoethylenically unsaturated monomer.

30 21. The porous absorbent structure of claim 19 wherein the weight ratio of the superabsorbent polymer material to the absorbent particles is 1.1 : 1.

22. The porous absorbent structure of claim 19 wherein the porous absorbent structure has a Peak Stretch of at least about 10%.

35

23. The porous absorbent structure of claim 19 wherein the porous absorbent

5 structure has a Peak Energy of at least about 150 g/cm.

24. The porous absorbent structure of claim 19 further comprising a nonwoven material.

10 25. The porous absorbent structure of claim 24 wherein the nonwoven material and porous absorbent structure form a wiper.

26. An absorbent article comprising:

15 an outer cover adapted to be secured to a person, the outer cover having an inner side;

    a porous absorbent structure comprising

    absorbent particles and

    a superabsorbent polymer material substantially coating the

20 absorbent particles and connecting the particles into a porous network to form an absorbent core that is positioned on the inner side of the outer cover, wherein the ratio by weight of the superabsorbent polymer material to the absorbent particles in the porous absorbent structure is greater than 0.8:1 and less than 1.4:1.

25

27. The absorbent article of claim 26 wherein the superabsorbent polymer material has less than about 1000 parts per million residual monoethylenically unsaturated monomer.

30 28. The absorbent article of claim 26 wherein the porous absorbent structure has a Peak Stretch of at least about 10%.

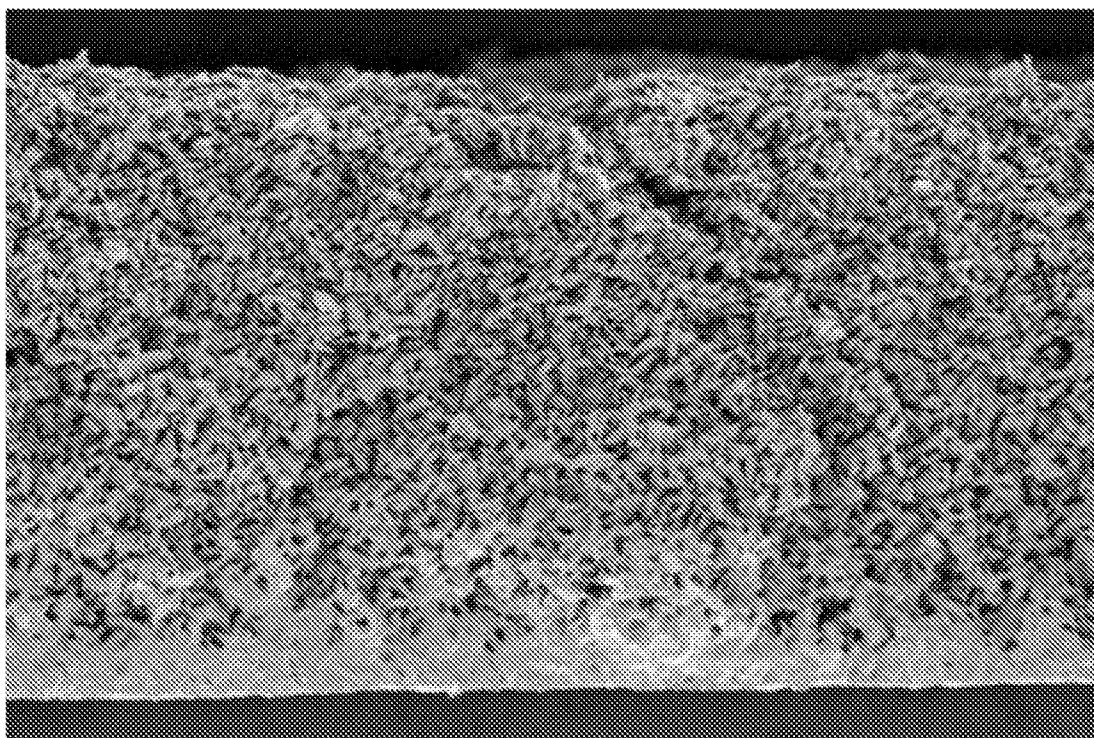


FIG. 1

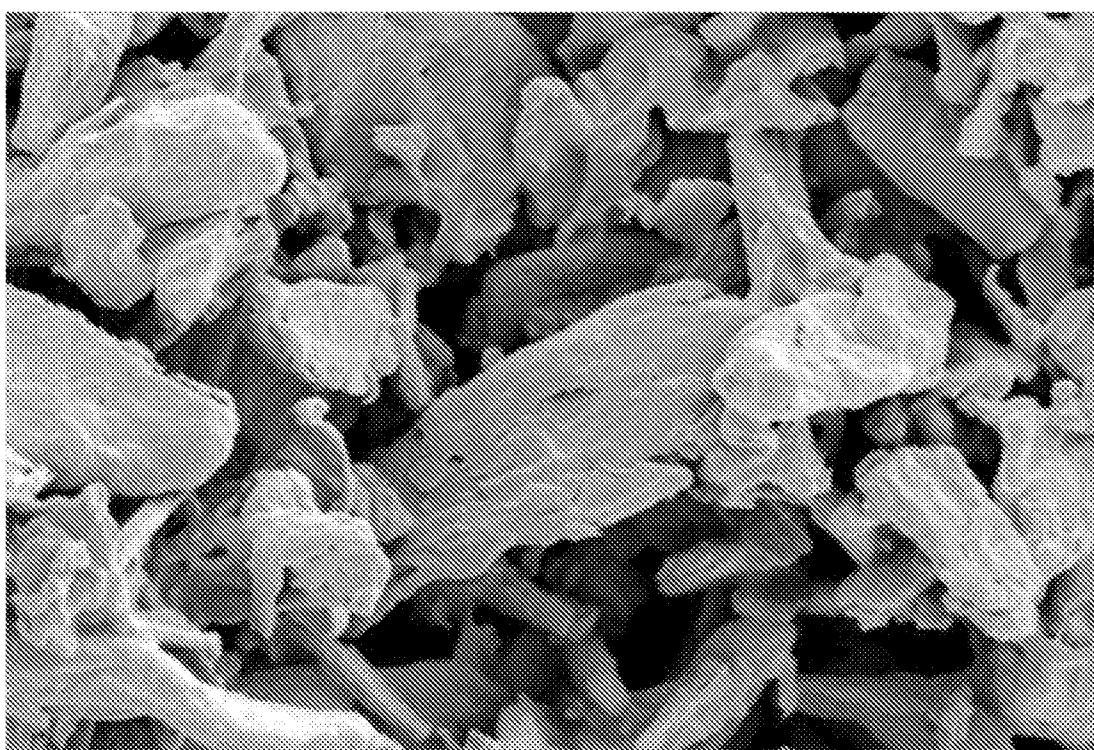


FIG. 2

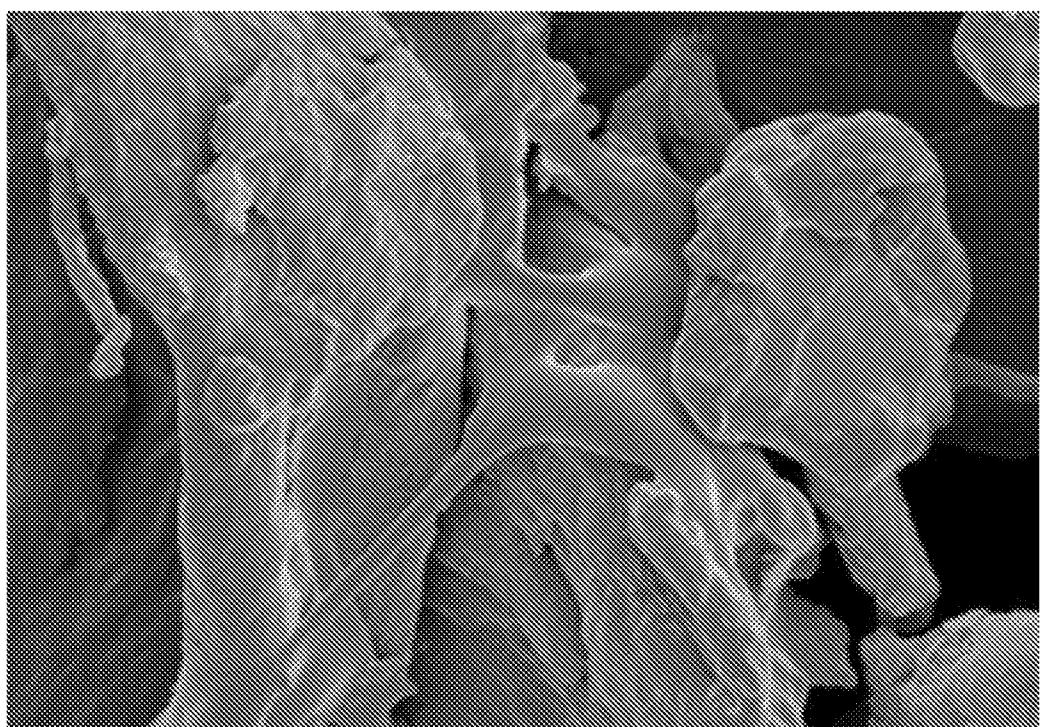


FIG. 3



FIG. 4



FIG. 5

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB2014/059472

## A. CLASSIFICATION OF SUBJECT MATTER

A61L 15/16(2006.01)i, A61F 13/15(2006.01)i

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

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A61L 15/16; D21H 11/20; A01K 29/00; A61F 13/15; A61L 15/60; D06M 13/192

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
eKOMPASS(KIPO internal) & Keywords: absorbent, superabsorbent polymer, SAP, mix, blend, spray, dry, ratio

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96-04024 A1 (PEARLSTEIN, L.) 15 February 1996 See abstract; claims 1-15.	1-28
A	WO 2005-108669 A2 (RAYONIER PRODUCTS AND FINANCIAL SERVICES COMPANY) 17 November 2005 See abstract; claims 1-5, 15.	1-28
A	WO 03-059228 A2 (TYCO HEALTHCARE RETAIL GROUP, INC.) 24 July 2003 See abstract; claims 1-5, 16.	1-28
A	US 8148598 B2 (TSANG, P. et al.) 3 April 2012 See abstract; claims 1-7; figure 3.	1-28
A	US 2008-0022940 A1 (KIRSCH, B. et al.) 31 January 2008 See abstract; claim 1; figure 1.	1-28

 Further documents are listed in the continuation of Box C. See patent family annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

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Name and mailing address of the ISA/KR

International Application Division  
Korean Intellectual Property Office  
189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701,  
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

Han, Inho

Telephone No. +82-42-481-3362



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/IB2014/059472**

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 96-04024 A1	15/02/1996	AU 2966395 A BR 9508490 A EP 0689867 A1 EP 0689867 B1 EP 0697217 A1 EP 0880367 A1 IL 114709 A JP 08-080429 A JP 09-503954 A MX 9700779 A US 05539019 A US 05549590 A US 05611973 A US 05849816 A WO 97-27884 A1	04/03/1996 03/11/1998 03/01/1996 11/11/1998 21/02/1996 04/09/2002 16/07/2000 26/03/1996 22/04/1997 31/05/1997 23/07/1996 27/08/1996 18/03/1997 15/12/1998 07/08/1997
WO 2005-108669 A2	17/11/2005	EP 1745175 A2 EP 1745175 A4 US 2005-0247419 A1 WO 2005-108669 A3	24/01/2007 08/07/2009 10/11/2005 04/10/2007
WO 03-059228 A2	24/07/2003	US 2003-0129915 A1 WO 03-059228 A3	10/07/2003 09/10/2003
US 8148598 B2	03/04/2012	CA 2643482 A1 CN 101426461 A US 2007-0197987 A1 US 2012-175056 A1 WO 2007-098492 A2 WO 2007-098492 A3	30/08/2007 06/05/2009 23/08/2007 12/07/2012 30/08/2007 21/02/2008
US 2008-0022940 A1	31/01/2008	CA 2607676 A1 CA 2607750 A1 CA 2703443 A1 US 2005-0005869 A1 US 2005-0005870 A1 US 2005-0175577 A1 US 2007-0289543 A1 US 2008-0029039 A1 US 2008-0184939 A1 US 2008-0251027 A1 US 2009-0217882 A1 US 2010-0136336 A1 US 7964529 B2 WO 2005-120221 A2 WO 2005-120221 A3	01/05/2008 01/05/2008 15/11/2010 13/01/2005 13/01/2005 11/08/2005 20/12/2007 07/02/2008 07/08/2008 16/10/2008 03/09/2009 03/06/2010 21/06/2011 22/12/2005 18/05/2007