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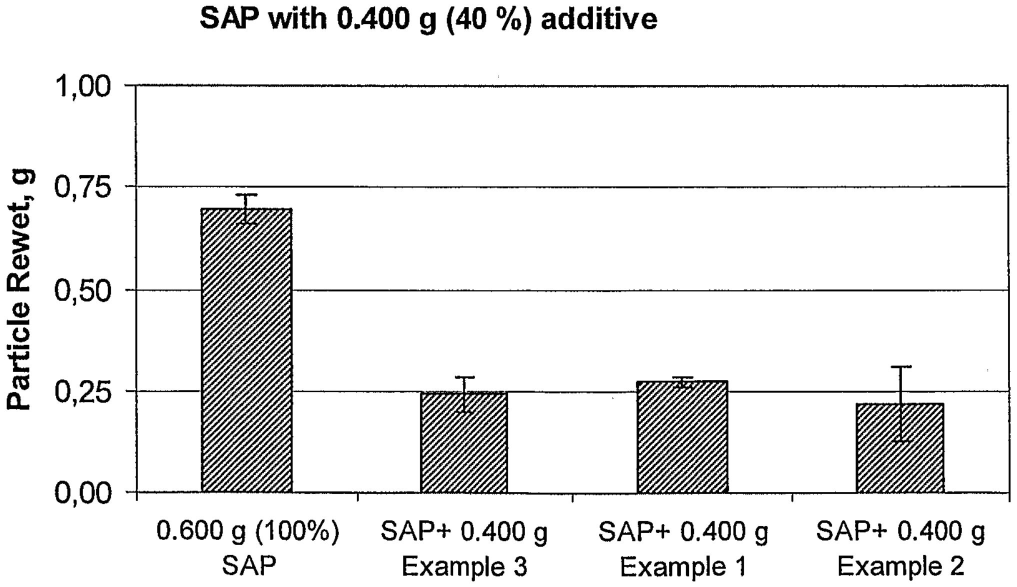
(54) **Title:** POLYSACCHARIDE-INORGANIC COMPOSITE PARTICLES AS PERFORMANCE ADDITIVES FOR SUPERABSORBENT POLYMERS



(57) **Abstract:** The present invention relates to discrete particulate composite additives for superabsorbent polymers and includes a method of making same. The discrete particulate composite additives generally comprise a polysaccharide and an inert inorganic component. Advantageously, these discrete particulate composite additives functionally improve superabsorbent performance. They are suitable for a number of applications, including the use and manufacture of hygiene products.

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TITLE OF THE INVENTION

POLYSACCHARIDE-INORGANIC COMPOSITE PARTICLES AS PERFORMANCE ADDITIVES FOR SUPERABSORBENT POLYMERS

FIELD OF THE INVENTION

The present invention relates to additives that improve the performance of superabsorbent polymers. The invention further includes the use of such additives as well as means for producing same.

BACKGROUND OF THE INVENTION

Superabsorbent polymers can be employed in various applications, such as in disposable sanitary products (*i.e.* diapers, incontinence articles, feminine hygiene products, and absorbent dressings), airlaids, household articles, sealing materials, humectants (*i.e.* agricultural products for soil conditioning), mining and oil drilling, anti-condensation coatings, water-storing materials (for use in fields as diverse as agriculture, horticulture and forestry), absorbent paper products, surgical absorbents, pet litter, bandages, wound dressings, chemical absorbents, polymeric gels for cosmetics and pharmaceuticals, artificial snow, in fire-fighting techniques, and in applications related to the transportation of fresh food or seafood, as well as in food packaging applications.

The largest use of superabsorbent materials or polymers (also referred to as SAP), however, is in disposable personal hygiene products. These products include, in the order of volume of superabsorbent materials used, diapers, training pants, adult incontinence products and feminine hygiene products.

Superabsorbent polymers and fluff cellulose pulp are usually mixed uniformly in diapers and incontinence products. This mixture of fluff and superabsorbents is formed in absorbent structures called "absorbent cores". Unfortunately, physiological fluids are excreted and absorbed over only a small area of these absorbent cores. The superabsorbent performance of these absorbent cores is therefore not optimal.

Fluid acquisition or fluid distribution layers have been added to diapers and incontinence garments for some time. (See, for example, United States Patent No. 5,137,600 (Barnes *et al*).) These nonwoven .textiles increase liquid diffusion along the length and width of absorbent structures (i.e., along the X and Y axes), and in this way increase the amount of superabsorbents that is placed in contact with fluids. However, nonwoven textiles do not enhance the performance of superabsorbents. Nonwoven textiles can only be placed at the surface of absorbent structures, and this minimizes their impact on liquid penetration through the absorbent structures (i.e., along the Z axis). Furthermore, they are usually very expensive. Due to their high cost, fluid distribution layers are usually placed over a small area in absorbent structures and thus have only a limited effect on liquid diffusion.

Superabsorbent polymers (SAP) can be mixed with inorganic additives, such as clays, zeolites or silicates. Several additives have been mixed with superabsorbent polymers or in hygiene products for odor control purposes. (See, for example, United States Patent No. 6,225,524 and European Patent No. 0751 791 (Guarracino *et al*); United States Patent No. 6,096,299; International Patent Application No. WO 91/12031 (Ryan *et al*); International Patent Application Nos. WO 99/30754 and 99/30752 (Carlucci *et al*); United States Patent No. 5,980,879 (Hiroki *et al)*; Japanese Patent No. 04-114741 (Takahashi *et al*); United States Patent No. 6,175,055 (Schöne); International Patent Application No. WO 91/11977 (Furio *et al)*; International Patent Application No. WO 81/01643 (Dodwel *et al*) and United States Patent No. 4,826,497 (Marcus *et al*). However, not all of these additives were reported to improve superabsorbent performance in diapers or incontinence garments.

Wong *et al* (United States Patent Application No. 2003/131,799), Brehm *et al* (United States Patent Application No. 2003/158,296 and United States Patent No. 5,248,709) and Brüggeman *et al* (United States Patents Nos. 5,847,031 and 5,721,295) describe absorbent polymer compositions made from matrix bound (melt bound) particles of superabsorbent polymers and additives. The additives are either polysaccharides or clays. As described in Pietsch (*Agglomeration Processes*: *Phenomena, Technologies, Equipment,* Wiley-VCH, 2002, ISBN 3-527-30369-3, at page 44), matrix forming binder components fill entire pore spaces, and therefore drastically reduce porosity and accessible surface area. High specific surface areas and porosity provide higher driving forces for fluid transport through the absorbent structure, as demonstrated by Roe (United States Patent No. 5,419,956).

Superabsorbent material was also reported to play a role as a matrix material or binder. Hiroki *et al* (United States Patent No. 5,980,879) teaches that superabsorbent particles occlude odor control additives, such as zeolites. Jiro *et al* (Japanese Patent No. 59-008711) and Herfert *et al* (United States Patent Application No. 2005/239,942) describe superabsorbent particles that occlude additives, such as clays, alumina or silica. Suskind *et al* (United States Patent Nos. 5,539,019 and 5,849,816) discuss solid cores covered with absorbent polymers. Murukami *et al* (United States Patent No. 4,418,163) and Herfert *et al* (United States Patent Application No. 2005/245,393) are concerned with superabsorbents coated with inorganic particles (clay, calcium carbonate, magnesium silicate, barium sulphate). Kobayashi *et al* (United States Patent No. 5,489,469) and Sears (United States Patent No. 6,855,182) describe composites made from fibers, swollen absorbent polymers and water insoluble inorganic materials, such as alumina, silica, zeolite and clays. The absorbent materials will therefore fill pore spaces, drastically reducing accessible surface area.

Takahashi *et al* (Japanese Patent No. 04-114741), Chmelir *et al* (European Patent No. 0318989), Obayashi *et al* (United States Patent No. 4,732,968), Yanagisawa *et al* (Japanese Patent No. 08-010616) and Woodrum *et al* (United States Patent No. 4,914,066) report agglomerated particles made from silicates and fine superabsorbent particles. Takai *et al* (United States Patent No. 6,284,362) is concerned with agglomerated particles made from metal oxides and fine superabsorbent particles. Reeves *et al* (United States Patent No. 6,387,495), Skidmore *et al* (International Patent Application No. WO 00/16816), Luke *et al* (United States Patent No. 5,609,123) and Toth *et al* (United States Patent No. 5,339,769) teach agglomerated particles made from clays and fine superabsorbent particles. Yen *et al* (United States Patent 3,900,378) describe agglomerated particles made from diatomaceous earth, clay or magnesium silicate and fine superabsorbent particles. As reported by Berg *et al* (United States Patent No. 5,300,565) water-agglomerated superabsorbent fine particles dissociate upon contact and/or swelling with an aqueous solution. This results in a concentration of swollen free fine particles that will contribute to an increased gel blocking.

McKinley *et al* (United States Patent No. 4,500,670), Duchane (United States Patent No. 3,932,322) and Tsubakimoto *et al* (United States Patent Nos. 4,734,478 and 4,286,082) describe optimized superabsorbents mixed with additives, such as silica, diatomaceous earth and clays. As discussed in Roe (United States Patent No. 5,419,956), none of the foregoing appears to have adequately understood and addressed the problems associated with the transport rate of fluids in both the X-Y plane and in the Z-direction. Moreover, these additives are not made from organic components.

Kodaira *et al* (Japanese Patent No. 01-004653) and Sun *et al* (United States Patent No. 6,124,391) report superabsorbent compositions comprising inorganic substances, especially kaolin. Sun emphasizes anti-caking effects of inorganic substances, but also demonstrates improved SAP performances attributed to the inorganic component. However, Sun and Kodaira don't describe additives made from organic components.

Biodegradability and sustainable development issues were raised recently in the superabsorbent industry when increases in oil prices created provisioning problems (*Kuster B.,* Nonwovens World, Dec-Jan 2005, p. 57). One solution to the "SAP shortage" was to propose a reduction of the SAP content in hygiene articles. However, this strategy does not necessarily involve SAP optimization.

As alternatives, the Groupe Lysac proposed many absorbent compositions made from biodegradable and renewable feedstocks. (See, for example, Canadian Patent No. 2,308,537 (Huppé *et al*); Canadian Patent No. 2,362,006 (Couture *et al*); Canadian Patent No. 2,426,478 (Bergeron); Canadian Patent No. 2,462,053 (Thibodeau *et al)*; and Canadian Patent No. 2,483,049 (Berrada *et al*).) However, these patents do not relate to additives that have the effect of improving the performance of superabsorbents.

Takahiro *et al* (Japanese Patent No. 01-296933), Marx (United States Patent No. 4,615,923) and Brander *et al* (United States Patent No. 6,376,034) describe inorganic additives (kieselguhr, clays, diatomaceous earth) added to biodegradable superabsorbents. However, none of these patents teach additives made from organic components.

Richman *et al* (United States Patent No. 4,454,055) and Spence (United States Patent No. 4,272,514) report the use of starch, a natural and biodegradable polymer, as an additive for superabsorbent polymers. Richman and Spence also teach the use of inorganic additives for enhancing the performance of superabsorbent polymers. However, neither Richman nor Spence describes the use of both organic (starch) and inorganic components in a single particle.

There thus remains a need for an additive that effectively improves the performance of superabsorbents. Ideally, such an additive would be cost-efficient and be composed of mainly renewable resources. Moreover, the additive would combine synergistically, in a single particle, organic components as well as inorganic components.

The present invention seeks to meet these and other needs.

The following description refers to a number of documents, the contents of which are herein incorporated by reference in their entirety.

SUMMARY OF THE INVENTION

The present invention relates to novel composite functional additives. These additives are composed of discrete particles that are suitable to be blended with superabsorbent polymers and that improve superabsorbent performance. These discrete particles are generally comprised of a polysaccharide and an inorganic component.

In one embodiment, the present invention is concerned with superabsorbent compositions comprising a superabsorbent polymer and a composite additive.

The present invention further includes hygiene articles comprising the absorbent composition, as well as a process for the manufacture of the additive. Non limiting examples of means for making the additive of the present invention include tumble growth agglomeration, pressure agglomeration and matrix melt formation.

In another embodiment, the present invention concerns the use of the absorbent composition for the absorption of fluids. The absorbent compositions would be used to absorb fluids including but not limited to water, aqueous solutions, saline solutions and physiological solutions.

Other objects, advantages and features of the present invention will become more apparent upon reading of the following non restrictive description of embodiments thereof, given by way of example with reference to the accompanying figures.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 illustrates a scanning electron micrograph (Magnification 250 times) of an agglomerated composite additive according to an embodiment of the present invention.

Figure 2 illustrates a scanning electron micrograph (Magnification 1,000 times) of the agglomerated composite additive shown in Figure 1.

Figure 3 illustrates a scanning electron micrograph (Magnification 250 times) of a semi-uniform composite additive, according to another embodiment of the present invention.

Figure 4 illustrates a scanning electron micrograph (Magnification 1,000 times) of the semi-uniform composite additive shown in Figure 3.

Figure 5 illustrates a scanning electron micrograph (Magnification 250 times) of a uniform composite additive, according to yet another embodiment of the present invention.

Figure 6 illustrates a scanning electron micrograph (Magnification 1,000 times) of the uniform composite additive shown in Figure 5.

Figure 7 illustrates a side elevation view of a twin screw extruder (TSE) that may be used to make the composite additives of the present invention.

Figure 8 is a bar graph showing the relative rewet performances of absorbent compositions comprising additives (20 %) in accordance with an embodiment of the present invention.

Figure 9 is a bar graph showing the relative rewet performances of absorbent compositions comprising additives (40 %) in accordance with another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

In order to provide a clear and consistent understanding of the terms used in the present specification, a number of definitions are provided below. Additionally, the present description refers to a number of routinely used chemical and technical terms. Unless otherwise defined, the terms used in the present description have the meanings that would be understood by one of skill in the art.

Definitions

The use of the word “a” or “an” when used in conjunction with the term “comprising” in the claim(s) and/or the specification may mean “one”, but it is also consistent with the meaning of “one or more”, “at least one”, and “one or more than one”. Similarly, the word “another” may mean a second or more.

The words “comprising” (and any form comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “include” and “includes”), or “containing” (and any form of containing, such as “contain” and "contains"), are inclusive or open-ended. They do not exclude additional, unrecited elements or method steps.

The term "about" is used to indicate that a value includes an inherent variation of error for the device or the method being employed to determine the value.

As used herein, the term "percent" or "%" refers to percentages in weight (W/W).

As used herein, the term "additive for superabsorbent polymers" refers to a substance, added to superabsorbent polymer, in contents up to 50 % (w/w). Such a substance may be a composite according to the present invention which is added to a superabsorbent but does not exceed more than 50% of the absorbent composition.

As used herein, the term "discrete particle" refers to individual particles.

As used herein, the term "superabsorbent polymers" also called "SAP", refers to hydrogel forming absorbent polymers having a Centrifuge Retention Capacity (CRC) of at least 15 g/g. These superabsorbent polymers are best when dry and in the form of discrete particles.

As used herein, the term "discrete additive particles for superabsorbent polymers" refers to individual additive particles which are added to individual superabsorbents.

As used herein, the term "functional additive for superabsorbent polymers" refers to additives for superabsorbent polymers which, by their action, will improve superabsorbent performances. This improvement may be determined with the absorbent compositions or directly in hygiene articles. Non-limiting examples of improved characteristics for superabsorbent particles that may evaluated are higher free swell capacity, higher centrifuge retention capacity, higher absorption under load and lower particle rewet. Non-limiting examples of improved characteristics in hygiene articles are lower rewet, lower penetration time and higher stain area.

As used herein, the term "composite particle" refers to particles made from two or more constituent materials that remain distinct on a micrometric level while forming a single particle.

As used herein, the term "polysaccharide" refers to polymers comprising a backbone comprised mainly of (at least 90%) monosaccharide repeating units and/or derivatized monosaccharide repeating units. Non-limiting examples include starches, modified starches, amylopectin, modified amylopectin, amylose, modified amylose, chitosan, chitin, guar gum, modified guar gum, locust bean gum, tara gum, konjac gum, konjac flour, fenugreek gum, mesquite gum, aloe mannans, cellulose, modified cellulose (representative examples include carboxyalkylated cellulose and carboxymethyl cellulose), oxidized polysaccharides, sulfated polysaccharides, cationic polysaccharides (such as, but not limited to, the chitosan, quaternary ammonium derivatives of polysaccharides or guanidinated polysaccharides, as described in Canadian Patent No. 2,519,417 (Berrada)), pectin, arabic gum, karaya gum, xanthan, kappa, iota or lambda carrageenans, agar-agar, alginates and mixture thereof.

As used herein, the term "monosaccharide unit", refers to cyclic C_5-C_6 aldoses or ketoses. Non limiting examples of C_5-C_6 aldoses include allose, altrose, glucose, mannose, gulose, idose, galactose, talose, ribose, arabinose, xylose, lyxose. Non limiting examples of C_5-C_6 ketoses include ribulose, xylulose, fructose, sorbose and tagatose.

As used herein, the term "monosaccharide derivatives" refers to any chemically or enzymatically modified monosaccharide unit.

As used herein, the term "inorganic material" refers to materials which are not member of a large class of chemical compounds whose molecules contain carbon.

As used herein, the term "inert inorganic material" refers to inorganic materials which will not significantly react chemically or dissolve in water.

As used herein, the term "swelling clay" refers to clays which will be able to swell in deionized water. Non-limiting examples of such clays are smectites, hectorites, bentonites, montmorillonites, Laponites™, celites, illites and mixture thereof.

As used herein, the term "molten polysaccharides" refers to polysaccharides for which a sufficient amount of water and heat has been provided to break their native crystalline pattern. A synonymous term, "gelatinized", is often used when referring to starch.

As used herein, the term "agglomerated composite" refers to the morphology of composite particles, wherein the polysaccharide and the inorganic component are discrete particles bound together.

As used herein, the term "uniform composite" refers to the morphology of composite particles, wherein the polysaccharide is a uniform amorphous polysaccharide occluding the inorganic components.

As used herein, the term "semi-uniform composite" refers to the morphology of composite particles, wherein the polysaccharide comprises uniform and agglomerated morphologies. This morphology could be very specific and exhibit various shapes, such as sponge-like designs, as shown in Figures 3 and 4.

As used herein, the term "discrete blending" or "discrete blend" refers to a process wherein the additive is mixed with a superabsorbent polymer, but wherein both the superabsorbent polymer and the additive particles retain their discrete characters.

As used herein, the term "Liquid-SAP ratio" refers to the amount of saline solution that is used, for example, in a hygiene article or poured in a particle rewet test, per gram of a given superabsorbent polymer. Liquid-SAP ratio higher than CRC of the given SAP will exhibit interstitial water between SAP particles; while a liquid-SAP ratio lower than CRC of the given SAP will exhibit partially swollen SAP.

As used herein, the term "Free Swell Capacity" (FSC), also called "Total Absorption", refers to the amount (g) of fluid absorbed per gram of the composition. A typical fluid used for this determination is saline solution (0.9% Weight/Weight NaCl solution, hereinafter called 0.9% NaCl solution or saline).

As used herein, the term "Centrifuge Retention Capacity" (CRC), also called "Retention", refers to the amount (g) of fluid retained per gram of the composition, following exposure of the composition to a centrifugation force of 250G. A typical fluid used for this determination is saline solution (0.9% NaCl solution or saline).

As used herein, the term "Absorption Under Load" (AUL) at 0.3 PSI, 0.7 PSI or 0.9 PSI, also called "Absorption Against Pressure" (AAP), refers to the amount (g) of fluid absorbed per gram of the composition under a given applied pressure. A typical fluid used for this determination is saline solution (0.9% NaCl solution or saline).

As used herein, the term "particle rewet" or "powder rewet" refers to the amount of fluid released under an applied pressure (0.7 PSI) for a given amount of superabsorbent material.

As used herein, the term "rewet" or "wet-back" refers to a physical characteristic of hygiene articles, such as a diaper, a sanitary napkin, an airlaid, a C-Fold, an absorbent core or an incontinence garment, and is a measure of the capacity of these absorbent products to retain fluids under applied pressure (0.7 PSI).

As used herein, the term "stain area" or "diffusion" refers to a physical characteristic of hygiene articles, such a diaper, a sanitary napkin, an airlaid, a C-fold, an absorbent core or an incontinence garment, and is a measure of the staining area (cm^2) produced for a given amount of a liquid.

As used herein, the term "penetration time" or "acquisition time" refers to a physical characteristic of hygiene articles, such as a diaper, a sanitary napkin, an airlaid, a C-fold, an absorbent core or an incontinence garment, and is a measure of the time taken by an absorbent product to absorb a given amount of a liquid.

As used herein, the term "airlaid" refers to a type of absorbent core, usually located inside sanitary napkins and baby diapers. Airlaids are manufactured using cellulose "fluff" fibers. However, they can also be manufactured using, in addition to fluff, absorbent or superabsorbent materials, and/or bi-component fibers. Airlaids are generally made using an air-suspension of particles and fibers which are forcibly deposited on a vacuumed screen. The deposit is then compressed, resulting in an airlaid.

As used herein, the term "C-fold" refers to a type of absorbent core, usually located inside sanitary napkins, which is manufactured using an airlaid (see Canadian Patent 2,483,049 (Berrada *et al*)). The interior spacing of the "C-fold" usually comprises superabsorbent polymers or a superabsorbent composition.

As used herein, the term SEM refers to Scanning Electron Microscopy.

In a broad sense, the present invention relates to novel additives improving superabsorbent performances. More specifically, the present invention relates to discrete additive particles for superabsorbent polymers. Yet more specifically, the additive particles are composite particles, comprising a polysaccharide and an inert inorganic component. In an embodiment of the present, the additive of the present invention is a functional additive, improving superabsorbent polymer characteristics.

The polysaccharide part of the composite will provide biodegradability and renewability. Therefore, the polysaccharide content in the composite will be relatively high, ranging from about 40 to about 90 %. The polysaccharide may be crystalline or amorphous. If the polysaccharide is crystalline, it is preferably comprised in the composite in a particle state.

Yet more specifically, polysaccharides that are suitable for use in the composite particle may be selected from the following non-limited group: starches, modified starches, amylopectin, modified amylopectin, amylose, modified amylose and mixture thereof. Amongst these polysaccharides, starch is frequently chosen as a polysaccharide for use in the agglomerated particle. Nonlimiting examples of such starches are starch granules, pregelatinized starches, glass-like starches, waxy starches, anionic starches, cationic starches, fractionated starches, cross-linked starches, hydroxyalkylated starches, alkylated starches and mixture thereof.

Starch that is suitable for the present invention may be obtained from many sources, including but not limited to wheat, maize, buckwheat, potato, cassava, sorghum, millet, oat, arrowroot, barley, beans, peas, rice, rye, waxy starches and mixture thereof. A commonly used starch is wheat starch.

Naturally occurring starch is usually organized in a semi-crystalline, water insoluble pattern, which is sometimes referred to as a “starch granule”.

The form of these starch granules is characteristic of their botanical origin, and their mean particle size may range from about 1 µm to about 60 µm.

Another part of composite additives of the present invention is the inert inorganic component. The inert inorganic component will provide porosity and will drive the water more efficiently through the superabsorbent polymer. The typical inert inorganic component content ranges from about 1 % to about 40 %. The particle size of the inert inorganic component ranges from about 10 µm to about 150 µm. Water adsorbents, such as molecular sieves, zeolites, clays, silicates, silica gel, insoluble salts and mixture thereof may preferably be used. Among this class, swelling clays may also be used.

Non limiting examples of inert inorganic substances are calcium sulfate, silica gel, zeolites and mixtures thereof. Gypsum is a good source of calcium sulfate. Clinoptilolite is a good source of zeolites. Non-limiting examples of swelling clays are smectites, hectorites, bentonites, montmorillonites, Laponites™, celites, illites and mixture thereof. Bentonite has been found to be quite suitable.

The composite of the present invention may have multiple morphologies. The composite may be uniform, semi-uniform or agglomerated. Each morphology will exhibit its own behavior and will act differently on the performances of the superabsorbent. A uniform composite will result in increases in FSC and CRC.

Process conditions will strongly influence morphology of the composite additives. The composites of the present invention may be formed by pressure agglomeration, tumble growth agglomeration or matrix melt formation.

In order to obtain composite additive particles, the polysaccharide and the inorganic component are uniformly blended together before they will be bound to each other. An agglomerating agent or a binder may optionally be mixed with other components. Non-limiting examples of suitable binders are gelling polysaccharides, such as sodium carboxymethyl cellulose.

Matrix melt formation will be used to form uniform and semi uniform composites. In matrix melt formation, the polysaccharide component of the additive is partially molten (for semi uniform) or totally molten (for uniform) and act as matrix material. Extrusion is a very efficient way to melt a polysaccharide, such as described by Canadian Patent 2,308,537 (Huppé *et al*) or Canadian Patent 2,462,053 (Thibodeau *et al*).

Agglomerates may be manufactured in several ways. They may be prepared by tumble growth agglomeration. Agglomerates may also be made by pressure agglomeration. A useful pressure agglomeration process is extrusion. Other agglomeration techniques are described exhaustively by Pietsch (*Agglomeration Processes*: *Phenomena, Technologies, Equipment,* Wiley-VCH, 2002, ISBN 3-527-30369-3).

The resulting particles are porous and sponge-like, concave or have a clustered shape, as illustrated in Figures 3, 5 and 1, respectively. Once formed, additive particles may be ground to specific particle size distributions. Ideally, the discrete additive particles have particle size distributions that are similar to those of the superabsorbents for which they are intended. Additives of the present invention will typically comprise particles ranging from about 150 µm to about 850 µm in size.

The additive particles of the present invention are to be discretely blended with superabsorbent polymers. The resulting absorbent composition is especially useful. Additive particles may be pre-blended with a superabsorbent polymer. Additive particles may also be blended *in situ* in a hygiene article (i.e. a diaper), along with fluff pulp and other components in the manufacturing process. Additives of the present invention may be used with a variety of superabsorbent polymers such as natural based SAPs, hybrid SAPs, synthetic SAPs and mixture thereof.

Natural based superabsorbent polymers may be selected from gelling polysaccharides, gelling proteins and mixtures thereof. Non-limiting examples of natural based polymers are galactomannans, glucomannans, carboxyalkyl polysaccharides, borate cross-linked galactomannans (United States Patent Nos. 4,624,868 and 4,333,461 (Muller *et al*)), synergistic compositions of polysaccharides (Canadian Patent No. 2,426,478 (Bergeron)), cross-linked polysaccharides (Canadian Patent 2,362,006 (Couture *et al*), amylopectin networks (Canadian Patent 2,462,053 (Thibodeau *et al*)), absorbent polysaccharides nanocomposites (Canadian Patent No. 2,483,049 (Berrada *et al*)), guanidinated polysaccharides (Canadian Patent No. 2,519,417 (Berrada)) and modified proteins (United States Patent Nos. 6,821,331 and 5,847,089 (Srinivasan *et al*)).

Synthetic based superabsorbent polymers are essentially made from polymerized ethylenically unsatured hydrophilic monomers. They may be obtained by radical polymerization or radical graft polymerization. Synthetic SAPs are cross-linked, forming hydrophilic, swelling networks. Non-limiting examples of monomers which could be used to form superabsorbent polymers are acrylic acid, acrylate salts, acrylic ester, acrylic anhydride, methacrylic acid, methacrylate salts, methacrylic esters, methacrylic anhydride, maleic anhydride, maleic salts, maleate esters, acrylamide, acrylonitrile, vinyl alcohol, vinyl pyrrolidone, vinyl acetate, vinyl guanidine, aspartic acid, aspartic salts and mixtures thereof. Examples of such synthetic based superabsorbent polymers are detailed in (United States Patent No. 6,087,450 (Breitbach *et al*); United States Patent No. 5,610,220 (Klimmek *et al*); United States Patent No. 5,612,384 (Ross *et al)*; United States Patent No. 5,453,323 (Chambers *et al*); and United States Patent No. 5,075,344

(Johnson) as well as in Buchholz *et al Modern Superabsorbent Technology*, Wiley-VCH, 1998, ISBN: 0471194115).

Hybrid superabsorbents are superabsorbents made from graft polymerization of ethylenically unsatured hydrophilic monomers on a natural polymer, usually a polysaccharide. Superabsorbent polysaccharide-based grafted-polymers are obtained via the grafting of an unsaturated monomer (acrylonitrile, acrylic acid, acrylamide) onto starch, or, less frequently, cellulose. The so-obtained polymers, also called "Super Slurper", have shown a water absorption ranging from 700 to 5300 g/g in deionised water, and up to 140 g/g in a 0.9 % saline solution (Riccardo P.O., Water-Absorbent Polymers: A Patent Survey. J. Macromol. Sci., Rev. Macromol. Chem. Phys., 1994, 607-662 and references cited therein).

The hygiene market, and more specifically, the baby diapers market, is quite diversified. Some products, which are designated as "high tier" or "deluxe", will contain large amounts of SAP. However, in developing countries, where diaper cost is more of a concern, the SAP content is generally much lower. In fact, SAP content could range from 1.5 g to 15 g in a baby diaper. Additives of the present invention are ideally suited for use in absorbent products having a moderate to high content of superabsorbent polymers. The content of superabsorbent polymers may be calculated by determining the liquid-SAP ratio. It has been found that the additives of the present invention are especially useful with hygiene articles having a liquid-SAP ratio up to 35 ml per gram of SAP. It should be noted, however, that the liquid-SAP ratio is specific to the superabsorbent material. The liquid-SAP ratio will change with the SAP used. Best results have been observed with liquid-sap ratios ranging from about 85 % to about 115 % the CRC value of the used SAP.

The absorbent compositions (SAP + additive) of the present invention may be used in hygiene articles. Non-limiting examples of hygiene articles are diapers, incontinence products, airlaids, sanitary napkins, C-folds and absorbent cores.

The absorbent compositions (SAP + additive) of the present invention may be used to absorb water, aqueous solutions, saline solutions and physiological solutions, amongst other fluids. The compositions (SAP + additive) of the present invention may also be used in a method for the absorption of fluids. Non-limiting examples of fluids are water, aqueous solutions, saline solutions and physiological solutions. The method involves placing the absorbent composition in contact with the fluid.

EXPERIMENTAL

Materials

Synthetic, sodium polyacrylate superabsorbent were obtained from Stockhausen GmbH (Krefeld, Germany) and BASF (Ludwigshafen, Germany). Grade A wheat starch was obtained from Archer Daniels Midland® (Decatur, USA). Corn starch was obtained from Cargill (Minneapolis, USA). National™ Premium WT-200 bentonite was purchased from Bentonite Performance Minerals® (Denver, USA). Terra Alba, gypsum was obtained from United States Gypsum Company® (Chicago, USA). Clinoptilolite zeolite was obtained from Cycletrol® (Carson City, USA).

Eirich Intensive Mixer

An Eirich Intensive Mixer type RO2 from Maschinenfabrik Gustav Eirich, (Hardheim, Germany) was used to agglomerate the polysaccharide and the inorganic component.

Twin-screw extruder

Two twin screw extruders were used. A Coperion Werner & Pfleiderer ZSK58 MC (Stuttgart, Germany), and a Baker-Perkins Twin-screw extruder MPF-50D from APVBaker Invensys, (Grand Rapids, USA) were used to manufacture the composite.

As illustrated in Figure 7, the motor powered (4) extrusion lines (1) were composed of feeders, either volumetric or gravimetric, (2) feeding premixed solid components or each component individually into a solid entry port (8), a liquid injection port for water addition (3), a die plate (5) and a die-face pelletizer (7). Both twin screw extruders have 9 temperature control zones, noted as Z1, Z2, Z3, Z4, Z5, Z6, Z7, Z8 and Z9 and a pressure transducer (6).

The Baker-Perkins twin-screw extruder configuration starts with a zone of conveying elements, followed by zones of pumping elements, kneading elements and ends with pumping elements just before a die plate of either 6 or 9mm die openning.

The Coperion twin-screw extruder configuration starts with a zone of conveying elements, followed by zones of pumping elements, kneading elements and ending with pumping elements. The extrudate is further fed into a single screw ESA150 attached with a EGR pelletizer mounted with a die plate of 3mm die opening.

It should be noted that Buss-Kneader extruders could also be used. Extruders may be cooled. Extrudates exiting the extruders could be pumped for pressure build-up or final moisture removal. This can be done by various systems, such as single screw extruders or gear pumps. The extrusion can also be done on longer or shorter machines. Extruders having a length/diameter ratio (L/D ratio) ranging from about 15 to about 50 could be used. The extruder may have a side feeder for feeding additional ingredients downstream. This side feeder may also act as a devolatalizer removing the moisture from the ingredients or removing entrapped gases. The position of the degassing side feeder can be from about 12 L/D ratio to about 24 L/D ratio. A side feeder can also be installed in the vicinity to the exit of the extruder to remove excess moisture. This is usually done after the water is added to the product. An upstream vent, prior to injection of water, may be used to allow air to escape.

Convection oven

Samples were dried in a Lab tray drier TY 2, National Drying Machinery Company, (Philadelphia, USA).

High speed chopper

Urschel Comitrol model 3600 with 3B030030 blade was used (Valparaiso, USA).

Grinder

A Quaker City (Straub® Co, Philadelphia, USA) grinding mill model F-4 was used to grind the produced additives samples.

Sieve Shaker

When indicated, samples were sieved using a Tyler Ro-Tap™ test sieve shaker. Another sieve shaker, refered as vibrating siever was used; Kason model K24-3-SS, (Scarborough, Canada).

Test methods

As discussed in Modern Superabsorbent Polymer Technology (Buchholz F.L. and Graham A.T. Eds., Wiley-VCH, New York, 1998, section 4.6.1. Swelling Capacity: Theory and Practice, p. 147), several methods of measurement may be used in order to characterize the swelling capacity of a polymer. In the field of superabsorbents, the Gravimetric Swelling Capacity [also called the Free Swell Capacity (FSC)] and the Centrifuge Capacity [also called the Centrifuge Retention Capacity (CRC)] are recommended methods. The FSC and the CRC are used to compare the swelling capacities of the obtained absorbent products.

Tea bags for FSC and CRC measurements

Tea bags (10 X 10 cm) are made from heat sealable Ahlstrom™ filter paper (16.5 ±0.5) g/m^2.

FSC measurements

The Free Swell Capacity (FSC) in a 0.9% NaCl solution is determined in accordance with the recommended test method 440.2-02 from EDANA.

CRC measurements

The Centrifuge Retention Capacity (CRC) in a 0.9% NaCl solution was determined in accordance with the recommended test method 441.2-02 from EDANA.

Particle rewet

Rewet is a measurement especially useful in the hygiene industry. To better reflect the influence of the additive of the present invention on this characteristic, the rewet test was adapted for particles. In a 50 ml centrifuge test tube, 0,600 g of SAP was carefully weighed. A precise quantity of additive was weighed and blended with the superabsorbent polymer. Saline solution (18 ml) was added to the absorbent composition (liquid SAP ratio of 30 ml/g) and the composition let to absorb for precisely 30 minutes. About 4.5-5.0 g of filter paper was carefully weighed and placed on a Plexiglas plate. Over the filter paper, a 26 gsm nonwoven (Carded-Thermobonded Polypropylene from Industrias Maquin S.A., Huejotzingo, Mexico) was placed over the filter papers.

Alternatively, other acquisition distribution layers may be used. Swollen absorbent composition is poured on the nonwoven fabric. An aluminum piston, exerting a pressure of 0.7 Psi on the absorbent composition, was by placed on the nonwoven fabric. The filter paper was allowed to absorb for precisely 2 minutes, then the filter papers were carefully weighed. The particle rewet is the amount of fluid absorbed by the filter paper ($W_{paper\ wet} - W_{paper\ dry}$).

Scanning electron micrographs

Scanning electron micrographs were recorded using a Hitachi® S 3000N scanning electron microscope. Samples were placed on two-sided adhesive paper, glued to an aluminum plate. Any non-glued particles were removed with an air jet. A thin (about 10 nm) gold layer was then applied to the surface of the glued sample by a sputter coater. The surface was then scanned and recorded.

EXAMPLES

EXAMPLE 1

STARCH, ZEOLITE, CLAY COMPOSITE ADDITIVE SEMI-UNIFORM MORPHOLOGY

A mixture comprised of 70% wheat starch, 24% bentonite and 6% zeolite was compounded using the Baker Perkins twin-screw extruder with a die opening of 9 mm. The solid composition was mixed and wetted with 30 % tap water. The mixture was fed with a volumetric feeder and extruded at a throughput of 31 kg/h. Cooling was applied to the extruder using tap water, and all zones were 16°C. Zone 1 was not used. The screw speed was set at 200 RPM. The agglomerated material exited the extruder at about 75°C with a die pressure of about 270 psig. The motor load was at about 30-40%. This indicates that frictional heat was generated in the process.

The extrudates were then placed in a convection oven at 85°C for at least 3 hours and ground. The ground product was sieved using a RO-Tap sieve shaker. Samples larger than 30 Mesh were discarded, as well as samples smaller than 40 Mesh, in order to avoid any particle size effect interference on performances of the absorbent composition. The additives produced were characterized as described in Example 4. SEM of this sample was illustrated in Figures 3 and 4. The porosity of the additive can be observed from these figures.

EXAMPLE 2

STARCH, ZEOLITE, CLAY COMPOSITE ADDITIVE UNIFORM MORPHOLOGY

A mixture comprising of 70% wheat starch, 24% of bentonite and 6% of zeolite was compounded using the Baker Perkins twin-screw extruder with a die opening of 6 mm. The solid composition was mixed and wetted with 26 % tap water. The mixture was fed with a volumetric feeder and extruded at a throughput of about 18 kg/h. Temperature zones were : Z_1 zone was not used, Z_2=32°C, Z_3=38°C, Z_4=48°C, Z_5=65°C, Z_6=82°C, Z_7=93°C, Z_8=104°C, Z_9=115°C. The screw speed was set at 100 RPM. The agglomerated material exited the extruder about 131°C. The motor load was about 40%.

The extrudates were then placed in a convection oven at 85°C for at least 3 hours and ground using a high-speed chopper. The ground product was sieved using a RO-Tap sieve shaker. Samples larger than 30 Mesh were discarded, as well as samples smaller than 40 Mesh, in order to avoid any particle size effect interference on performances of the absorbent composition The additives produced were characterized as described in Example 4. SEM of this sample was illustrated in Figures 5 and 6. The porosity of the additive can be observed from these figures, as well as their concave design.

EXAMPLE 3

STARCH, ZEOLITE, CLAY COMPOSITE ADDITIVE AGGLOMERATED MORPHOLOGY

A mixture comprising of 70% corn starch, 24% of bentonite and 6% of zeolite was compounded using the Coperion twin-screw extruder. The mixture was fed with a volumetric feeder at a rate of 194 Kg/h and 26 % of cold water added. Corn starch, bentonite and zeolite were fed separately in the Coperion extruder with gravimetric feeders at the rate of 300 lbs/h, 103 lbs/h and 26 lbs/h, respectively. Tap water was injected at a rate of 155 lbs/hr, corresponding to a 26 % addition. The extrusion throughput was about 580 lbs/hr. Temperature zones were: Z_1=15°C, Z_2=34°C, Z_3=35°C, Z_4=35°C, Z_5=34°C, Z_6=36°C, Z_7=41°C, Z_8=43°C, Z_9=47°C. The screw speed was set at 220 RPM. The agglomerated material exited the extruder about 35°C. The motor load was about 15%.

The extrudates were then placed in a convection oven at 85°C for at least 3 hours and ground using a high-speed chopper. The ground product was sieved using a RO-Tap sieve shaker. Samples larger than 30 Mesh were discarded, as well as samples smaller than 40 Mesh, in order to avoid any particle size effect interference on performances of the absorbent composition. The additives produced were characterized as described in Example 4. SEM of this sample was illustrated in Figures 1 and 2. The clustered design of the additive can be observed from these figures.

EXAMPLE 4

ABSORBENT COMPOSITIONS

Synthetic superabsorbent polymer (BASF Hysorb 8650) was carefully weighed (0.600 g). To this mass, 0.150 g (20 %) or 0.400 g (40%) of additives particles were added and blended. Particle rewet values are reported in Figures 8 and 9. CRC was also characterized, as shown in Table 1. As it may be appreciated, the agglomerated morphology improves significantly particle rewet of superabsorbent polymer. However, matrix melt formation yields a better CRC.

Table 1. CRC performances in Examples 1 to 3 for additives at various concentrations

SAP Content	Additive and content	CRC (g/g)
100%SAP		33.2
80%SAP	20 % Example 3	26.8
80% SAP	20 % Example 1	26.8
80%SAP	20 % Example 2	**27.4**
60% SAP	40 % Example 1	20.3
60% SAP	40 % Example 3	20.4
60% SAP	40 % Example 2	**21.4**

EXAMPLE 5

STARCH ZEOLITE AGGLOMERATES WITH A BINDER

A dry powder is prepared by physically blending of 50% of starch, 49 % of zeolite. One (1) % of carboxymethylcellulose (CMC) was swelled with 30 % of aqueous solution, and then compacted. The obtained paste was dried overnight in an oven at 60°C. The resulting pellet was ground with a Quarker City mill and sieved, keeping only particles having a size ranging from 150 μm to 600 μm. Finally, this powder was blended with superabsorbent polymers (Stockhausen Favor SXM 9145) with additives charge varying from 10% to 20%. The powder performances of the so-obtained formulation were reported in Table 2.

Table 2: Performance of SAP-Additive blends, with the Example 5 agglomerated additive

Agglomerates (% w/w)	SAP (% w/w)	FSC	CRC
0	100	52.1	31.7
10	90	50.3	31.7
15	85	50.1	31.0
20	80	48.3	30.7

EXAMPLE 6

STARCH GYPSUM CLAY BY TUMBLE GROWTH AGGLOMERATION

A mixture comprising of 80% wheat starch, 18% of bentonite and 2% of gypsum was micropelletized using an Eirich Intensive Mixer. The following agglomeration procedure was applied: 1500g of the mixture is fed into the mixer, the agitation is set at 855 RPM and 643g of water is then added to the mixture over a period of 30 seconds. This agitation is maintained for 1 minute after the water addition. After the 1 minute period, the agitation speed is increased to 1765 RPM for another minute, then the agitation speed is increased to 3490 RPM and 700g of the mixture is fed in the mixer over a period of 1 minute. Once all the mixture is added, the agitation is maintained for 1 minute at 3490 RPM. The resulting moist agglomerated mixture is sieved and the -850µm/+150µm fraction is then dried in an oven at 60°C to bring the moisture down to 7 %. Table 3 shows the performances of various blends of SAP (Favor SXM 9145) and the dried agglomerated mixture (-850µm/+150µm fraction).

Table 3: Performances of blends of SAP and starch, clay, gypsum agglomerates

Agglomerates (% w/w)	SAP (% w/w)	FSC	CRC
0	100	52.1	31.7
10	90	48.0	28.3
15	85	45.8	26.3
20	80	43.8	26.0

CLAIMS:

1. A discrete particulate composite additive for superabsorbent polymers, wherein said composite comprises a polysaccharide and an inert inorganic component.

2. A discrete particulate composite additive, as described in claim 1, wherein said additive is a functional additive.

3. A discrete particulate composite additive, as described in claim 1, wherein said polysaccharide content in the discrete particulate composite additive is ranging from about 40 % to about 90 %.

4. A discrete particulate composite additive, as described in claim 1, wherein said polysaccharide is selected from the group of starches, modified starches, amylopectin, modified amylopectin, amylose, modified amylose and mixture thereof.

5. A discrete particulate composite additive, as described in claim 4, wherein said polysaccharide is selected from the group consisting of starch granules, pregelatinized starches, glass-like starches, waxy starches, anionic starches, cationic starches, cross-linked starches, hydroxyalkylated starches, alkylated starches and mixture thereof.

6. A discrete particulate composite additive, as described in claim 5, wherein said starch granules have a diameter ranging from 1 µm to 60 µm.

7. A discrete particulate composite additive, as described in claim 4, wherein said starch is coming from sources selected from the group consisting of wheat, maize, buckwheat, potato, waxy starches, cassava, sorghum, millet, oat, arrowroot, barley, beans, peas, rice, rye and mixture thereof.

8. A discrete particulate composite additive, as described in claim 1, wherein said inert inorganic component content ranges from about 1 % to about 40 %.

9. A discrete particulate composite additive, as described in claim 1, wherein said inert inorganic component particle size ranges from about 10 μm to about 150 μm.

10. A discrete particulate composite additive, as described in claim 1, wherein said inert inorganic component is selected from the group consisting of swelling clays, zeolites, silica gel, insoluble salts and mixture thereof.

11. A discrete particulate composite additive, as described in claim 11, wherein said swelling clay is selected from the group consisting of smectites, hectorites, bentonites, montmorillonites, Laponites™, celites, illites and mixture thereof.

12. A discrete particulate composite additive, as described in claim 1, wherein the morphology of the said discrete particulate composite additive is uniform, semi-uniform or agglomerated.

13. A discrete particulate composite additive, as described in claim 1, wherein said discrete particulate composite additive comprises a binder.

14. A discrete particulate composite additive, as described in claim 1, wherein said discrete particulate composite additive particulates have a size ranging from about 150 μm to about 850 μm.

15. A process for the manufacture of a discrete composite additive, as described in claim 1, wherein said additive was formed by pressure agglomeration, tumble growth agglomeration or matrix melt formation.

16. A process for the manufacture of a discrete composite additive, as described in claim 15, wherein said additive was formed by extrusion.

17. An absorbent composition comprising a superabsorbent polymer and a discrete composite additive, as described in claim 1.

18. An absorbent composition as described in claim 17, wherein said superabsorbent polymer comprises a superabsorbent polymer selected from the group consisting of natural superabsorbents, synthetic superabsorbents, hybrid superabsorbents and mixture thereof.

19. An absorbent composition as described in claim 18, wherein the composition is placed in contact with an amount of saline solution corresponding to a liquid-SAP ratio less than 35 ml per gram of the superabsorbent polymer in the absorbent composition.

20. An absorbent composition as described in claim 18, wherein the composition is placed in contact with an amount of saline solution corresponding to a liquid-SAP ratio ranging from 85 % to 115 % the CRC value of the superabsorbent polymer in the absorbent composition.

21. A hygiene article comprising an absorbent composition as described in claim 18.

22. The use of the absorbent composition described in claim 18 to absorb fluids selected from the group consisting of water, aqueous solutions, saline solutions and physiological solutions.

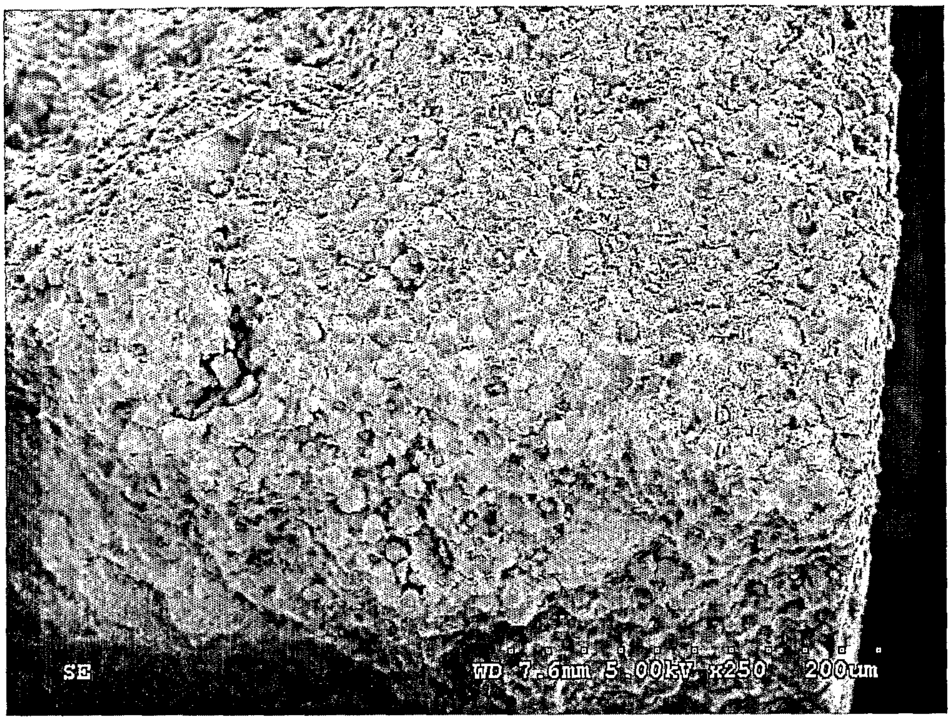

Fig. 1.

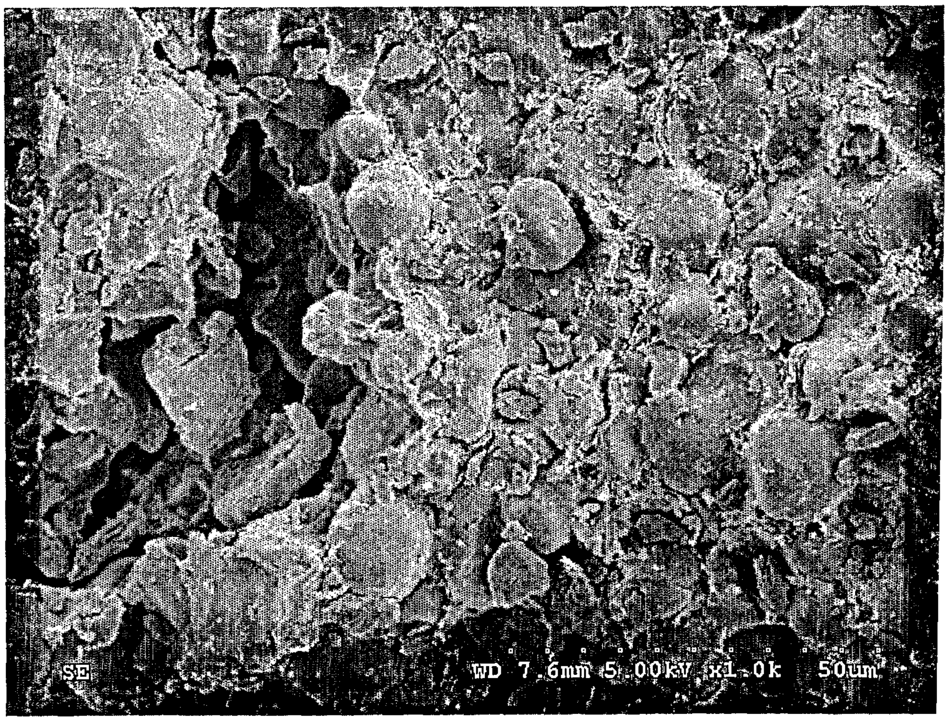

Fig. 2.

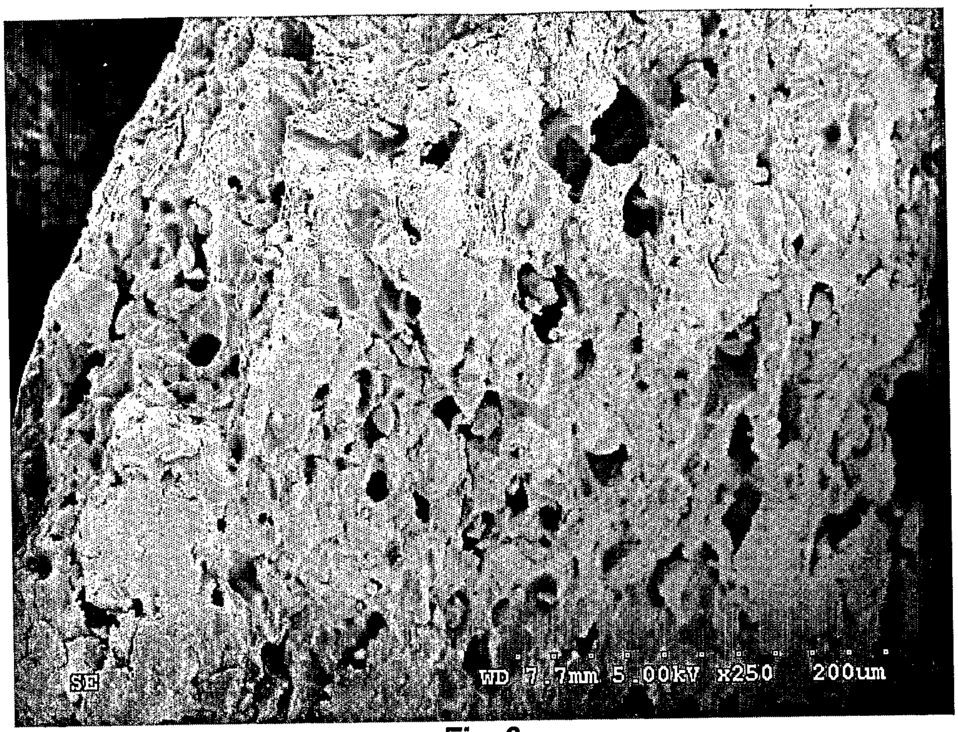

Fig. 3.

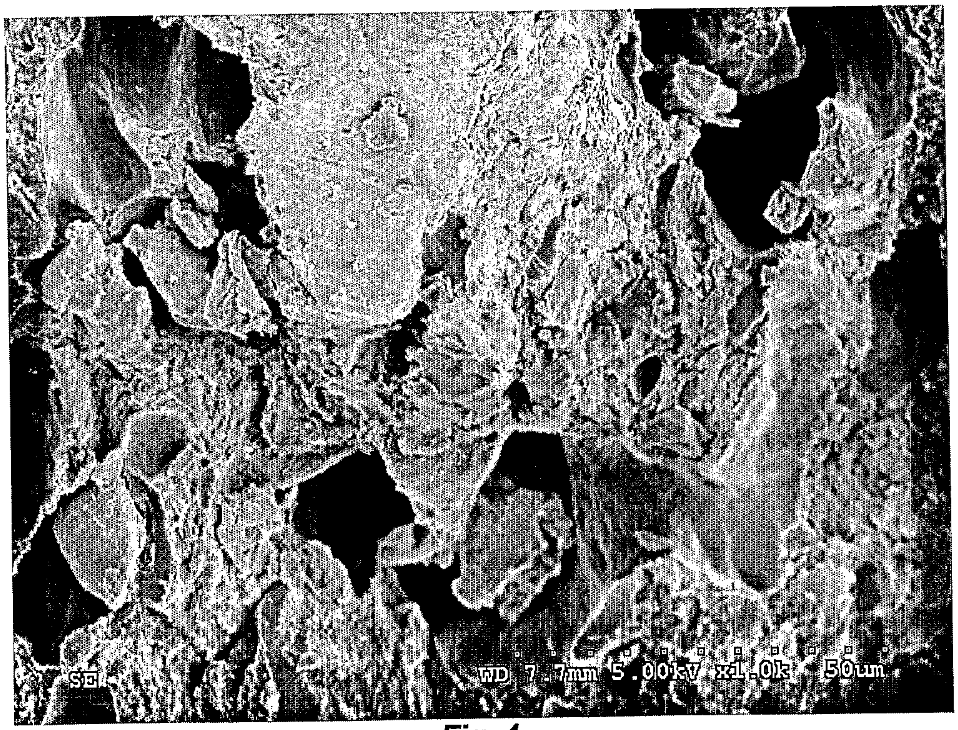

Fig. 4.

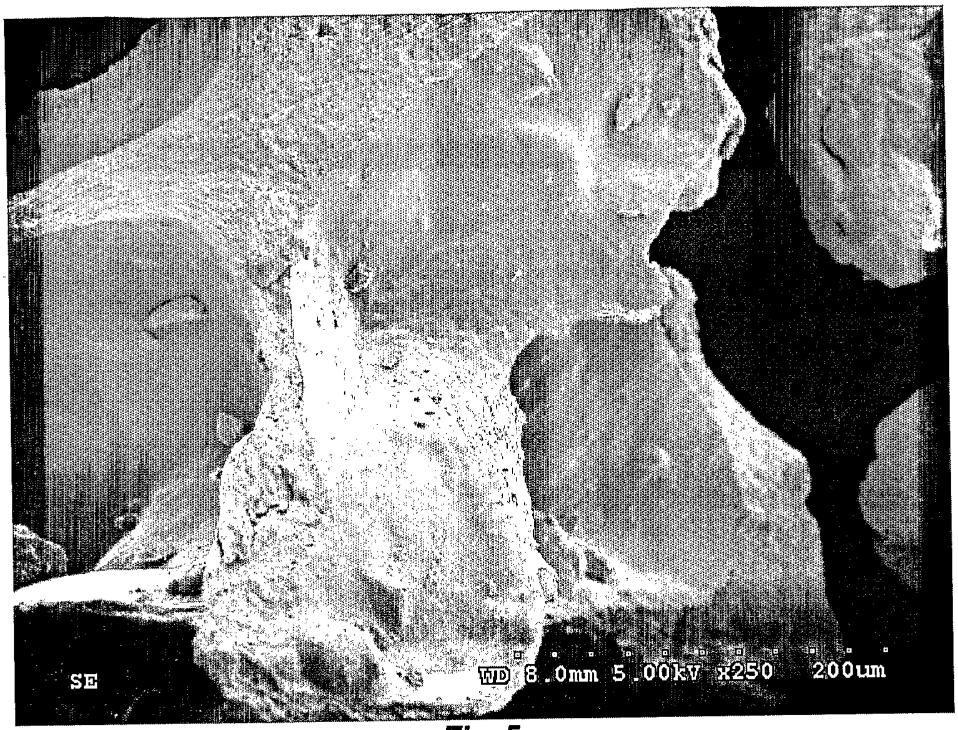

Fig. 5.

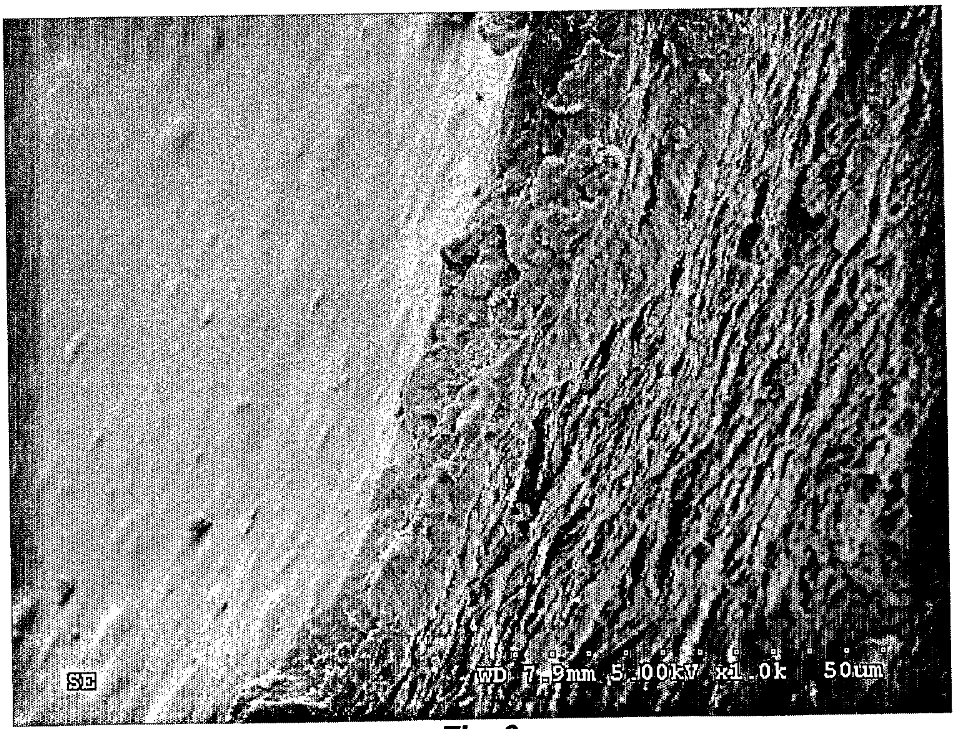

Fig. 6.

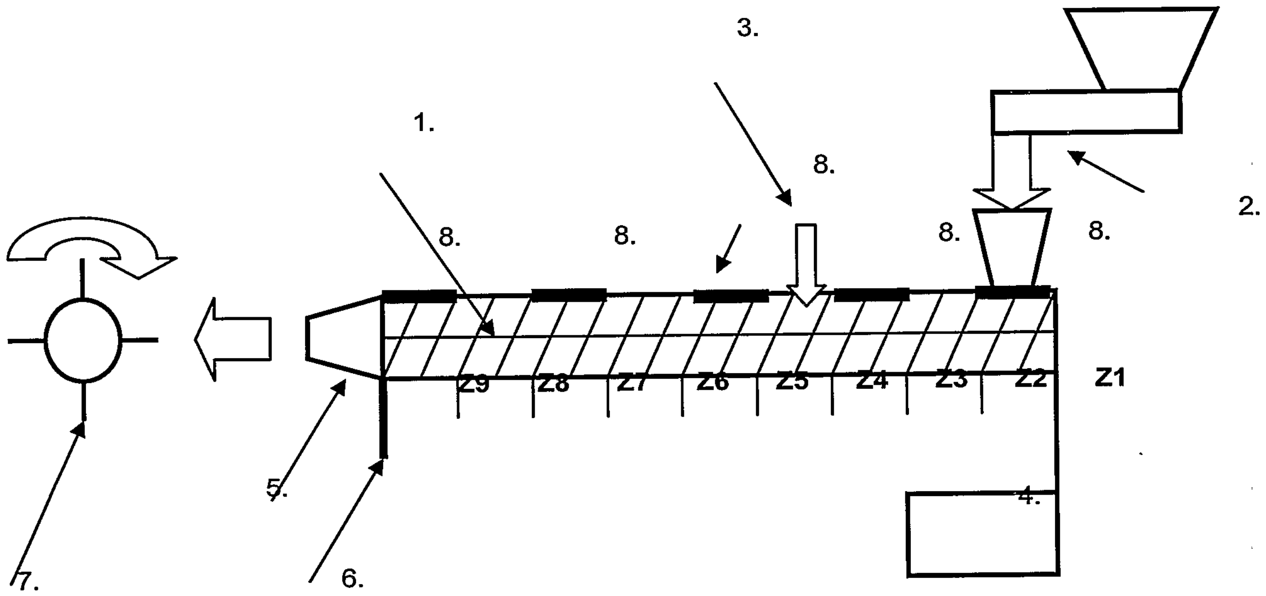

Fig. 7.

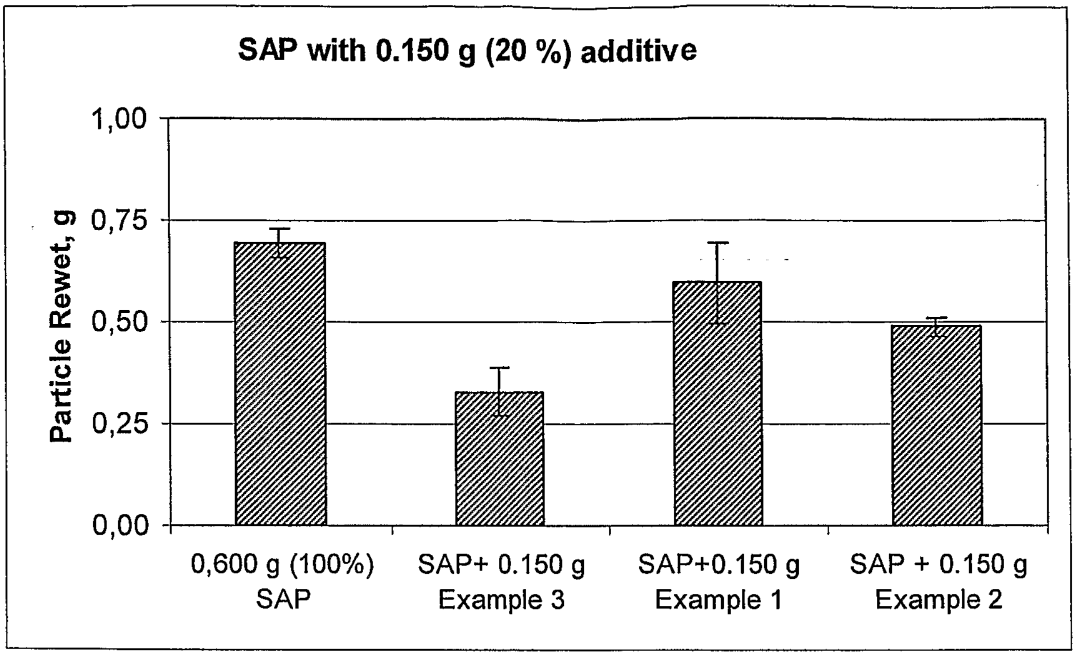
SAP with 0.150 g (20 %) additive
Particle Rewet, g
1,00
0,75
0,50
0,25
0,00
0,600 g (100%) SAP
SAP+ 0.150 g Example 3
SAP+0.150 g Example 1
SAP + 0.150 g Example 2

Fig. 8.

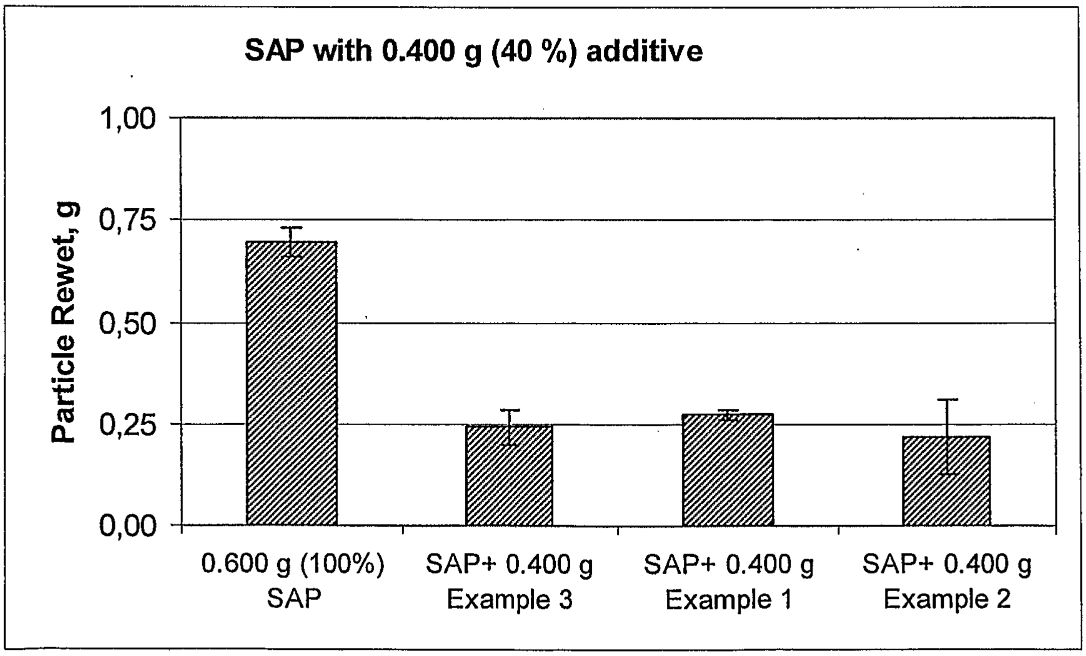
SAP with 0.400 g (40 %) additive
Particle Rewet, g
1,00
0,75
0,50
0,25
0,00
0.600 g (100%) SAP
SAP+ 0.400 g Example 3
SAP+ 0.400 g Example 1
SAP+ 0.400 g Example 2

Fig. 9.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2006/000136

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***B01J 20/22*** (2006.01) , ***C08L 3/00*** (2006.01) , ***C08K 13/04*** (2006.01) , ***C08K 3/34*** (2006.01) , ***C08J 3/20*** (2006.01) , ***A61F 13/53*** (2006.01) , ***A61L 15/18*** (2006.01) , ***A61L 15/28*** (2006.01)

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)

IPC: B01J, C08L, C08K, C08J, A61F & A61L.

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)

Canadian patent database, Delphion, Esp@cenet, USPTO, Scopus & Oxford online.

Keywords: “superabsorbent”, “absorbent”, “polysaccharide”, “inorganic”, “starch”, “gypsum”, “zeolite” & “particle”.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4454055 (Richman et al.) 12 June, 1984 (12-06-1984) Abstract & Column 7	1-22
X	EP 0087001 (Crampton et al.) 11 January, 1995 (11-01-1995) Page 4, lines 30-47	1-22
X	CA 2405618 (Pesce et al) 24 April, 2001 (24-04-2001) Pages 20-25 & Claims	1-22
P, X	CA 2483049 (Berrada et al) 29 September, 2005 (29-09-2005) Pages 26-27 & Claims	1-22
A	US 4272514 (Spence) 9 June, 1981 (09-06-1981)	1-22

[ ] Further documents are listed in the continuation of Box C. [X] 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
“E”	earlier application or patent but published on or after the international filing date
“L”	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
“O”	document referring to an oral disclosure, use, exhibition or other means
“P”	document published prior to the international filing date but later than the priority date claimed
“T”	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“X”	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“Y”	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“&”	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 May 2006 (12-05-2006)	15 May 2006 (15-05-2006)

Name and mailing address of the ISA/CA
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Authorized officer

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2006/000136

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US4454055	12-06-1984	DE3132976 A1	08-04-1982
		FR2488901 A1	26-02-1982
		GB2082614 A	10-03-1982
EP0087001	31-08-1983	DE3362488D D1	17-04-1986
		ES519925D D0	16-03-1984
		US4657881 A	14-04-1987
CA2405618	01-11-2001	AT300963T T	15-08-2005
		AU5720501 A	07-11-2001
		DE60112421D D1	08-09-2005
		EP1149596 A1	31-10-2001
		EP1276514 A1	22-01-2003
		JP2003530969T T	21-10-2003
		MXPA02010031 A	12-02-2003
		US6833487 B2	21-12-2004
		WO0180915 A1	01-11-2001
CA2483049	29-03-2005	CA2443059 A1	29-03-2005
		US2005214541 A1	29-09-2005
		WO2005030279 A1	07-04-2005
US4272514	09-06-1981	NONE	