

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
17 February 2005 (17.02.2005)

PCT

(10) International Publication Number
WO 2005/014062 A1

(51) International Patent Classification⁷: **A61L 15/00**,
15/60, 15/42, C08J 9/00

(DE). **URANKAR, Edward** [US/US]; 8834 Charleston
Hill Court, Mason, OH 45040 (US).

(21) International Application Number:
PCT/US2004/025640

(74) Common Representative: **THE PROCTER & GAM-
BLE COMPANY**; c/o T. David Reed, 6110 Center Hill
Road, Cincinnati, OH 45224 (US).

(22) International Filing Date: 5 August 2004 (05.08.2004)

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, IT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/492,819 6 August 2003 (06.08.2003) US

(71) Applicant (for all designated States except US): **THE
PROCTER & GAMBLE COMPANY** [US/US]; One
Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **SCHMIDT, Mat-
tias** [DE/DE]; Charlotte-Rosenthal-Str. 21, 65510 Idstein
(DE). **MEYER, Axel** [DE/DE]; Robert-Mayer Strasse
34, 60486 Frankfurt am Main (DE). **FOSSUM, Renae,
Dianna** [US/US]; 501 South Main Street, Middletown,
OH 45044 (US). **EHRNSPERGER, Bruno, Johannes**
[DE/DE]; Bonner Strasse 5, 65812 Bad Soden (DE).
GOLDMAN, Stephen, Allen [US/IT]; Via Colle di Moro
62, Citta Sant' Angelo, I-60513 Pescara (IT). **DIVO,
Michael** [DE/DE]; Feldbergstr. 14, 61381 Friedrichsdorf

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR MAKING WATER-SWELLABLE MATERIAL COMPRISING COATED WATER-SWELLABLE
POLYMERS

(57) Abstract: This invention is directed to a process for making solid, typically particulate, water-swella-
ble material comprising coated water-swella-
ble, preferably hydrogel-forming polymers, which are coated with a coating agent, which is such that it does
not rupture when the polymers swell in a liquid, e.g. water or saline water. Hereto, the coating agent is extensible in wet state and
comprises thereto a wet-extensible material that has a tensile stress at break in the wet state of at least 1MPa. Typically, the coating
agent comprises thereto an elastomeric polymeric material. The invention also relates to solid (particulate) water-swella-
ble material obtainable by the process of the invention.



WO 2005/014062 A1

**PROCESS FOR MAKING WATER-SWELLABLE MATERIAL COMPRISING
COATED WATER-SWELLABLE POLYMERS**

FIELD OF THE INVENTION

This invention is directed to a process for making water-swellaable materials, typically solid, particulate, water-swellaable materials comprising coated water-swellaable, preferably hydrogel-forming polymers, whereby the coating is such that it substantially does not rupture when the polymers swell in 0.9% saline, the coating being highly extensible in the wet state. The coating comprises preferably an elastomeric polymeric material. The invention also relates to solid (particulate) water-swellaable materials obtainable by the process of the invention, and to products, e.g. disposable absorbent articles, comprising such solid (particulate) water-swellaable material.

BACKGROUND OF THE INVENTION

An important component of disposable absorbent articles such as diapers is an absorbent core structure comprising water-swellaable polymers, typically hydrogel-forming water-swellaable polymers, also referred to as absorbent gelling material, AGM, or super-absorbent polymers, or SAP's. This polymer material ensures that large amounts of bodily fluids, e.g. urine, can be absorbed by the article during its use and locked away, thus providing low rewet and good skin dryness.

Especially useful water-swellaable polymer materials or SAP's are often made by initially polymerizing unsaturated carboxylic acids or derivatives thereof, such as acrylic acid, alkali metal (e.g., sodium and/or potassium) or ammonium salts of acrylic acid, alkyl acrylates, and the like in the presence of relatively small amounts of di- or poly-functional monomers such as N,N'-methylenebisacrylamide, trimethylolpropane triacrylate, ethylene glycol di(meth)acrylate, or triallylamine. The di- or poly-functional monomer materials serve to lightly cross-link the polymer chains thereby rendering them water-insoluble, yet water-swellaable. These lightly crosslinked absorbent polymers contain a multiplicity of neutralized carboxylate groups attached to the polymer backbone. It is generally believed, that these carboxylate groups generate an osmotic driving force for the absorption of body fluids by the crosslinked polymer network.

In addition, the polymer particles are often treated as to form a surface cross-linked layer on the outer surface in order to improve their properties in particular for application in baby diapers.

Water-swellaable (hydrogel-forming) polymers useful as absorbents in absorbent members and articles such as disposable diapers need to have adequately high sorption capacity, as well as

adequately high gel strength. Sorption capacity needs to be sufficiently high to enable the absorbent polymer to absorb significant amounts of the aqueous body fluids encountered during use of the absorbent article. Together with other properties of the gel, gel strength relates to the tendency of the swollen polymer particles to resist deformation under an applied stress in the absorbent article. The gel strength needs to be high enough in the absorbent article so that the particles do not deform and fill the capillary void spaces to an unacceptable degree causing so-called gel blocking. This gel-blocking inhibits the rate of fluid uptake or the fluid distribution, i.e. once gel-blocking occurs, it can substantially impede the distribution of fluids to relatively dry zones or regions in the absorbent article and leakage from the absorbent article can take place well before the water-swellaable polymer particles are fully saturated or before the fluid can diffuse or wick past the "blocking" particles into the rest of the absorbent article. Thus, it is important that the water-swellaable polymers (when incorporated in an absorbent structure or article) maintain a high wet-porosity and have a high resistance against deformation thus yielding high permeability for fluid transport through the swollen gel bed.

Absorbent polymers with relatively high permeability can be made by increasing the level of internal crosslinking or surface crosslinking, which increases the resistance of the swollen gel against deformation by an external pressure such as the pressure caused by the wearer, but this typically also reduces the absorbent capacity of the gel undesirably.

The inventors have found that often the surface crosslinked water-swellaable polymer particles are constrained by the surface-crosslinking 'shell' and cannot absorb and swell sufficiently, and/ or that the shell is not strong enough to withstand the stresses of swelling or the stresses associated with performance under load.

The inventors have found that the coatings or shells of the water-swellaable polymers, as used in the art, including surface cross-linking 'coatings', break when the polymer swells significantly or that the 'coatings' break after having been in a swollen state for a period of time. They also have found that, as a result thereof, the coated and / or surface-crosslinked water-swellaable polymers or super-absorbent material known in the art deform significantly in use thus leading to relatively low porosity and permeability of the gel bed in the wet state, especially under pressure. They have found that this could be detrimental to the optimum absorbency, liquid distribution or storage performance of such polymer materials.

Thus, the inventors have found that what is required are water-swellaable materials comprising coated water-swellaable polymers that have a coating that can exert a force in the wet state and that does substantially not rupture when the polymers swell in body liquid under typical in-use conditions. In the context of this invention, the inventors have found that as a good representative

for body liquids such as urine, a 0.9% sodium chloride by weight in water solution, further called "0.9% saline" can be used. Therefore the inventors have found that it is required to have coated water-swellaable materials where the coating does substantially not rupture when the materials swell in 0.9% saline.

The inventors have now developed a process for making a new water-swellaable material and a new water-swellaable material, comprising water-swellaable polymers that are coated with a coating agent, which is extensible, e.g. elastomeric coatings which are elastically extensible, so that when the internal core of the hydrogel polymers swells, the coating can extend and remains substantially intact, i.e. without breaking.

Moreover, they have found that not all extensible materials are suitable in every application as coating agents, because some materials have a good extensibility (elongation) when in a dry state, but not in a wet state. Thus, they have found that it is important to provide the water-swellaable polymers with a coating agent that is wet-extensible.

The inventors further have found that the process of applying and subsequently treating the coating agents may be important in order to impart high extensibility (elongation) in the wet state.

SUMMARY OF THE INVENTION

The present invention relates to a process for making a water-swellaable material, comprising coated water-swellaable polymers, the process comprising the steps of:

- a) obtaining water-swellaable polymers; and
- b) simultaneously or subsequently to step a), applying at least 1% by weight of the water-swellaable material, of a coating agent, as described herein, to at least part of said water-swellaable polymers to obtain said water-swellaable material comprising said coated water-swellaable polymers; and in one embodiment of the invention:
- c) annealing and / or curing the resulting coated water-swellaable polymers of step b),

whereby said coating agent in step b) comprises a material that is wet- extensible and has tensile stress at break in the wet state of at least 1MPa, as determined by the Wet-elongation test defined herein.

Preferably, the coating agent comprises a material that has a wet-elongation at break of at least 400% or more preferably 500%, as determined by the same test.

For said test, a film or an annealed film or a cured film, and/ or an annealed and cured film of the coating agent or wet-extensible material is first prepared by the method described herein, and then tested. Hereby, an annealed film is tested when the process herein has the annealing step c) as a compulsory step; a cured film is tested if the process herein has the curing step as a compulsory step; an annealed and cured (preferably in that order) film is tested when the process herein has both the annealing and curing step, preferably in that order, as compulsory step.

Thus for example, a wet-extensible material or coating agent, used or useful in a process herein, which has an annealing step but not a curing step, has a tensile stress at break in the wet state of at least 1MPa, and preferably a wet-elongation of at least 400% or even at least 500%, when tested in the form of an annealed film; a wet-extensible material or coating agent used or useful in a process herein, which does not involve an annealing step and/ or curing step, has a tensile stress at break in the wet state of at least 1MPa, and preferably a wet-elongation of at least 400% or even at least 500%, when tested in the form of a film which has not been annealed or cured.

In other words, in a first embodiment of the invention, the process of the invention is as defined above and the wet-extensible material or coating agent used in step b) is such that a film thereof, which has not been annealed or cured, has a tensile stress at break in the wet state of at least 1MPa, and preferably a wet-elongation of at least 400% or even at least 500%. In a second, independent embodiment of the invention, the process is as defined above, except that the annealing and/ or the curing step is compulsory and the wet-extensible material or coating agent used in step b) is such that an annealed and/ or cured film thereof has a tensile stress at break in the wet state of at least 1MPa, and preferably a wet-elongation of at least 400% or even at least 500%.

Preferably, the process comprises the step d): prior to, simultaneous with or subsequent to step b) or c), obtaining said water-swellaable polymers or coated water-swellaable polymers in solid form.

The invention also relates to water-swellaable material obtainable by the processes of the invention.

The resulting coating is preferably substantially uniform, as described herein.

Preferably the water-swellaable polymers and the resulting water-swellaable material, comprising the coated water-swellaable polymers, is solid, preferably in the form of particles.

In a preferred process, step b) involves: applying at least twice a coating agent; preferred materials obtainable thereby comprise thus more than one coating layer.

It may be preferred that the coating agent is in the form of a powder, or that the coating agent in step b) is fluid, preferably being in the form of a solution, dispersion, or hotmelt when applied in the process. However, the coating agent may also for example be applied from the gas or vapour phase.

Step b) is preferably done in a fluidised bed or Wurster coater, or in a plough-share mixer, such as a Loedige mixer.

During the annealing or curing step, the coated polymers may be dried, or alternatively, a separate drying step may take place, simultaneously with, or after step b) or after step c).

The water-swellaable polymers are preferably hydrogel forming polymers, preferably being (partially neutralized) polyacrylates.

The water-swellaable polymers may be (surface) crosslinked prior to the coatings step b) and/ or the process may be such that the coated polymers are further subjected to (surface) cross-linking.

DETAILED DESCRIPTION

Water-swellaable material

The water-swellaable material of the invention is such that it swells in water by absorbing the water; it may thereby form a gel. It may also absorb other liquids and swell. Thus, when used herein, 'water-swellaable' means that the material swells at least in water, but typically also in other liquids or solutions, preferably in water based liquids such as 0.9% saline (0.9% NaCl solution).

The water-swellaable material of the invention comprises water-swellaable polymers that are coated by the process of the invention, as described below. The coating agent is preferably present at a level of 1% to 50% by weight of the water-swellaable material, more preferably from 1% to 30% by weight or even from 1% to 20% by weight or even from 2% to 15% by weight.

The coating agent is applied such that the resulting coating layer is preferably thin; preferably the coating layer has an average caliper (thickness) between 1 micron to 100 microns (μm), or even from 1 to 50 microns or even to 20 microns, or even 2 to 10 microns.

The coating is preferably uniform in caliper and/ or shape. Preferably, the average caliper is such that the ratio of the smallest to largest caliper is between 1 to 1 and 1 to 5, preferably between 1 to 1 and 1 to 2.

The water-swellaable material of the invention may also comprise other components, such as fillers, flowing aids, process aids, anti-caking agents, odor control agents, colouring agents, coatings to impart wet stickiness, hydrophilic surface coatings, etc.

The water-swellaable material may also contain water-swellaable polymers that are not coated. However, the coated water-swellaable polymers are preferably present at a level of at least 20% by weight (of the water-swellaable material), more preferably between 50% and 100% by weight or even from 80% to 100% by weight, and most preferably between 90% and 100% by weight.

The water-swellaable material is obtainable by the process described herein, which is preferably such that the resulting material is solid; this includes gels, flakes, fibers, agglomerates, large blocks, granules, powder particles, spheres and other forms known in the art for superabsorbent or water-swellaable polymers described herein.

Preferably, the material is in the form of particles having a mass median particle size between 10 μ m and 2mm, or even between 50microns and 1mm, or preferably between 100 μ m and 800 μ m, as can for example be measured by the method set out in for example EP-A-0691133.

In one embodiment of the invention the water-swellaable material of the invention is in the form of (free flowing) particles with particle sizes between 10 μ m and 1200 μ m or even between 50 μ m and 800 μ m and a mass median particle size between 100 μ m and 800 μ m or even 600 μ m.

In addition, or in another embodiment of the invention, the water-swellaable material comprises particles that are essentially spherical.

In yet another preferred embodiment of the invention the water-swellaable material of the invention has a relatively narrow range of particle sizes with the majority (e.g. at least 80% or preferably at least 90% or even at least 95%) of particles having a particle size between 50 μ m and 800 μ m, preferably between 100 μ m and 600 μ m, and more preferably between 200 μ m and 500 μ m.

The water-swellaable material of the invention preferably comprises less than 20% by weight of water, or even less than 10% or even less than 8% or even less than 5%, or even no water. The

water-content of the water-swellaable material can be determined by the Edana test, number ERT 430.1-99 (February 1999) which involves drying the water-swellaable material at 105 °Celsius for 3 hours and determining the moisture content by the weight loss of the water-swellaable materials after drying.

The material of the invention may be in the form of so-called core-shell particles, whereby the water-swellaable polymer(s) is (are) present in the internal structure or core and the coating agent forms a coating shell around the water-swellaable polymers, as described below in more detail.

In one preferred embodiment of the invention, the coating is an essentially continuous coating layer or shell around the water-swellaable polymer (core), and said coating layer covers the entire surface of the polymer(s), i.e. no regions of the polymer's surface (core surface) are exposed. Hereby, it is believed that maximum tangential forces are exerted around the water-swellaable polymer in the 'core' when the water-swellaable material swells in a liquid, as described below. In particular in this embodiment, the coating materials and the resulting coatings are preferably highly water permeable such as to allow a fast penetration/ absorption of liquid into the water-swellaable material (into the core).

In another preferred embodiment of the invention, the coating shell or layer is porous, e.g. in the form of a network comprising pores for penetration of water, such as for example in the form of a fibrous network, e.g. that is connected and circumscribing the particle as defined herein.

In other words, it is highly preferred that the resulting coating or coating layer or shell, formed in the process herein, is pathwise connected and more preferably that the coating layer is pathwise connected and encapsulating (completely circumscribing) the water-swellaable polymer(s) (see for example E. W. Weinstein et. al., Mathworld – A Wolfram Web Resource for 'encapsulation' and 'pathwise connected').

The coating layer is preferably a pathwise connected complete surface on the surface of the ('core' of the) water-swellaable polymer(s). This complete surface consists of first areas where the coating agent is present and which are pathwise connected, e.g. like a network, and it may comprise second areas, where no coating agent is present, being for example micro pores, whereby said second areas are a disjoint union. Preferably, each second area, e.g. micropore, has a surface area of less than 0.1 mm^2 , or even less than 0.01 mm^2 preferably less than $8000 \text{ } \mu\text{m}^2$, more preferably less than $2000 \text{ } \mu\text{m}^2$ and even more preferably less than $80 \text{ } \mu\text{m}^2$.

It is most preferred that no second areas are present, and that the coating agent forms a complete encapsulation around the water-swellaable polymer (s).

Preferred may be that the water-swellaable material comprises two or more layers of coating agent (shells), obtainable by coating the water-swellaable polymers twice or more. This may be the same coating agent herein, or a different coating agent.

Especially preferred water-swellaable materials made by the process of the invention have a high sorption capacity measured by the Cylinder Centrifugation Retention Capacity, CCRC test outlined below.

Especially preferred water-swellaable materials made by the process of the invention have a high permeability for liquid such as can be measured by the SFC test disclosed in US 5,599,335, US 5,562,646 and US 5,669,894 all of which are incorporated herein by reference.

In addition, especially preferred water-swellaable materials made by the process of the invention have a high wet porosity (i.e. this means that once an amount of the water-swellaable material of the invention is allowed to absorb a liquid and swell, it will typically form a (hydro)gel or (hydro)gelbed, which has a certain wet porosity, in particular compared to the uncoated water-swellaable polymers, as can be measured by the SFC test discussed below (or PHL test disclosed in US 5,562,646 which is incorporated herein by reference; if the water-swellaable material and water-swellaable polymers are to be tested at different pressures than described in the test method, the weight used in this test should be adjusted accordingly).

50% or even at least 100%, or even at least 150%.

Most preferred water-swellaable materials made by the process of the invention have a high sorption capacity such as is preferably measured by the CCRC test outlined below in combination with a high permeability (SFC) and high wet porosity (that are increased by the use of the coating agent).

Water-swellaable polymers

The water-swellaable polymers herein are preferably solid, preferably in the form of particles, flakes, fibers, agglomerated particles; most preferably, the water-swellaable polymers are particles having a mass median particle size as specified above for the water-swellaable material, plus the

thickness (caliper) of the coating; when the coating is very thin, e.g. 1 to 20 microns, then the mass median particle size/ distribution is the same as cited above.

As used herein, the term "water-swellaable polymer" refers to a polymer which is substantially water-insoluble, water-swellaable and preferably water-gelling, forming a hydrogel, and which has typically a Cylinder Centrifuge Retention Capacity (CCRC) as defined below of at least 10 g/g. These polymers are often also referred to in the art as (super-) absorbent polymers (SAP) or absorbent gelling materials (AGM).

These polymers are typically (lightly) crosslinked polymers, preferably lightly crosslinked hydrophilic polymers. While these polymers may in general be non-ionic, cationic, zwitterionic, or anionic, the preferred polymers are cationic or anionic. Especially preferred are acid polymers, which contain a multiplicity of acid functional groups such as carboxylic acid groups, or their salts, preferably sodium salts. Examples of acid polymers suitable for use herein include those which are prepared from polymerizable, acid-containing monomers, or monomers containing functional groups which can be converted to acid groups after polymerization. Such monomers include olefinically unsaturated carboxylic acids and anhydrides, and mixtures thereof. The acid polymers can also comprise polymers that are not prepared from olefinically unsaturated monomers. Examples of such polymers also include polysaccharide-based polymers such as carboxymethyl starch and carboxymethyl cellulose, and poly(amino acid) based polymers such as poly(aspartic acid). For a description of poly(amino acid) absorbent polymers, see, for example, U.S. Patent 5,247,068, issued September 21, 1993 to Donachy et al.

The above-cited patents and all following cited documents are incorporated herein by reference.

Some non-acid monomers can also be included, usually in minor amounts, in preparing the absorbent polymers herein. Such non-acid monomers can include, for example, monomers containing the following types of functional groups: carboxylate or sulfonate esters, hydroxyl groups, amide-groups, amino groups, nitrile groups, quaternary ammonium salt groups, and aryl groups (e.g., phenyl groups, such as those derived from styrene monomer). Other optional non-acid monomers include unsaturated hydrocarbons such as ethylene, propylene, 1-butene, butadiene, and isoprene. These non-acid monomers are well-known materials and are described in greater detail, for example, in U.S. Patent 4,076,663 (Masuda et al.), issued February 28, 1978, and in U.S. Patent 4,062,817 (Westerman), issued December 13, 1977.

Olefinically unsaturated carboxylic acid and anhydride monomers useful herein include the acrylic acids typified by acrylic acid itself, methacrylic acid, α -chloroacrylic acid, α -cyanoacrylic acid, β -methylacrylic acid (crotonic acid), α -phenylacrylic acid, β -acryloxypropionic acid, sorbic acid, α -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid, β -stearylacrylic

acid, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, tricarboxyethylene, and maleic anhydride.

Preferred water-swellaable polymers contain carboxyl groups, such as the above-described carboxylic acid/ carboxylate containing groups. These polymers include hydrolyzed starch-acrylonitrile graft copolymers, partially neutralized hydrolyzed starch-acrylonitrile graft copolymers, starch-acrylic acid graft copolymers, partially neutralized starch-acrylic acid graft copolymers, hydrolyzed vinyl acetate-acrylic ester copolymers, hydrolyzed acrylonitrile or acrylamide copolymers, slightly network crosslinked polymers of any of the aforementioned copolymers, polyacrylic acid, and slightly network crosslinked polymers of polyacrylic acid. These polymers can be used either solely or in the form of a mixture of two or more different polymers. Examples of these polymer materials are disclosed in U.S. Patent 3,661,875, U.S. Patent 4,076,663, U.S. Patent 4,093,776, U.S. Patent 4,666,983, and U.S. Patent 4,734,478.

Most preferred polymer materials used for making the water-swellaable polymers herein are polyacrylates/ acrylic acids and derivatives thereof, preferably (slightly) network crosslinked polymers partially neutralized polyacrylic acids and/or -starch derivatives thereof.

Preferred may be that partially neutralized polymeric acrylic acid is used in the process herein.

The water-swellaable polymers useful herein can be formed by any polymerization and/or crosslinking techniques. Typical processes for producing these polymers are described in U.S. Reissue Patent 32,649 (Brandt et al.), issued April 19, 1988, U.S. Patent 4,666,983 (Tsubakimoto et al.), issued May 19, 1987, and U.S. Patent 4,625,001 (Tsubakimoto et al.), issued November 25, 1986; US 5,140,076 (Harada); US 6,376,618 B1, US 6,391,451 and US 6,239,230 (Mitchell); US 6,150,469 (Harada). Crosslinking can be affected during polymerization by incorporation of suitable crosslinking monomers. Alternatively, the polymers can be crosslinked after polymerization by reaction with a suitable reactive crosslinking agent. Surface crosslinking of the initially formed polymers is a preferred way to control to some extent the absorbent capacity, porosity and permeability.

The water-swellaable polymers may also be surface-crosslinked, prior to, simultaneously with or after the coating step of the process herein. Suitable general methods for carrying out surface crosslinking of absorbent polymers according to the present invention are disclosed in U.S. Patent 4,541,871 (Obayashi), issued September 17, 1985; published PCT application WO92/16565 (Stanley), published October 1, 1992, published PCT application WO90/08789 (Tai), published August 9, 1990; published PCT application WO93/05080 (Stanley), published March 18, 1993;

U.S. Patent 4,824,901 (Alexander), issued April 25, 1989; U.S. Patent 4,789,861 (Johnson), issued January 17, 1989; U.S. Patent 4,587,308 (Makita), issued May 6, 1986; U.S. Patent 4,734,478 (Tsubakimoto), issued March 29, 1988; U.S. Patent 5,164,459 (Kimura et al.), issued November 17, 1992; published German patent application 4,020,780 (Dahmen), published August 29, 1991; ; US 5,140,076 (Harada); US 6,376,618 B1, US 6,391,451 and US 6,239,230 (Mitchell); US 6,150,469 (Harada); and published European patent application 509,708 (Gartner), published October 21, 1992.

Most preferably, the water-swellaable polymers comprise from about 50% to 95% (mol percentage), preferably about 75% neutralized, (slightly) polyacrylic acid [i.e., poly (sodium acrylate/acrylic acid)]. Crosslinking renders the polymer substantially water-insoluble and, in part, determines the absorptive capacity and extractable polymer content characteristics of the absorbent polymers. Processes for crosslinking these polymers and typical crosslinking agents are described in greater detail in U.S. Patent 4,076,663.

While the water-swellaable polymer is preferably of one type (i.e., homogeneous), mixtures of water-swellaable polymers can also be used herein. For example, mixtures of starch-acrylic acid graft copolymers and slightly network crosslinked polymers of polyacrylic acid can be used herein. Mixtures of (coated) polymers with different physical properties, and optionally also different chemical properties, could also be used, e.g. different mean particle size, absorbent capacity, absorbent speed, SFC value, such as for example disclosed in US 5,714,156 which is incorporated herein by reference.

The water-swellaable polymers herein preferably have, prior to coating, a Cylinder Centrifuge Retention Capacity (CCRC) of at least 30 g/g, preferably at least 40 g/g, more preferably at least 50 g/g, and further even more preferably of at least 80 g/g or even at least 100 g/g.

The water-swellaable polymers preferably have a low amount of extractables, preferably less than 15% (by weight of the polymers; 1 hour test value), more preferably less than 10% and most preferably less than 5% of extractables, or even less than 3%. The extractables and levels thereof and determination thereof is further described in for example US5,599,335; US5,562,646 or US5,669,894.

Coating agents and wet-extensible material thereof

The wet-extensible material and preferably the coating agent as a whole have a tensile stress at break in the wet state of at least 1 MPa, or even at least 3MPa and more preferably at least 5 MPa, or even at least 8 MPa. This can be determined by the Wet Tensile test method, (wherein a wet film of the wet-extensible material is submitted to specific conditions, in order to measure the

wet-elongation at break; the wet-extensible material is therefore thus a material that can be formed into a film, i.e. film-forming).

Also, the a wet-extensible material and preferably the coating agent as a whole, have preferably a wet-elongation at break of at least 400%, or more preferably at least 500%, as determined by the Wet elongation and Wet Tensile test method described herein below. Preferably, the coating agent and/ or the wet-extensible material thereof has a wet-elongation at break of at least 800%, or even at least 100% or even at least 1100% or even at least 1200%, or even at least 1600%.

It should be understood for the purpose of the invention that the coating formed from the wet-extensible material and the coating agent typically extend (in wet state) their surface area, without (substantially) expanding in volume by liquid (e.g. water; saline solution) absorption. The wet-extensible polymeric material and the coating agent are thus typically substantially non-water-swelling. Preferred may be that the wet-extensible material and or coating agent is non-water-swelling, as for example may be determined by the method set out herein below. The inventors have found that the coatings or films formed from materials that are substantially not swellable in water or saline solution have typically a higher wet elongation compared to materials that swell significantly in water or saline solution. This means in practice that the coating agent has preferably a water-swelling capacity of less than 1g/g, or even less than 0.5g/g, or even less than 0.2g/g or even less than 0.1g/g, as may be determined by the 'Method of determining water-swelling capacity of a polymeric material' as set out below.

The wet-extensible material is preferably an elastomeric polymer (an elastomeric polymer being a polymer that, when deformed by stress, partially or completely recovers its mechanical properties when the deformation stress is removed). It is believed that a coating of the elastomeric polymeric materials provide a return force when being extended and thus enable the coating (shell/ layer) to provide tangential forces around the water-swelling polymer, and thus will thereby act like the elastic membrane of a balloon and thus aid in providing a resistance to deformation for the water-swelling material of the invention.

Typically, the wet extensible materials and/ or the coating agent will have a secant wet elastic modulus at 400% elongation of less than 10 MPa.

Particularly preferred wet extensible materials/ coating agents herein can be formed into a film and have a wet secant elastic modulus at 400% elongation ($SM_{wet\ 400\%}$) of at least 0.25 MPa,

preferably at least about 0.50 MPa, more preferably at least about 0.75 or even at least 2.0 MPa, and most preferably of at least about 3.0 MPa.

Preferred wet-extensible materials herein have a ratio of [wet secant elastic modulus at 400% elongation ($SM_{\text{wet } 400\%}$)] to [dry secant elastic modulus at 400% elongation ($SM_{\text{dry } 400\%}$)] of 1.4 or less, preferably 1.2 or less, or even 1.0 or less, and it may be preferred that the ratio is at least 0.6 or even at least 0.7.

The coating agent is preferably such that the resulting coating on the water-swellaable polymers herein is water-permeable, but not water-soluble and, preferably not water-dispersible. The water permeability of the coating should be high enough such that the coated water-swellaable material has a sufficiently high free swell rate as defined herein, preferably a free swell rate (FSR) of at least 0.05 g/g/sec, preferably at least 0.1 g/g/sec, and more preferably at least 0.2 g/g/sec.

The coating formed of the coating agent is preferably breathable to some extent at least, so that moisture vapour can pass. Thereto, the coating agent or wet-extensible material thereof is such that a specific film thereof, with a specific caliper, as is described below in the MVTR test, is at least moderately breathable, having a Moisture Vapour Transmission rate (MVTR) of 800 to $\text{g/m}^2/\text{day}$, or even from 1200 $\text{g/m}^2/\text{day}$, to 1400 $\text{g/m}^2/\text{day}$, but preferably being breathable with a MVTR of at least 1500 $\text{g/m}^2/\text{day}$, up to 200 $\text{g/m}^2/\text{day}$ or even more preferably, the coating agent or material is highly breathable with a MVTR of 2100 $\text{g/m}^2/\text{day}$ or more.

Preferred coating agents herein include natural or synthetic elastomeric polymeric materials, preferably elastomeric polymeric materials selected from the group of natural rubber, synthetic rubber and thermoplastic elastomeric polymers that are elastic at 35°C.

Preferred is also that the wet-extensible material, or the coating agent as a whole, as a first glass transition temperature of 20°C or below, preferably of 0°C or below.

Preferred coating agents herein comprise polymers that form a film by any film forming method known in the art, e.g. when being applied (as a spray) from a solution, dispersion or as hotmelt, for example under the process conditions described below.

Further preferred are polymers that form elastomeric films that are wet extensible but that are not tacky or sticky in the dry state. Especially preferred are coating agents that are not tacky or sticky in the dry state but are sticky or tacky in the wet state.

The wet extensible polymers useful in coating agents herein are optionally polymers that can be self-crosslinking i.e. form covalent crosslinks in the polymer network to make it thermoset. Alternatively, crosslinking agents may be added to the polymers to cause crosslinking after activation, e.g. with high temperature, described hereinafter under the discussion of the annealing step c).

While it is generally preferred to apply the coating agents in such a way in the process that the wet-extensible polymers thereof have already been made by a polymerization reaction, this does not generally need to be the case and the coating agent may also be formed from precursor materials that are polymerizable and are polymerized during the process of making the coated water-swallowable particles (e.g. step b,) such as for example by interfacial polymerization on the surface of the water-swallowable polymers or by depositing the precursor polymerizable materials via Chemical Vapor Deposition (CVD) as it is known in the art and subsequently polymerizing them to form the wet-extensible material of the coating agent. It should be noted that surface crosslinking alone is not understood to be part of the invention since this will not lead to an additional polymer coating layer but rather form additional crosslinks in the already polymerized surface of the water-swallowable polymer.

In a preferred embodiment, the wet extensible polymers useful in coating agents herein may be reactive with the water-swallowable polymers, preferably thereto being a carboxylated wet-extensible polymeric (elastomeric) material.

Preferred wet-extensible materials herein are phase-separating, having at least two phases and at least a first glass transition temperature T_{g1} and a second glass transition temperature T_{g2} , the difference between T_{g1} and T_{g2} being at least 30°C. Phase-separation occurs due to the thermodynamic incompatibility of different units or segments in a block copolymer or incompatibility of the polymers used in a blend. Incompatible regions in a block copolymer separate to form domains that are comprised of aggregates of blocks of only one type of unit. Phase-separating polymers will exhibit two glass transition temperatures, T_g , that arise due to molecular motion of the polymer chains and are dependent on the test method and testing rate. Below the T_g , the polymer will be glassy and brittle, whereas above the T_g , molecular motion of the polymer chains can occur and the material is rubbery (see for example Thermoplastic

Elastomers: A Comprehensive Review, eds. Legge, N.R., Holden, G., Schroeder, H.E., 1987, Chapter 2).

The preferred wet extensible materials or coating agents described herein have a first T_g that is below room temperature, and a second T_g above room temperature. The T_g of a polymer can be routinely measured using differential scanning calorimetry, DSC, to measure the change in specific heat of the polymer relative to an inert reference material (eg. Indium), as described herein after.

When phase-separating polymer(s) are used in or as the coating agent, the optional annealing step is performed at temperatures at least 20° C above the highest T_g. If the polymer or polymer mixture is crystalline or semi-crystalline, the optional annealing step is performed above the highest T_g, preferably at least 20°C or more above the highest T_g, but in any event at least 20 °C below the melting temperature, T_m. To determine the appropriate annealing temperature, thermal analysis of the polymer transitions that occur with heating can be performed using a technique such as differential scanning calorimetry, DSC, as described herein.

It should be understood that, for the purpose of the invention, the wet-extensible material itself (i.e. before incorporation into the coating agent or before formation into the coating on the water-swallowable polymers) has the herein specified properties, but that typically, the wet-extensible material maintains these properties once in the coating agent and/ or in the coating, and that the resulting coating (or the coating agent, as tested in the form of a film) should thus preferably have the same properties.

Thus, the wet-extensible material may be a mixture of two or more different polymers that each have a different T_g and that form a phase-separating mixture.

Preferred phase-separating wet-extensible materials comprise a mixture of at least a (co)polymer selected of the following group A and a (co)polymer selected of the following group B:

A: poly ethylene (co) polymers, polypropylene (co) polymers, polybutylene (co) polymers, polyisoprene (co) polymers, polybutadiene (co)polymers, polyethylene-co-polypropylene, polyethylene-co-polybutylene, polyethylethylene-co-polypropylene, polyether (co) polymers, polyester (co) polymers; which all may optionally be grafted and/or be partially modified with chemical substituents (e.g. hydroxyl groups or carboxylates);

B: polyvinyl (co) polymers (e.g. styrene, vinylacetate, vinylformamide), polyurethanes (co) polymers, polyester (co) polymers, polyamide (co) polymers, polydimethylsiloxanes, proteins; which all may optionally be grafted and/or be partially modified with chemical substituents (e.g. hydroxyl groups or carboxylates).

More preferably, the wet-extensible comprises one or more phase-separating block copolymer (s), with each two or more Tg's, preferably having a weight average molecular weight Mw of at least 50 kDa, preferably at least 70 kDa.

Preferably, the wet-extensible material has one or more first (soft) phase(s) with a Tg₁ which is less than 25°C, preferably less than 20°C, more preferably less than 0°C, or even less than -20°C, and one or more second (hard) phase(s) with a Tg₂ of at least 50°C or even at least 55°C, but more preferably more than 60°C or even more than 70°C, or in certain embodiments, more than 100°C, provided the temperature difference between Tg₁ and Tg₂ is at least 30°C, preferably at least 50°C or even at least 60°C, or in certain embodiments at least 90°C.

Such a block copolymer has at least a first polymerized homopolymer segment (block) and at least a second polymerized homopolymer segment (block), polymerized with one another, whereby preferably the first (soft) segment has a Tg₁ of less than 25°C or even less than 20°C, or even less than 0°C, and the second (hard) segment has a Tg₂ of at least 50°C, or of 55°C or more, preferably 60°C or more or even 70°C or more.

The total weight average molecular weight of the hard second segments (with a Tg of at least 50°C), is preferably at least 28 kDa, or even at least 45 kDa.

The preferred weight average molecular weight of a first segment is at least 500 Da, preferably at least 1000 Da or even at least 2000 Da, but preferably less than 8000 Da, or even less than 5000 Da.

It may be preferred that the block copolymer comprises a mixture of different soft segments and/or a mixture of different hard segments, for example a mixture of different soft segments that each have a different Tg, but all less than 25°C or even less than 20°C, or even less than 0°C, or for example a mixture of hard segments, each having a different Tg, but all greater than 50°C.

The precise weight level (in the block copolymer) of the first segments that have a T_g of less than 25°C, or even less than 20°C or even less than 0°C, will depend on the required tensile strength of the resulting coating, e.g. by decreasing the weight level of the first segments in the block copolymer, the tensile strength may increase. However, when the weight percentage of the first segments is too low, the MVTR may be lower than desirable.

However, the total of the total of the first (soft) segments is typically 20% to 95% by weight of the total block copolymer, or even from 20% to 70% or more preferably from 30% to 60% or even from 30% to 40% by weight. Furthermore, when the total weight level of soft segments is more than 70%, it is even more preferred that an individual soft segment has a weight average molecular weight of less than 5000 Da.

The block copolymers useful herein are preferably block copolymers that have intermolecular H-bonding.

The block copolymers useful herein are preferably selected from: polyurethane (co) polyethers, polyurethane (co)polyesters, polyurethane/urea- co-polyethers or -co(poly) esters, polystyrene block copolymers, hydrogenated polystyrene block copolymers, polyester (co) polyethers, polyester (co)polyethers, polyamide- co-polyethers or -co(poly) esters, polyoxyethylene-co-polyepichlorohydrin.

Preferred are polyurethane-co- poly(ethyleneglycol), polyurethane-co- poly(tetramethylene glycol), and polyurethane-co- poly(propylene glycol) and mixtures thereof.

The polyurethane (hard) segments are preferably derived from a polymerisation reaction of a diisocyanate with a diol, such as for example butane diol, or cyclohexane diol, or preferably from a polymerisation reaction of an aromatic diisocyanate and an aliphatic diol such as ethylene glycol, butane diol, propane diol, or mixtures thereof.

A preferred diisocyanate used to form the polyurethane segments of the block copolymers herein is methylene bis (phenyl isocyanate).

The hard segments are then reacted with macrodiols to form the preferred phase-separating polyurethane block co-polymer.

Preferred may be that the elastomeric phase-separating material comprises a block copolymer with poly(tetramethylene glycol), or more preferably poly(ethylene glycol) segments (as first (soft) segments with a T_g of less than 20°C), because poly(ethylene glycol) provides a higher

breathability of the resulting coating. Also, the molecular weight percentage (by weight of the total block copolymer; as discussed above) of these first (soft) segments can be selected to provide the required breathability, e.g. a higher percentage of these segments will provide a more breathable coating.

Preferred block copolymers are Vector 4211, Vector 4111, Septon 2063, Septon 2007, Estane 58245, Estane 4988, Estane 4986, Estane T5410, Irogran PS370-201, Irogran VP 654/5, Pellethane 2103-70A, Elastollan LP 9109; Estane is a trade name of Noveon Inc., 9911 Brecksville Road, Cleveland, OH 44 141 – 3247, USA. Vector is a trade name of Dexco Polymers, 12012 Wickchester Lane, Houston, TX 77079, USA; Septon is a trade name of the Septon Company of America, A Kuraray Group Company, 11414 Choate Road, Pasadena, TX 77507, USA; Irogran is a trade name of Huntsman Polyurethanes, 52 Kendall Pond Road, Derry, NH 03038, USA; Pellethane is a trade name of the Dow Chemical Company, 2040 Dow Center, Midland, MI 48674, USA; and Elastollan is a trade name of BASF, 1609 Biddle Avenue, Wyandotte, MI 48192.

Another class of preferred materials useful in the coating agent herein are commercially available wet-extensible, elastomeric latex materials, such as for example from the Hystretch, Vinamul, Dur-O-Set Elite, GenFlo and AcryGen series, in particular Hystretch V43, Hystretch V60, Hystretch V23, Vinamul 3301, Vinamul Dur-O-Set Elite Ultra, Vinamul Dur-O-Set Elite 21, Rovene 4151, Rovene 5550, GenFlo 3075, GenFlo 3088, GenFlo 3000, Suncryl CP-75, AcryGen DV242DX, AcryGen 1900 D.

Hystretch is a trade name of Noveon Inc., 9911 Brecksville Road, Cleveland, OH 44 141 – 3247, USA. Vinamul and Dur-O-Set Elite are trade names of Vinamul Polymers, De Asselen Kuil 20, 6161 RD Geleen, NL. Rovene is a trade name of Mallard Creek Polymers, 14 700 Mallard Creek Road, Charlotte, NC 28262, USA. GenFlo, AcryGen and Suncryl are trade names of Omnova Solutions Inc., 2990 Gilchrist Road, Akron, OH 44305 – 4418, USA.

Particularly preferred coating agents comprise Surface Hydrophilic Elastic Latexes (SHEL) as described for example in US 4,734,445; US 4,835,211, US 4,785,030; EP 0 799 258 B1 all of which are incorporated herein by reference. These particularly preferred SHEL materials typically comprise: (1) a liquid phase selected from the group consisting of water, water-miscible solvents and mixtures thereof; and (2) an effective amount of latex particles dispersed in the liquid phase. These particles comprise an elastomeric hydrophobic core and an outer hydrophilic shell integral with the elastomeric core. The hydrophilic shell of the particles ultimately translates into

the hydrophilic surface of films formed there from, and also advantageously stabilizes the particles as colloids in the liquid phase. The shell comprises hydrophilic moieties -X which are attached to the core via linking group L-. When the liquid phase is removed, the particles form an elastomeric film having a substantially permanent hydrophilic surface. The SHEL compositions have the desirable property of forming elastomeric films having a hydrophilic surface and surface hydrophilicity, combined with other properties such as flexibility, elasticity and strength.

Also mixtures of wet-extensible materials may be present in the coating agent.

In addition to the wet-extensible material, the coating agent may also comprise other components.

Preferred polymeric elastomeric materials for use in the coating agent herein are strain hardening and/ or strain crystallizing. Strain Hardening occurs after the rubbery plateau and is the rapid increase in stress with increasing strain. Strain hardening can introduce orientation in the film producing greater resistance to extension in the direction of drawing.

While there are some elastomeric polymers that are strain crystallizing, this property can also be imparted by the addition or blending of materials into the polymer. Hereto, the coating agent may comprise additional components that increase the strain hardening and/ or strain crystallization of the wet-extensible material, such as organic or inorganic fillers. Nonlimiting examples of inorganic fillers include various water-insoluble salts, and other (preferably nanoparticulate) materials such as for example chemically modified silica, also called active or semi-active silica that are for example available as fillers for synthetic rubbers. Examples for such fillers are UltraSil VN3, UltraSil VN3P, UltraSil VN2P, and UltraSil 7000GR available from Degussa AG, Weißfrauenstraße 9, D-60287 Frankfurt am Main, Germany.

Preferred fillers are organic or inorganic compounds which are useful as flow agents in the processes described herein, and which typically reduce the stickiness of the coated water-swallowable materials or the water-swallowable polymers to be coated. Examples of such flow aids are semi-active or hydrophobic silica, urea formaldehyde, (sodium) silicate, diatomaceous earth, clays.

The coating agent and/ or the wet-extensible material is preferably hydrophilic and in particular surface hydrophilic. The surface hydrophilicity may be determined by methods known to those skilled in the art. In a preferred execution, the hydrophilic coating agents or wet-extensible materials are materials that are wetted by the liquid that is to be absorbed (0.9% saline; urine). They may be characterized by a contact angle that is less than 90 degrees. Contact angles can for

example be measured with the Video-based contact angle measurement device, Krüss G10 - G1041, available from Krüss, Germany or by other methods known in the art.

It may also be preferred that the resulting water-swellaable material is hydrophilic. The hydrophilicity of water-swellaable materials may be measured as described in co-pending application EP03014926.4

If the wet-extensible material or the coating agent itself is not hydrophilic, it can be made hydrophilic for example by treating it with surfactants, plasma coating, plasma polymerization, or other hydrophilic surface treatments as known to those skilled in the art.

Preferred compounds to be added to make the hydrophilic coating agent, or subsequently added to the resulting coated water-swellaable polymers are for example: N-(2-Acetamido)-2-aminoethansulfonic acid, N-(2-Acetamido)-imino-diacetic acid, N-acetyl-glycine, β -Alanine, Aluminum-hydroxy-acetate, N-Amidino-glycine, 2-Amino-ethyl-hydrogenphosphate, 2-Amino-ethyl-hydrogen sulfate, Amino-methansulfonic acid, Maleinic acid, Arginine, Asparaginic acid, Butane-diacid, Bis(1-aminoguanidinium) sulfate, 2-Oxo-propionic acid, Tri-Calcium dicitrate, Calcium gluconate, Calcium saccharate, Calcium-Titriplex®, Carnitin, Cellobiose, Citrullin, Creatin, Dimethylaminoacetic acid, THAM-1,2-disulfonic-acid, Ethylendiammonium sulfate, Fructose, Fumaric acid, Galactose, Glucosamine, Gluconic acid, Glutamine, 2-Amino-glutaric acid, Glutaric acid, Glycine, Glycylglycin, Imino-diacetic acid, Magnesium glycerophosphate, Oxalic acid, Tetrahydroxy-adipinic acid, Taurin, N-Methyl-aurin, N-Tris-(hydroxymethyl)-aminomethane, N-(Tris-(hydroxymethyl)-methyl)-2-aminoethansulfonicacid.

Alternatively, the coating agent can be made hydrophilic with a hydrophilicity boosting composition comprising a hydrophilicity-boosting amount of nanoparticles. By hydrophilicity boosting amount, it is intended that an amount of nanoparticles be present in the hydrophilicity boosting compositions, which are sufficient to make a substrate to which it is applied more hydrophilic. Such amounts are readily ascertained by one of ordinary skill in the art; it is based on many factors, including but not limited to, the substrate used, the nanoparticles used, the desired hydrophilicity of the resulting water-swellaable material.

Nanoparticles are particles that have a primary particle size, that is diameter, which is in the order of magnitude of nanometers. That is, nanoparticles have a particle size ranging from about 1 to about 750 nanometers. Nanoparticles with particle sizes ranging from about 2 nm to about 750 nm can be economically produced. Non-limiting examples of particle size distributions of the nanoparticles are those that fall within the range from about 2 nm to less than about 750 nm, alternatively from about 2 nm to less than about 200 nm, and alternatively from about 2 nm to less than about 150 nm.

The particle size of the nanoparticles is the largest diameter of a nanoparticle and may be measured by any methods known to those skilled in the art.

The mean particle size of various types of nanoparticles may differ from the individual particle size of the nanoparticles particles. For example, a layered synthetic silicate can have a mean particle size of about 25 nanometers while its particle size distribution can generally vary between about 10 nm to about 40 nm. (It should be understood that the particle sizes that are described herein are for particles when they are dispersed in an aqueous medium and the mean particle size is based on the mean of the particle number distribution. Non-limiting examples of nanoparticles can include crystalline or amorphous particles with a particle size from about 2 to about 750 nanometers. Boehmite alumina can have an average particle size distribution from 2 to 750 nm.

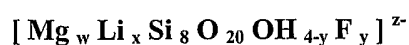
The hydrophilicity boosting composition may consist of the nanoparticles, and then the nanoparticles are directly added to the surface-treatment agent or to the process, e.g. in step b).

Alternatively, the nanoparticles are present in a composition with other carrier ingredients, e.g. solvents or dispersant liquids; in one preferred embodiment the nanoparticles are applied in step b) as a dispersion in a liquid. If the hydrophilicity boosting composition does not consist of the nanoparticles, but comprises other ingredients, then it is preferred that the nanoparticles are present in the hydrophilicity boosting compositions at levels of from about 0.0001% to about 50%, preferably from about 0.001% to about 20 % or even to 15%, and more preferably from about 0.001% to about 10%, by weight of the composition.

Either organic or inorganic nanoparticles may be used in the hydrophilicity boosting composition; inorganic nanoparticles are preferred. Inorganic nanoparticles generally exist as oxides, silicates, carbonates and hydroxides. Some layered clay minerals and inorganic metal oxides can be examples of nanoparticles. The layered clay minerals suitable for use herein include those in the geological classes of the smectites, the kaolins, the illites, the chlorites, the attapulgites and the mixed layer clays. Typical examples of specific clays belonging to these classes are the smectites, kaolins, illites, chlorites, attapulgites and mixed layer clays. Smectites, for example, include montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite. Kaolins include kaolinite, dickite, nacrite, antigorite, anauxite, halloysite, indellite and chrysotile. Illites include bravaisite, muscovite, paragonite, phlogopite and biotite, and vermiculite. Chlorites include corrensite, penninite, donbassite, sudoite, pennine and clinocllore. Attapulgites include sepiolite and polygorskite. Mixed layer clays include alleverdite and vermiculitebiotite. Variants and isomorphic substitutions of these layered clay minerals offer unique applications.

Layered clay minerals may be either naturally occurring or synthetic. An example of one non-limiting embodiment of the coating composition uses natural or synthetic hectorites, montmorillonites and bentonites. Another embodiment uses the hectorites clays commercially available, and typical sources of commercial hectorites are the LAPONITES™ from Southern Clay Products, Inc., U.S.A; Veegum Pro and Veegum F from R. T. Vanderbilt, U.S.A.; and the Barasyls, Macaloids and Propaloids from Baroid Division, National Read Comp., U.S.A.

In one preferred embodiment herein the nanoparticles comprise a synthetic hectorite a lithium magnesium silicate. One such suitable lithium magnesium silicate is LAPONITE™, which has the formula:



wherein $w = 3$ to 6 , $x = 0$ to 3 , $y = 0$ to 4 , $z = 12 - 2w - x$, and the overall negative lattice charge is balanced by counter-ions; and wherein the counter-ions are selected from the group consisting of selected Na^+ , K^+ , NH_4^+ , Cs^+ , Li^+ , Mg^{++} , Ca^{++} , Ba^{++} , $\text{N}(\text{CH}_3)_4^+$ and mixtures thereof. (If the LAPONITE™ is “modified” with a cationic organic compound, then the “counter-ion” could be viewed as being any cationic organic group ®.)

Other suitable synthetic hectorites include, but are not limited to isomorphous substitutions of LAPONITE™, such as, LAPONITE B™, LAPONITE S™, LAPONITE XLS™, LAPONITE RD™, LAPONITE XLG™, and LAPONITE RDS™.

The nanoparticles may also be other inorganic materials, including inorganic oxides such as, but not limited to, titanium oxide silica, zirconium oxide, aluminum oxide, magnesium oxide and combinations thereof. Other suitable inorganic oxides include various other inorganic oxides of alumina and silica.

In one preferred embodiment herein the nanoparticles comprise a Boehmite alumina ($[\text{Al}(\text{O})(\text{OH})]_n$) which is a water dispersible, inorganic metal oxide that can be prepared to have a variety of particle sizes or range of particle sizes, including a mean particle size distribution from about 2 nm to less than or equal to about 750 nm. For example, a boehmite alumina nanoparticle with a mean particle size distribution of around 25 nm under the trade name Disperal P2™ and a nanoparticle with a mean particle size distribution of around 140 nm under the trade name of Dispal® 14N4-25 are available from North American Sasol, Inc.

In one preferred embodiment herein the nanoparticles are selected from the group consisting of titanium dioxide, Boehmite alumina, sodium magnesium lithium fluorosilicates and combinations thereof.

Use of mixtures of nanoparticles in the hydrophilicity boosting compositions is also within the scope herein.

Optionally, in addition to or in place of water, the carrier can comprise a low molecular weight organic solvent. Preferably, the solvent is highly soluble in water, e.g., ethanol, methanol, acetone, methyl ethylene ketone, dimethylformamide, ethylene glycol, propanol, isopropanol, and the like, and mixtures thereof. Low molecular weight alcohols can reduce the surface tension of the nanoparticle dispersion to improve wettability of the substrate. This is particularly helpful when the substrate is hydrophobic. Low molecular weight alcohols can also help the treated substrate to dry faster. The optional water-soluble low molecular weight solvent can be used at any suitable level. The carrier can comprise any suitable amount of the composition, including but not limited to from about 10% to about 99%, alternatively from about 30% to about 95%, by weight of the coating composition.

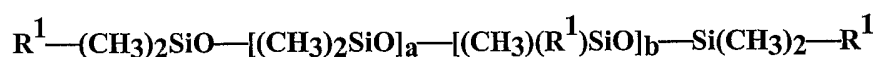
The hydrophilicity boosting composition may also comprise organic, e.g. latex nanoparticles, so-called nanolatexes. A "nanolatex", as used herein, is a latex with particle sizes less than or equal to about 750 nm. A "latex" is a dispersion of water-insoluble polymer particles that are usually spherical in shape. Nanolatexes may be formed by emulsion polymerization. "Emulsion polymerization" is a process in which monomers of the latex are dispersed in water using a surfactant to form a stable emulsion followed by polymerization. Particles are typically produced which can range in size from about 2 to about 600 nm. When the nanolatexes are wet-extensible material, e.g. film-forming elastomeric polymers, then they are considered coating agents for the purpose of the invention, and not (part of) a hydrophilicity boosting composition.

Surfactants are especially useful as additional ingredient of the coating agent herein, or as additional ingredients in the process step a) or b) herein, e.g. as wetting agents to facilitate the dispersion of the coating agent onto the substrate. Surfactants are preferably included when the coating composition is used to treat a hydrophobic substrate.

Suitable surfactants can be selected from the group including anionic surfactants, cationic surfactants, nonionic surfactants, amphoteric surfactants, ampholytic surfactants, zwitterionic surfactants and mixtures thereof. Nonlimiting examples of surfactants useful in the compositions herein are disclosed in McCutcheon's, Detergents and Emulsifiers, North American edition (1986), published by Allured Publishing Corporation; McCutcheon's, Functional Materials, North American Edition (1992); U.S. Pat. Nos. 5,707,950 and 5,576,282; and U. S. Patent No. 3,929,678, to Laughlin et al., issued December 30, 1975.

When a surfactant is used in the coating composition, it may be added at an effective amount to provide or facilitate application of the coating composition. Surfactant, when present, is typically employed in compositions at levels of from about 0.0001% to about 60%, preferably from about 0.001% to about 35 %, and more preferably from about 0.001% to about 25%, by weight of the composition.

Nonlimiting examples of surfactants, including preferred nonionic surfactants, useful herein typically at levels from about 0.001% to about 60%, by weight, include nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like. Another class of useful surfactants are silicone surfactants and/or silicones. They can be used alone and/or alternatively in combination with the alkyl ethoxylate surfactants described herein. Nonlimiting examples of silicone surfactants are the polyalkylene oxide polysiloxanes having a dimethyl polysiloxane hydrophobic moiety and one or more hydrophilic polyalkylene side chains, and having the general formula:



wherein $a + b$ are from about 1 to about 50, and each R^1 is the same or different and is selected from the group consisting of methyl and a poly(ethyleneoxide/propyleneoxide) copolymer group having the general formula: $-(CH_2)_n O(C_2 H_4 O)_c (C_3 H_6 O)_d R^2$, wherein n is 3 or 4; total c (for all polyalkyleneoxy side groups) has a value of from 1 to about 100, alternatively from about 6 to about 100; total d is from 0 to about 14; alternatively d is 0; total $c+d$ has a value of from about 5 to about 150, alternatively from about 9 to about 100 and each R^2 is the same or different and is selected from the group consisting of hydrogen, an alkyl having 1 to 4 carbon atoms, and an acetyl group, alternatively hydrogen and methyl group. Each polyalkylene oxide polysiloxane has at least one R^1 group being a poly(ethyleneoxide/propyleneoxide) copolymer group. Silicone superwetting agents are available from Dow Corning as silicone glycol copolymers (e.g. Q2-5211 and Q2-5212).

It is also within the scope of the present invention to use a mixture of surfactants.

The coating agent is preferably applied in fluid form, e.g. as melt (or so-called hotmelt), solution or dispersion. Preferred are water-based solutions or dispersions. In the context of this invention and as it is typically used in the art, the latexes referred herein are thus typically applied as water based dispersions of specific latex polymers, whereby the polymeric latex particles – typically of spherical shape – are suspended or dispersed (stable) in a water based liquid.

Thus, the coating agent may also comprise a solvent or dispersing liquid, such as water, THF (tetrahydrofuran), methylethyl ketone, dimethylformamide, toluene, dichloromethane, cyclohexane or other solvents or dispersing liquids that are able to dissolve or disperse the wet-extensible material (e.g. elastomeric polymer) and subsequently can be evaporated such as to form a (dry) coating shell or layer.

As it is known to those skilled in the art, in particular for latex dispersions with lower amounts of the polymer in the water dispersion, the viscosity is decreased, which enables good spreading of the coating agent. On the other hand, it is preferred to have higher amounts of polymer in the water dispersion to aid film quality and coalescence, and to minimize the amount of liquid that needs to be dried-off or evaporated. Thus, the skilled person would know how to select a high enough, but not too low concentration to obtain the desired coating.

Preferably, the coating agent comprises from 0% to 95% by weight of a dispersing liquid or solvent, such as water. Preferred is that the coating agent comprises at least 10% by weight (of the coating agent) of the wet-extensible material, more preferably from 20% to 80% or even from 30% to 70%, the remaining percentage being said liquid and/ or fillers/ or hydrophilicity aids, spreading aids etc, as described herein.

In addition to providing the right mechanical properties in the wet state as it is outlined above, preferred coating agents of the invention preferably also have other desired properties such as high resistance against mechanical abrasion in order to survive processing into absorbent articles or structures, without significant deterioration of their properties. They also are preferably colorless or white and opaque and may in addition contain other materials such for example to control odor, release perfumes, and the like.

Process of the invention for making the solid water-swellaable material

The process of the invention comprising the steps of:

- a) obtaining water-swellaable polymers; and
 - b) simultaneously or subsequently to step a), applying a coating agent to at least part of said water-swellaable polymers, whereby said coating agent is as defined herein; and in one embodiment, the step of:
 - c) annealing and/ or curing the resulting coated water-swellaable polymers of step b);
- to obtain the water-swellaable material herein.

In step a) 'obtaining' the water-swellaable polymers, as described herein above, includes using commercially available water-swellaable polymers, or forming the water-swellaable polymers by any known process from precursors. It includes also for example the possibility that step a) and b) are done simultaneously and that step a) involves reacting the relevant polymer precursors to form the water-swellaable polymer in the same reaction conditions/ medium as the coating step b): for example, the polymer precursors and coating agent can be mixed together. It should be noted

that optional process steps may take place prior to, or simultaneous with step a) and/ or b), such as that the water-swellaable polymer may be surface crosslinked prior to step b), or that the coating agent or water-swellaable polymers may be submitted to a hydrophilic treatment, to render them more hydrophilic, prior to step b).

In general, the step a) involves obtaining the water-swellaable polymers in solid form, e.g. in particulate form.

The coating step b) may be done by any known method, for example by mixing or dispersing the water-swellaable polymers (or precursors thereto) in the coating agent, or melt or solution or dispersion thereof; by spraying the coating agent, or (hot) melt, solution or dispersion thereof onto the polymers; by introducing the coating agent, or melt, dispersion or solution thereof, and the water-swellaable polymers (or precursors thereto) in a fluidised bed or Wurster coater; by agglomerating the coating agent, or melt, solution or dispersion thereof, and the water-swellaable polymers (or precursors thereof); by dip-coating the (particulate) water-swellaable polymers in the coating agent, melt, dispersion or solution thereof. Other suitable mixers include for example twin drum mixers, so called "Zig-Zag" mixers, plough-share mixers, such as Lödige mixers, cone screw mixers, or perpendicularly cylindrical mixers having coaxially rotating blades. Examples of preferred coating processes are for example described in US5,840,329 and US6,387,495.

In an alternative embodiment of the invention, the coating step b) may be done by applying the coating agent in the form of a foam, preferably in the form of an open-cell foam, leading to a porous coating. In yet an alternative embodiment the coating step may be done by forming a fibrous network on the surface of the water-swellaable material such as for example by applying the coating agent in the form of meltblown microfibers, such that an essentially connected coating is formed (as described herein).

To apply the coating agent, it may also comprise solvents such as water and/ or organic, optionally water-miscible, solvents. Suitable organic solvents are, for example, aliphatic and aromatic hydrocarbons, alcohols, ethers, esters, amides and ketones. Suitable water-miscible solvents are, for example, aliphatic alcohols, polyhydric alcohols, ethers, amides and ketones.

If the coating agent is in the form of a (commercially available) latex dispersion, it may be further preferred to add processing aids (such for example coalescing aids) subsequently or prior to the coating step b), e.g. in order to aid a good film formation of the coating layer.

The inventors found that in certain embodiments, a subsequent heat treatment, resulting in annealing and/ or curing of the coating agent, may be important in order to impart high extensibility in the wet state. While some wet extensible materials may already have high wet elongation per se, (e.g. after a film is formed, for example from a dispersion, optionally followed by drying at medium temperatures that are high enough to cause the material to coalesce as known to those skilled in the art, and as is further explained for example in: Paul A. Steward et. al., *Advances in Colloid and Interface Science* 86 (2000) 195-267 "Literature Review of polymer latex film formation and properties"), it may be useful to applying a annealing and/ or a curing step (both heat treatment steps).

Without wishing to be bound by any theory, it is believed, that in particular for latex materials that are strongly hydrophilic, and/or that have hydrophilic shells that are formed around the (typically spherical) polymer particles, the additional temperature treatment annealing step is beneficial since it enables a more efficient interparticle chain diffusion of polymer chains leading to entanglement of the chains and thus to a "blurring" of the particle boundaries. It is believed that the heat treatment annealing step increases the degree of chain interdiffusion and enhances film strength. It may reinforce the wet strength of films if it breaks the hydrophilic cell walls thus promoting interparticle chain diffusion (see for example M. Joanicot, et. al., *Macromolecules* 1996, 29, 4976 – 4984 "Interdiffusion in latex films").

The additional step c) of annealing and/ or curing the coated water-swellaable polymers may be done by methods known in the art. The annealing step c) typically involves a step (typically heat treatment) resulting in a further strengthened or more continuous or more completely connected coating; curing typically involves invoking chemical reactions within the coating, e.g. invoking cross-linking of the polymers in the coating. Annealing and curing are phenomena known to the skilled person and the skilled person would know how to select annealing and/ or curing temperatures that are appropriate for the coating agent used. For example, the annealing temperature of a coating formed from a curable latex emulsion will be selected to be below temperatures where curing occurs, e.g. below a temperature whereby cross-linking occurs.

In any event, the skilled person would select the annealing or curing temperatures such that no decomposition of the coating will occur.

The annealing and/ or curing step may be a single heat treatment step whereby both annealing and curing takes place.

Alternatively, either an annealing (e.g. heat treatment) step or a curing (e.g. heat treatment) step may take place, or alternatively, an annealing step and a curing step may both take place as separate process steps. In the latter case, it is preferred that first annealing takes place and then curing.

In a first embodiment, the annealing and/ or curing step may be done at a temperature of at least 50°C, or even at least 70°C, or even at least 100°C, or even at least 120°C or even at least 130°C or even at least 140°C, and preferably for at least 15 minutes, or even at least 30 minutes or even at least 1 hour or even at least 2 hours.

In a preferred embodiment, the wet-extensible material or coating agent is semi-crystalline or crystalline and has a specific melting temperature T_m , and then the optional annealing step is done at a temperature below the T_m , preferably at least 20°C below the T_m .

In another preferred embodiment, the wet-extensible material or coating agent is phase separating has two or more T_g 's, as described herein. Then, an annealing step is typically done by subjecting the coated water-swellaable polymers to a temperature above the highest T_g (but below the polymer's melting temperature and the polymer's decomposition temperature) and such temperatures can be determined by thermal analysis techniques known in the art, as described herein.

Typically, the temperature difference between two T_g 's is at least 30°C and the annealing temperature is at least 20°C or even at least 50°C above the highest temperature, provided it is below the T_m .

For example, the annealing heat treatment involves heating the coated water-swellaable polymers at a temperature of at least 70°C, or even at least 100°C, or even at least 120°C or even at least 130°C up to 200°C or even up to 250°C or even up to 300°C. For example, the annealing step may be done for at least 5 minutes, or even for at least 10 minutes or even for at least 15 minutes, or even at least 30 minutes or even at least 1 hour or even at least 2 hours.

The (annealed) coating may optionally be cured, for example to (further) introduce covalent cross-links and to further increase the wet-extensibility.

Preferred curing temperatures will depend on the coating agent or wet-extensible material used, and preferred curing temperatures are typically higher than annealing temperatures. For example, it may be preferred that the curing step involves subjecting the coated water-swellaable polymers to a temperature of at least 140°C, or even at least 160°C, for at least 10 minutes, at least 30 minutes or even at least 1 hour or even at least 2 hours, to invoke curing, e.g. chemical reactions, such as further polymerising or cross-linking the wet-extensible polymers of the coating agent.

As said above, the annealing step and/ or curing step involves typically a heat treatment of the resulting coated water-swellaable polymers of step b); it may be done by for example radiation heating, oven heating, convection heating; azeotropic heating; (optionally, also involving placing the coated polymers under vacuum); and it may for example take place in conventional equipment used for drying, such as fluidized bed driers.

Preferred may be that a vacuum is applied as well or that the annealing is done under an inert gas (to avoid oxidation).

During the curing and/ or annealing step, the coated water-swellaable polymers may also be dried at the same time. However, as described below, in a preferred embodiment, the coated water-swellaable polymers are submitted to a separate drying step, which may involve any of the treatments described above as annealing/ curing treatment, but typically for a time period which is longer than the annealing time.

Typically, when the coating agent is applied in the form of a (water-based) latex dispersion or solution, such an annealing or curing step that is also a drying step has two main effects that are desired. Firstly, since the majority of the present liquid (e.g. water) will be removed from the coated water-swellaable polymers through the coating layer during the drying or curing/ annealing step, the coating will become water permeable, e.g. by forming "pores" in the coating, which is useful for future absorption of liquid (urine) in use. Secondly, the coating itself coalesces to form a wet-extensible, preferably elastic film. Typically, the temperature and time are adjusted in order to allow good coating (film) formation and good coalescence such as to form mechanically strong coatings (films). The drying time is preferably long, e.g. more than 2 hours, typically more than 4 hours, preferably up to 48 hours, so that the coating agent can coalesce completely (for example so that the latex 'particles' of the coating are deformed in order to form a solid coating film).

Preferably, when the coating agent is a film-forming agent or comprises a film forming wet-extensible material, the annealing and/ or curing temperature is also typically above the minimum film forming temperature (MFFT) of the coating agent or material thereof.

The resulting water-swellaable material is preferably solid and thus, if the water-swellaable polymers of step a) or the resulting coated polymers of step b) are not solid, a subsequent process step is required to solidify the resulting coated polymers of step b), e.g. a so-called solidifying or preferably particle forming step, as known in the art. This may preferably be done prior to, or simultaneously with step c).

The solidifying step includes for example drying the water-swellaable polymers and/ or the coated polymers of step b) (e.g. if the step b) involves a dispersion, suspension or solution of any of the ingredients) by increasing the temperature and/ or applying a vacuum, as described herein. The solidifying step may also include a cooling step, if for example a melt is used.

Subsequently, any known particle forming process may also be used here for, including agglomeration, extrusion, grinding and optionally followed by sieving to obtain the required particle size distribution.

The inventors found another preferred way to provide wet-extensible coatings on cores of water-swellaable polymers, namely by providing a coating that has a significantly larger surface area than the outer surface area of the water-swellaable polymer (core), so that when the polymers swell, the coating can 'unfold' and extend. The inventors found a very easy and convenient way to provide such coated water-swellaable polymers, namely by applying the coating agent on water-swellaable polymers, which are in swollen state due to absorption of a liquid (e.g. water), and then removing the liquid or part thereof, so that, the inventors believe, the water-swellaable polymers (in the core) shrink again, but the coating maintains its original surface area. The surface area of the coating is then larger than the surface area of the polymer core, and the coating is then typically wrinkled; it can unwrinkle when the water-swellaable polymers absorb water and swell, without encountering any strain/ stress on the coating due to the swelling of the water-swellaable polymers. Thus, the coating agent is wet-extensible, without much exposure to strain or stress and without the risk of rupturing.

A highly preferred process thus involves the step of obtaining water-swellaable polymers (particles) and immersing these in a dispersion or solution of a wet-extensible material in a liquid (water), typically under thorough stirring. The water-swellaable polymers will absorb the liquid, and thereby, the wet-extensible material is automatically 'transferred' to the surface of water-

swellable polymers (particles). The amount of water-swellable polymers and amount of water and wet-extensible material can be adjusted such that the water-swellable polymers can absorb about all water present in the dispersion and that when this is achieved, the water-swellable polymers, coated with the latex, are in the form of a gel "particles". The resulting coating is typically under zero strain/ stress.

The process may also involve addition of further processing aids in any of the steps, such as granulation aids, flow aids, drying aids. For some type of coating agents, the coated water-swellable polymers may potentially form agglomerates. Any flow aids known in the art may be added (for example prior to or during the coating step, or preferably during the drying and/ or annealing and/ or cross-linking step (s), as discussed below), for example Aerosil 200, available from Degussa has been found to be a good flow aid.

Highly preferred may be that the process involves addition of a spreading aid and/ or surfactant, as described above, which facilitates the coating step b).

If the coating agent is in the form of a latex dispersion, the choice of additional spreading aids or surfactants is dictated by the desired stability of the dispersion. If for example the dispersion contains also anionic emulsifiers, then an anionic surfactant may be used as a spreading aid without negatively impacting the stability of the latex dispersion.

Alternatively, it may be desired to use a cationic surfactant subsequently to precipitate the polymer in the latex dispersion on the surface of the water-swellable polymer. Preferred spreading aids are those that when added to the latex dispersion will provide a low contact angle of the latex dispersion on an already dried latex film. The specific choices of spreading agent/ surfactants will be readily recognizable by those skilled in the art, and they include those described herein above.

Use

The water-swellable materials of the invention are useful in a number of applications, including in absorbent structures such as disposable absorbent articles, such as preferably interlabial products, sanitary napkins, panty liners, and preferably adult incontinent products, baby diapers, nappies and training pants. However, the present invention does not relate to such absorbent structures listed herein.

Process examples and materials made by the process

Preparation of water-swellaable polymers that are especially useful for use in process step a) of the invention.

Example 1.1: Process for preparation of spherical water-swellaable polymer particles:

Spherical core polymer particles may be obtained UMSICHT (Fraunhofer Institut Umwelt, Sicherheits-, Energietechnik, Oberhausen, Germany), or made by following the adapted procedure below:

40 g glacial acrylic acid (AA) is placed into a beaker, and 1712 mg MethyleneBisAcrylAmide (MBAA) is dissolved in the acid. Separately, 13.224 g solid NaOH is dissolved in 58.228 g water and cooled. The NaOH solution is then slowly added to the acrylic acid, and the resulting solution is chilled to 4-10°C.

In a second beaker, 400 mg ammonium peroxodisulfate (APS) and 400 mg sodium metabisulfite are mixed and dissolved in 99.2 ml water. This solution is also chilled to 4-10°C.

With the use of two equal peristaltic pumps, both solutions are combined and pumped at equal rates through a short static mixer unit, after which they are dropped as individual droplets into 60 – 80°C hot silicone oil (Roth M 50, cat. # 4212.2) which is in a heated, about 2 m long, glass tube. The pump rate is adjusted such that individual droplets sink through the oil in the tube, while also avoiding premature polymerization in the mixer unit. The polymerization proceeds during the descent of the droplets through the oil, and particles (gelled polymer droplets) are formed, which can be collected in a heated 1 l Erlenmeyer flask attached to the bottom of the tube.

After completion of the addition, the oil is allowed to cool, and the spheres are collected by draining the oil. Excess oil is removed by washing with i-propanol, and the particles (spheres) are pre-dried by exposing them to excess i-propanol for 12 – 24 hours. Additional washings with i-propanol may be needed to remove traces of the silicone oil. The particles (spheres) are then dried in a vacuum oven at 60 – 100°C until a constant weight is obtained.

The amount of MBAA may be adjusted, depending on what properties are required from the resulting polymers, e.g. when 0.3mol % (per mol AA) MBAA is used, the resulting water-swellaable polymer particles have a CCRC of about 50g/g (absorption of 0.9% saline solution, as determined by methods known in the art and described herein); when 1.0mol % (per mol AA) MBAA is used, the resulting water-swellaable polymer particles have a CCRC of about 19g/g; when 2.0 mol % (per mol AA) MBAA is used, the resulting water-swellaable polymer particles have a CCRC of about 9 g/g.

All compounds were obtained by Aldrich Chemicals, and used without further purification.

Example 1.2: Process for the preparation of water-swellaable polymers useful herein:

To 300 g of glacial acrylic acid (AA), an appropriate amount of the core crosslinker (e.g. MethyleneBisAcrylAmide, MBAA) is added (see above) and allowed to dissolve at ambient temperature. A 2500 ml resin kettle (equipped with a four-necked glass cover closed with septa, suited for the introduction of a thermometer, syringe needles, and optionally a mechanical stirrer) is charged with this acrylic acid / crosslinker solution. Typically, a magnetic stirrer, capable of mixing the whole content, is added. An amount of water is calculated so that the total weight of all ingredients for the polymerization equals 1500 g (i.e. the concentration of AA is 20 w/w-%). 300 mg of the initiator ("V50" from Waco Chemicals) are dissolved in approx. 20 ml of this calculated amount of deionized water. Most of the water is added to the resin kettle, and the mixture is stirred until the monomer and water are well mixed. Then, the initiator solution is added together with any remaining water. The resin kettle is closed, and a pressure relief is provided e.g. by puncturing two syringe needles through the septa. The solution is then sparged vigorously with argon via a 80 cm injection needle while stirring at ~ 300 RPM. Stirring is discontinued after ~ 8 minutes, while argon sparging is continued. The solution typically starts to gel after 12 – 20 minutes total. At this point, persistent bubbles form on the surface of the gel, and the argon injection needle is raised above the surface of the gel. Purging with argon is continued at a lowered flow rate. The temperature is monitored, typically it raises from 20°C to 60 – 70°C within an hour. Once the temperature drops below 60°C, the kettle is transferred into a circulation oven and kept at 60°C for 15 – 18 hours.

After this time, the resin kettle is allowed to cool, and the resulting gel is removed into a flat glass dish. The gel is then broken or cut with scissors into small pieces (for example in pieces smaller than 2 mm max. dimension), and transferred into a 6 l glass beaker. The amount of NaOH (50%) needed to neutralize 75% of the acid groups of the polymer is diluted with DI water to 2.5 l, and added quickly to the gel. The gel is stirred until all the liquid is absorbed; then, it is covered and transferred into a 60°C oven and let equilibrate for 2 days.

After this time, the gel is allowed to cool, then divided up into 2 flat glass dishes, and transferred into a vacuum oven, where it is dried at 100°C under vacuum. Once the gel has reached a constant weight (usually 3 days), it is ground using a mechanical mill (e.g. IKA mill) and sieved to obtain water-swellaable polymer particles of the required particle size, e.g. 150 – 800 µm.

(At this point, key parameters of the water-swellaable polymer as used herein may be determined).

The amount of MBAA may be adjusted, depending on what properties are required from the resulting polymers, e.g. when 0.01mol % (per mol AA) MBAA is used, the resulting water-swellaable polymer particles have a CCRC of about 90g/g (absorption of 0.9% saline solution, as determined by methods known in the art and described herein); when 0.03mol % (per mol AA)

MBAA is used, the resulting water-swellaable polymer particles have a CCRC of about 73g/g; when 0.1 mol % (per mol AA) MBAA is used, the resulting water-swellaable polymer particles have a CCRC of about 56 g/g; when 2.0 mol % (per mol AA) MBAA is used, the resulting water-swellaable polymer particles have a CCRC of about 16g/g; when 5.0 mol % (per mol AA) MBAA is used, the resulting water-swellaable polymer particles have a CCRC of about 8 g/g.

(All compounds were obtained by Aldrich Chemicals, and used without purification.)

Example 1.3: Surface Cross-linking process step:

This example demonstrates surface crosslinking of water-swellaable polymers prior to subjecting them to the process step b) of the invention. A 150 ml glass beaker is equipped with a mechanical stirrer with a plastic blade, and charged with 4 g of a dry water-swellaable polymer in particulate form. The mechanical stirrer is selected in such a way that a good fluidization of the polymers can be obtained at 300 – 500 RPM. A 50 – 200 μ l syringe is charged with a 4% solution (w/w) of Denacol (= EthyleneGlycolDiGlycidylEther = EGDGE) in 1,2-propanediol; another 300 μ l syringe is charged with deionised water.

The water-swellaable polymers are fluidized in the beaker at 300RPM, and the surface cross-linking agent is added within 30 seconds. Mixing is continued for a total of three minutes. While stirring is continued, 300 μ l of water are then added within 3 – 5 seconds, and stirring is continued at 300 – 500 RPM for another 3 minutes. After this time, the mixture is transferred into a glass vial, sealed with aluminum foil, and is equilibrated for 1 hour. Then the vial is transferred to a 140°C oven, and kept at this temperature for 120 minutes. After this time, the vial is allowed to cool down, the contents are removed, and the surface cross-linked water-swellaable polymer is obtained. Any agglomerates may be carefully broken by gentle mechanical action. The resulting surface cross-linked water-swellaable polymer particles may then be sieved to the desired particle size.

The following examples show coating processes that are used to demonstrate the coatings step b) of the process of the invention.

Example 2.1: Process of providing coated water-swellaable materials by directly mixing them into a water based latex dispersion.

The following is a preferred process for making the water-swellaable material of the invention, involving swelling the water-swellaable polymers prior to, or simultaneously with the coating step. The amount of water-swellaable polymers to be coated, coating level and water needed to swell the water-swellaable polymers is chosen.

Then, the diluted dispersion of the coating agent or wet-extensible material is prepared, e.g. of the latex as described herein. This is done by mixing the commercial available coating agent or wet-extensible material and water (if required) under stirring, for example in a glass beaker using magnetic stirrers at about 300 rpm for about 5 minutes. At all times, care needs to be taken that no film is formed on the surface of the dispersion. Typically for latex dispersions, the dispersion contains at the most 70% by weight of wet-extensible polymer.

In order to monitor the coating process better, a staining color might be added to the dispersion, for example New Fuchsin Red.

Then, a mechanical stirrer with a double cross Teflon blade is used and the dispersion is stirred such that a vortex can be seen, the water-swellaable polymer (particles) are quickly added under continuous stirring. Once the water-swellaable polymers start absorbing the water from the dispersion (typically after about 15 seconds), the mixture will start to gel and the vortex will eventually disappear. Then, when about all of the free liquid has been absorbed, the stirring is stopped and the resulting coated water-swellaable polymers may be dried or post treated by any of the methods described herein.

Example 2.2: Process of providing coated water-swellaable materials by directly mixing:.

The following is a preferred process for making the water-swellaable material of the invention, which may involve swelling the water-swellaable polymers prior to, or simultaneously with the coating step.

The amount of water-swellaable polymers to be coated, coating level and water needed to swell the water-swellaable polymers is chosen.

Then, the solution of the coating agent or wet-extensible material is prepared, e.g. of the thermoplastic polymer as described herein. This is done by dissolving the commercial available coating agent or wet-extensible material in organic solvent (eg. THF or a mixture of water and THF), for example in a glass beaker for 1 hour to 24 hours.

In order to monitor the coating process better, a staining color might be added to the dispersion, for example New Fuchsin Red.

Then, the solution of polymer is added to the water-swellaable polymer that is being stirred or mechanically agitated to provide the coating. When the free liquid has been absorbed into the water-swellaable polymer, the stirring is stopped and the resulting coated water-swellaable polymers may be dried or post treated by any of the methods described herein.

Example 2.3: Process of providing individually coated water-swellaable materials

An alternative preferred coating process of the invention is as follows:

The (solid, particulate) water-swellaable polymers are placed on a surface that is preferably under an angle (30-45 degrees).

The coating agent, in the form of a dispersion, is applied in drops, e.g. by use of a pipette or by spraying, onto the polymers. Hereby, no air bubbles should be formed. Thus, a film is formed on the surface of the water-swellaable polymers.

These coated water-swellaable polymers are then dried, either at room temperature (20°C), or for example at 40°C / 80% humidity, for up to 2 days, or for example in an oven (if required, a vacuum oven) at a low temperature (up to 80°C).

The coated water-swellaable material can then be annealed or cured as described herein.

It may then also be formed into the desired form, e.g. particles.

Example 2.4: Alternative preferred coating process

In another preferred process, a dispersion of the water-swellaable polymers is prepared first and the coating agent is added thereto.

For example, 200 grams of a water-swellaable polymer (cross-linked polyacrylic acid based polymers, for example prepared by the method described above) is placed in a plastic beaker and n-heptane is added, until the heptane stands about 1 – 2 mm above the surface of the polymers in the beaker; this is typically about 100 g of n-heptane.

Using a household mixer (e.g. for whipping cream), the components are mixed at high speed. The coating agent, in the form of a water dispersion of a wet-extensible coating material, e.g. a latex dispersion as described above, is added to the beaker with the water-swellaable polymers by use of for example a pipette. The mixture is continuously stirred, avoiding the formation of lumps.

The resulting material can be spread out over a surface as a thin layer (e.g. less than 1cm) and allowed to air dry for at least 12 hours or in a (vacuum) oven (at any temperature up to about 70°C). The dried material may then additionally be annealed or cured.

After cooling or subsequent steps, the resulting material may be mechanically reduced or sieved to the desired particle sizes.

Example 2.5: Process of providing coated water-swellaable materials using a fluidized bed Wurster coater

Step b) may also be done in a fluidised bed or Wurster coater.

For example, a Lakso Wurster Model 101 (The Lakso Company, Leominster, MA) may be used, or a Glatt GPCG-3 granulator-coater may be used (supplied by Glatt Ingenieurtechnik GmbH,

Nordstrasse 12, 99427 Weimar, Germany). It may be desired that the coating equipment is pre-heated, for example to 70 °C, under air flow, for example for about 30 minutes.

For example, typically between 20 and 35 g of water-swellaable polymer is placed in the vessel.

The coating agent, preferably in fluid form, such as the polymer solutions/ dispersions listed below, is placed in a container on the stirring platform and stirred using a magnetic bar at low speed to prevent entrainment of air. The weight can be recorded.

The peristaltic pump is calibrated and then set to the desired flow rate (e.g. 5 g/minute) and the direction of flow of the coating agent is set forward. The desired inlet air flow and temperature are set to 50m³/hr and 60°C. Then, the 'atomising' air supply and pump are started. The outlet temperature of the system is maintained at 45°C by adjusting the solvent flow rate into the system.

(A higher speed may be used to advance the coating agent closer towards the inlet of the coater and then setting the correct speed for the experiment.)

The experiment is typically complete when stickiness prevents efficient fluidisation of the powder (between 10 and 60 minutes).

Then, the coating agent flow is stopped immediately and flow reversed. The weight of coating agent used in the experiment is recorded.

Optionally, the resulting coated water-swellaable polymers may be dried within the coater, which also may aid to reduce particle surface stickiness (drying time typically between 5 and 60 minutes).

Then, the material inside the coater is weighed.

In general, the material may be returned to the coating vessel to continue the process, if required, e.g. if more than one coating agent is to be applied or to add a flow aid, e.g. 0.5 – 2% hydrophobic silica.

In order to visualise the coating process, or for aesthetic purposes, a colouring agent or dye solution may be added to the coating agent, for example New Fuchsin Red (0.25g of New Fuchsin Red in 5 ml to 25ml deionised water (15 – 25°C), without entrainment of air bubbles). The dye solution can be added drop-wise to about 10ml of the coating agent under stirring and this can then be stirred into the remaining coating agent (sufficient for up to 70ml coating agent).

The following water-swellable materials were made by the process above, using a fluid bed coater or Wurster coater; in each case, 25 g of the uncoated water-swellable polymers, available as GV-A640 from Nippon Shokubai (lot 0019H 0000 ISA0331) was used and the specified amount of latex, at the specified weight-% solids concentration, was used.

After drying of the coated samples for 2 days at 35°C, each exemplified latex-coated material was cured in vacuum at 140°C for 2 hours.

Example:	Latex:	Latex concentration (% w/w):	Amount of Latex (% w/w)
1	Hystretch V43	12.5	16.7
2	Vinamul 3301	50	9.1
3	Vinamul Elite 21	50	9.1
4	Vinamul Elite 21	50	18.0
5	Vinamul Elite 21	25	10.7
6	Vinamul Elite 21	12.5	15.3
7	Vinamul Elite 21	25	10.7
8	Vinamul Elite 21	50	12.3
9	Rovene 4151	12.5	10.7
10	Rovene 4151	25	7.4
11	GenFlo 3075	50	9.1
12	GenFlo 3088	50	3.8
13	Suncryl CP-75	50	3.8

The following water-swellaable materials were made by the process below, using a fluidized bed coater or Wurster coater for example, a Lakso Wurster Model 101 (The Lakso Company, Leominster, MA); in each case, 500 g of the uncoated water-swellaable polymers, available as ASAP 500 base polymer from BASF is used and the specified amount of polymer, at the specified weight-% solids concentration, is used. The peristaltic pump is calibrated and then set to the desired flow rate (e.g. 5g/minute) and the direction of flow of the coating agent is set forward. The desired inlet air flow and temperature are set to 50 m³/hr and 60°C. Then, the 'atomising' air supply and pump are started. The outlet temperature of the system is maintained at 45°C by adjusting the solvent flow rate into the system. (A higher speed may be used to advance the coating agent closer towards the inlet of the coater and then setting the correct speed for the experiment. The experiment is typically complete when stickiness prevents efficient fluidisation of the powder (between 10 and 60 minutes). The samples were dried in the vacuum oven at 27 °C for 12 to 24 hours.

Example	Polymer	Polymer Concentration (% w/w)	Solvent	Amount of Polymer (% w/w)
---------	---------	-------------------------------	---------	---------------------------

14	Vector 4211	10	MEK	2.8
15	Vector 4211	12	MEK	5.5
16	Irogran 654/5	5	MEK	1.4
17	Irogran 654/5	5	MEK	1.6
18	Septon 2063	10	Toluene	6.7
19	Estane 58245	5	DMF	1.4

Hystretch and Estane are trade names of Noveon Inc., 9911 Brecksville Road, Cleveland, OH 44141 – 3247. Vinamul is a trade name of Vinamul Polymers, De Asselen Kuil 20, 6161 RD Geleen, NL. Rovene is a trade name of Mallard Creek Polymers, 14 700 Mallard Creek Road, Charlotte, NC 28262. Gen Flo and Suncryl are trade names of Omnova Solutions Inc., 2990 Gilchrist Road, Akron, OH 44305 – 4418. Vector is a trade name of Dexco Polymers, 12012 Wickchester Lane, Houston, TX 77079, USA, Septon is a trade name of the Septon Company of America, A Kuraray Group Company, 11414 Choate Road, Pasadena, TX 77507, USA, Irogran is a trade name of Huntsman Polyurethanes, 52 Kendall Pond Road, Derry, NH 03038, USA.

Example 2.6: Preferred subsequent drying process step

The process of the invention may comprise a step whereby a solution, suspension or dispersion or solution is used, e.g. whereby the water-swellaable polymers comprise a liquid (water) or whereby the coating agent is in the form of a dispersion, suspension or solution.

The following is a preferred process step of drying the coated water-swellaable polymers of step b):

The coated water-swellaable material comprising a liquid, e.g. water, is placed on a surface, for example, it is spread out in a Pyrex glass pan in the form of a layer which is not more than about 1cm thick. This is dried at about 70 Celsius for at least 12 hours (under vacuum).

If the amount of liquid present in the coated water-swellaable polymers is known, then, by measuring the coated water-swellaable material comprising said weight of liquid prior to drying and then subsequently after drying, one can determine the residual moisture in the resulting water-swellaable material (coated water-swellaable polymers) as known in the art. Typically, the resulting water-swellaable material/ coated water-swellaable polymers will be dried to less than 5% (by weight of the material) moisture content.

For some type of coating agents, coated water-swellaable polymers may potentially form agglomerates. Flow aids may be added prior to or during the coating step, preferably added as a

dispersion in the coating agent solution, or preferably during the drying and/or annealing step (and optionally cross-linking step), as known in the art, e.g. Aerosil 200, available from Degussa. The above drying step may also be done by spreading the coated water-swellaible polymers on a Teflon coated mesh in a very thin layer, e.g. less than 5mm, such as to enable convection through the layer.

The coated water-swellaible polymers or material may subsequently be annealed, for example in a vacuum oven at 120 Celsius for 2 hours, or at a temperature that is appropriate for the polymer that is used as determined by the thermal transitions that occur for that polymer, according to the methods described herein.

As alternative method, the coated water-swellaible polymers that contain a liquid (water), may also be directly dried and annealed in one step, e.g. placing the material in a vacuum oven at 120 Celsius for 2 hours, or at a temperature that is appropriate for the polymer that is used as determined by the thermal transitions that occur for that polymer.

Example 2.7: Method of Drying in Fluidized Bed

A Lakso Wurster coater as used in example 2.5 and other fluidized bed driers known in the art may also be used to dry the coated materials formed by step b) of the process. For example, the conditions of example 2.5 might be used, introducing the coated material (and thus using the Wurster coating equipment only for drying the coated material).

Example 2.8: Method of Azeotropic Distillation and Drying

The wet, coated polymers may be dried or dewatered at low-temperature via azeotropic distillation from a suitable liquid that does not dissolve the coating agent, for example cyclohexane, if the coating agent is not soluble in cyclohexane. For example, the coated polymers are transferred to a 2 liter resin kettle, equipped with a Trubore mechanical stirrer with Teflon blade and digital stirring motor, immersion thermometer, and Barrett type moisture receiver with graduated sidearm and water-cooled condenser. Approximately one liter of cyclohexane is added to the resin kettle. While stirring, a heating mantle is used to raise the temperature of the stirred cyclohexane/gel system to reflux. Heating and reflux is continued until the temperature of the system approaches the boiling point of cyclohexane (approximately 80°C) and only minimal additional quantity of water is delivered to the sidearm. The system is cooled and then filtered to obtain the dewatered or dried coated water-swellaible polymers, which may be further dried overnight under vacuum at ambient temperature (20C).

Test Methods used herein:

(Unless specified otherwise, each test to obtain a value parameter herein is done 3 times to obtain an average of 3 values).

Preparation of films of the coating agent

In order to subject the coating agents or wet-extensible polymeric material used herein to some of the test methods below, including the Wet-elongation test, films need to be obtained of said coating agents or wet-extensible polymeric material thereof.

The preferred average (as set out below) caliper of the (dry) films for evaluation in the test methods herein is around 60 μ m.

Methods to prepare films are generally known to those skilled in the art and typically comprise solvent casting, hot melt extrusion or melt blowing films. Films prepared by these methods may have a machine direction that is defined as the direction the film is drawn or pulled. The direction perpendicular to the machine direction is defined as the cross-direction.

For the purpose of the invention, the films used in the test methods below are formed by solvent casting, except when the coating agent or wet-extensible material cannot be made into a solution or dispersion of any of the solvents listed below, and then the films are made by hotmelt extrusion as described below. (The latter is the case when particulate matter from undissolved polymer is still visible in the mixture of the material or coating agent and the solvent, after attempting to dissolve or disperse it at room temperature for a period between 2 to 48 hours, or when the viscosity of the solution or dispersion is too high to allow film casting.)

It should be understood that in the first embodiment of the invention, when an annealing and/ or curing step is only optional, the films are prepared without the annealing and/ or curing step. In a second embodiment of the invention, the annealing and/ or curing step is required, and then, the films to be tested are made by a process below, involving an annealing and/ or curing step as well.

The resulting film should have a smooth surface and be free of visible defects such as air bubbles or cracks.

An example to prepare a solvent cast film herein from a wet-extensible polymeric material or coating agent:

The film to be subjected to the tests herein can be prepared by casting a film from a solution or dispersion of said material or coating agent as follows:

The solution or dispersion is prepared by dissolving or dispersing the wet-extensible material or coating agent, at 10 weight %, in water, or if this is not possible, in THF (tetrahydrofuran), or if this is not possible, in dimethylformamide, or if this is not possible in methyl ethyl ketone, or if this is not possible, in dichloromethane or if this is not possible in toluene, or if this is not possible in cyclohexane (and if this is not possible, the hot melt extrusion process below is used).

Next, the dispersion or solution is poured into a Teflon boat with aluminum film cover and the solvent or dispersant is slowly evaporated at a temperature above the minimum film forming temperature of the polymer, typically about 25°C, for a long period of time, e.g. during at least 48 hours, or even up to 7 days. (For the drying it is important to slow down evaporation by covering the drying films during drying, for example with aluminum foil). Then, the films are placed in a vacuum oven for 6 hours, at 25°C, to ensure any remaining solvent is removed.

The process to prepare a hotmelt extruded film herein is as follows:

If the solvent casting method is not possible, films of the coating agent or wet-extensible material herein may be extruded from a hot melt using a rotating single screw extrusion set of equipment operating at temperatures sufficiently high to allow the material to flow. If the coating agent or material has a melt temperature T_m , then the extrusion should takes place at least 20 °C above said T_m of the polymer. If the coating agent or wet-extensible material is amorphous (i.e. the polymer does not have a T_m), steady shear viscometry can be performed to determine the order to disorder transition for the polymer, or the temperature where the viscosity drops dramatically. The extrusion temperature should be below the decomposition temperature of the material or coating agent. The direction that the film is drawn from the extruder is defined as the machine direction and the direction perpendicular to the drawing direction is defined as the cross direction.

For example	Wet-extensible material	Die Temperature	Screw rpm
20	Irogran VP 654/5	180 °C	40
21	Elastollan LP 9109	170 °C	30
22	Estane 58245	180 °C	30
23	Estane 4988	180 °C	30

24

Pellethane 2103-70A 185 °C

30

Annealing of the films:

If the process herein involves as compulsory step an annealing step, the films used in the test method are annealed. If the coating agent or wet-extensible material has two or more Tg's, then this annealing of the films (prepared and dried as set out above) should, for the purpose of the test methods below, be done by placing the film in a vacuum oven at a temperature which is 20°C above the highest Tg of the used coating agent or used wet-extensible material of the film, and this is done for 2 hours.

If the coating agent or wet-extensible material has a T_m, then this annealing of the films (prepared and dried as set out above) should, for the purpose of the test methods below, be done by placing the film in a vacuum oven at a temperature which is 20°C below the T_m of the coating agent or wet-extensible material of the film, and this is done for 2 hours.

If the coating agent has a (highest) Tg and a T_m, then said annealing of the films (prepared as set out above and to be tested by the methods below) is done at a temperature which is above the (highest) Tg and at least 20°C below the T_m and (as close to) 20°C above the (highest) Tg. For example, a wet-extensible material that has a T_m of 135°C and a highest Tg (of the hard segment) of 100°C, would be annealed at 115°C.

In the annealing steps, it is important that when the Tg is reached, the temperature should be increased slowly above the highest Tg to avoid gaseous discharge that may lead to bubbles in the film. For example, a material with a hard segment Tg of 70 °C might be annealed at 90 °C for 10 min, followed by incremental increases in temperature until the annealing temperature is reached.

Curing of the films:

If the water-swellaable material is used in a process involving as compulsory step a curing step, the films used in the test method are cured. This curing of the films (prepared and dried as set out above) should, for the purpose of the test methods below, be done by placing the film in a vacuum oven at 140°C for 2 hours.

Removal of films

If the dried and optionally annealed films are difficult to remove from the film forming substrate, then they may be placed in a warm water bath for 30 s to 1 min to remove the films from the substrate. The film is then subsequently dried for 6 – 24h at 25°C.

Wet-elongation Test and Wet-tensile-stress Test:

This test method is used to measure the wet-elongation at break (= extensibility at break) and tensile properties of films of water-extensible material or coating agents as used herein, by applying a uniaxial strain to a square flat sample 1" x 1" (2.54 cm x 2.54 cm) and measuring the force that is required to elongate the sample. The film samples are herein strained in the cross-direction, when applicable.

A preferred piece of equipment to do the tests is a tensile tester such as a MTS Synergie100 or a MTS Alliance, fitted with a computer interface and Testworks 4 software, available from MTS Systems Corporation 14000 Technology Drive, Eden Prairie, MN, USA, with a 25N or 50N load cell. This measures the Constant Rate of Extension in which the pulling grip moves at a uniform rate and the force measuring mechanisms moves a negligible distance (less than 0.13mm) with increasing force. The load cell is selected such that the measured loads (e.g. force) of the tested samples will be between 10 and 90% of the capacity of the load cell.

Each sample is die-cut from a film, each being 1 x 1 inch (2.5 x 2.5 cm), as defined above, using an anvil hydraulic press die to cut the film with the die into individual samples. (Thus, when the film is made by a process that does not introduce any orientation, the film may be tested in either direction.). Test specimens (minimum of three) are chosen which are substantially free of visible defects such as air bubbles, holes, inclusions, and cuts. They must also have smooth and substantially defect-free edges.

The thickness of each dry specimen is measured to an accuracy of 0.001 mm with a low pressure caliper gauge such as a Mitutoyo Caliper Gauge using a pressure of about 0.1 psi. Three different areas of the sample are measured and the average caliper is determined. The dry weight of each specimen is measured using a standard analytical balance to an accuracy of 0.001 g and recorded. Dry specimens are tested without further preparation for the determination of dry-elongation, dry-secant modulus, and dry-tensile stress values used herein.

For wet testing, pre-weighed dry film specimens are immersed in saline solution [0.9% (w/w) NaCl in distilled water] for a period of 24 hours, at ambient temperature (23C +/-2C). Films are secured in the bath with a 120-mesh corrosion-resistant metal screen that prevents the sample from rolling up and sticking to itself. The film is removed from the bath and blotted dry with an absorbent tissue such as a Bounty[®] towel, to remove excess or non-absorbed solution from the surface. The wet caliper is determined as noted for the dry samples. Wet specimens are used for tensile testing without further preparation. Testing should be completed within 5 minutes after

preparation is completed. Wet specimens are evaluated to determine wet-elongation, wet-secant modulus, and wet-tensile stress.

For the purpose of the present invention the Elongation to (or at) Break will be called Wet-elongation to (or at) Break and the tensile stress at break will be called Wet Stress at Break. (At the moment of break, the elongation to break % is the wet extensibility at break as used herein.)

Tensile testing is performed on a constant rate of extension tensile tester with computer interface such as an MTS Alliance tensile tester with Testworks 4 software. Load cells are selected such that measured forces fall within 10-90% of the cell capacity. Pneumatic jaws, fitted with flat 1"-square rubber-faced grips, are set to give a gauge length of 1 inch. The specimen is loaded with sufficient tension to eliminate observable slack, but less than 0.05N. The specimens are extended at a constant crosshead speed of 10"/min until the specimen completely breaks. If the specimen breaks at the grip interface or slippage within the grips is detected, then the data is disregarded and the test is repeated with a new specimen and the grip pressure is appropriately adjusted. Samples are run in triplicate to account for film variability.

The resulting tensile force-displacement data are converted to stress-strain curves using initial sample dimensions from which the elongation, tensile stress, and modulus that are used herein are derived. Tensile stress at break is defined as the maximum stress measured as a specimen is taken to break, and is reported in MPa. The break point is defined as the point on the stress-strain curve at which the measured stress falls to 90% of its maximum value. The elongation at break is defined as the strain at that break point and is reported relative to the initial gauge length as a percentage. The secant modulus at 400% elongation is defined as the slope of the line that intersects the stress-strain curve at 0% and 400% strain. Three stress-strain curves are generated for each extensible film coating that is evaluated. Elongation, tensile stress, and modulus used herein are the average of the respective values derived from each curve.

The dry secant elastic modulus at 400% elongation ($SM_{dry\ 400\%}$) is calculated by submitting a dry film, as obtainable by the methods described above (but without soaking it in the 0.9% NaCl solution), to the same tensile test described above, and then calculating the slope of the line intersecting with the zero intercept and the stress-strain curve at 400%, as done above.

Glass Transition Temperatures

Glass Transition Temperatures (Tg's) are determined for the purpose of this invention by differential scanning calorimetry (DSC). The calorimeter should be capable of heating/cooling rates of at least 20°C/min over a temperature range, which includes the expected Tg's of the sample that is to be tested, e.g. from -90° to 250°C, and the calorimeter should have a sensitivity of about 0.2 µW. TA Instruments Q1000 DSC is well-suited to determining the Tg's referred to

herein. The material of interest can be analyzed using a temperature program such as: equilibrate at -90°C , ramp at $20^{\circ}\text{C}/\text{min}$ to 120°C , hold isothermal for 5 minutes, ramp $20^{\circ}\text{C}/\text{min}$ to -90°C , hold isothermal for 5 minutes, ramp $20^{\circ}\text{C}/\text{min}$ to 250°C . The data (heat flow versus temperature) from the second heat cycle is used to calculate the T_g via a standard half extrapolated heat capacity temperature algorithm. Typically, 3-5 g of a sample material is weighed (± 0.1 g) into an aluminum DSC pan with a crimped lid.

As used herein T_{g1} will be a lower temperature than T_{g2} .

Polymer Molecular Weights

Gel Permeation Chromatography with Multi-Angle Light Scattering Detection (GPC-MALS) may be used for determining the molecular weight of the phase-separating polymers herein. Molecular weights referred to herein are the weight-average molar mass (M_w). A suitable system for making these measurements consists of a DAWN DSP Laser Photometer (Wyatt Technology), an Optilab DSP Interferometric Refractometer (Wyatt Technology), and a standard HPLC pump, such as a Waters 600E system, all run via ASTRA software (Wyatt Technology).

As with any chromatographic separation, the choice of solvent, column, temperature and elution profiles and conditions depends upon the specific polymer which is to be tested. The following conditions have been found to be generally applicable for the phase-separating polymers referred to herein: Tetrahydrofuran (THF) is used as the solvent and mobile phase; a flow rate of 1 mL/min is passed through two $300 \times 7.5\text{mm}$, $5\text{ }\mu\text{m}$, PLgel, Mixed-C GPC columns (Polymer Labs), placed in series, and are heated to $40\text{--}45^{\circ}\text{C}$ (the Optilab refractometer is held at same temperature); 100 μL of a 0.2% polymer in THF solution is injected for analysis. The dn/dc values are obtained from the literature where available or are calculated using the ASTRA utility. The weight-average molar mass (M_w) is calculated by with the ASTRA software using the Zimm fit method.

Moisture Vapor Transmission Rate Method (MVTR method)

MVTR method measures the amount of water vapor that is transmitted through a film under specific temperature and humidity. The transmitted vapor is absorbed by CaCl_2 desiccant and determined gravimetrically. Samples are evaluated in triplicate, along with a reference film sample of established permeability (e.g. Exxon Exxaire microporous material #XBF-110W) that is used as a positive control.

This test uses a flanged cup machined from Delrin (McMaster-Carr Catalog #8572K34) and anhydrous CaCl_2 (Wako Pure Chemical Industries, Richmond, Va.; Catalog 030-00525).

The height of the cup is 55 mm with an inner diameter of 30 mm and an outer diameter of 45 mm. The cup is fitted with a silicone gasket and lid containing 3 holes for thumb screws to completely seal the cup.

Desiccant particles are of a size to pass through a No. 8 sieve but not through a No. 10 sieve. Film specimens approximately 1.5" x 2.5" that are free of obvious defects are used for the analysis.

The cup is filled with CaCl_2 to within 1 cm of the top. The cup is tapped on the counter 10 times, and the CaCl_2 surface is leveled. The amount of CaCl_2 is adjusted until the headspace between the film surface and the top of the CaCl_2 is 1.0 cm. The film is placed on top of the cup across the opening (30 mm) and is secured using the silicone gasket, retaining ring, and thumb screws. Properly installed, the specimen should not be wrinkled or stretched.

The film must completely cover the cup opening, A, which is 0.0007065 m^2 .

The sample assembly is weighed with an analytical balance and recorded to $\pm 0.001 \text{ g}$. The assembly is placed in a constant temperature ($40 \pm 3^\circ\text{C}$) and humidity ($75 \pm 3\% \text{ RH}$) chamber for $5.0 \text{ hr} \pm 5 \text{ min}$. The sample assembly is removed, covered with Saran Wrap[®] and is secured with a rubber band. The sample is equilibrated to room temperature for 30 min, the plastic wrap removed, and the assembly is reweighed and the weight is recorded to $\pm 0.001 \text{ g}$. The absorbed moisture M_a is the difference in initial and final assembly weights. MVTR, in $\text{g/m}^2/24\text{hr}$ ($\text{g/m}^2/\text{day}$), is calculated as:

$$\text{MVTR} = M_a / (A \times 0.208 \text{ day})$$

Replicate results are averaged and rounded to the nearest $100 \text{ g/m}^2/24\text{hr}$, e.g. $2865 \text{ g/m}^2/\text{day}$ is herein given as $2900 \text{ g/m}^2/\text{day}$ and $275 \text{ g/m}^2/\text{day}$ is given as $300 \text{ g/m}^2/\text{day}$.

Method of determining the water-swellability capacity of wet-extensible materials used herein, considered non-water-swellable

The wet-extensible material herein is non-water swelling and / or absorbing, which means that it absorbs typically less than 1 g water/ g material, or even less than 0.5 g/g or even less than 0.2g/g/ or even less than 0.1g/g.

The water absorption can be determined as follows.

A certain pre-weighed amount of the water-extensible material (sample), with weight M (sample), is immersed in an excess amount of deionized water and is allowed to 'absorb' water for about 2.5 hours.

The sample is gently removed from the water; if possible, excess water is blotted from the sample with tissue towel for few seconds. The sample is then weighed again and the wet sample weight $M(\text{sample-wet})$ is determined.

The water absorption capacity of the sample, $X(\text{AC sample})$, is determined by the following formula:

$$X(\text{AC sample}) = \{M(\text{sample wet}) - M(\text{sample})\} / M(\text{sample})$$

The value X is reported in gram of absorbed fluid per gram of dry film sample.

The water absorption as determined is herein also called Water Swellability (or Swelling) Capacity of the wet-extensible material.

Cylinder Centrifuge Retention Capacity

The Cylinder Centrifuge Retention Capacity (CCRC) method determines the fluid retention capacity of the water-swellaable materials or polymers (sample) after centrifugation at an acceleration of 250g. Prior to centrifugation, the sample is allowed to swell in excess saline solution in a rigid sample cylinder with mesh bottom and an open top.

This method is particularly applicable to materials having fluid retention capacities that are substantially higher than 40 g/g and consequently not well-suited to evaluation by tea bag methods (e.g. EDANA 441.2-02, US 6,359,192 B1, US 5,415,643). Duplicate sample specimens are evaluated for each material tested and the average value is reported.

The CCRC can be measured at ambient temperature by placing the sample material (1.0 +/- 0.001 g) into a pre-weighed (+/- 0.01 g) plexiglass sample container that is open at the top and closed on the bottom with a stainless steel mesh (400) that readily allows for saline flow into the cylinder but contains the absorbent particles being evaluated. The sample cylinder approximates a rectangular prism with rounded-edges in the 67 mm height dimension. The base dimensions (78 X 58 mm OD, 67.2 X 47.2 MM ID) precisely match those of modular tube adapters, herein referred to as the cylinder stand, which fit into the rectangular rotor buckets (Heraeus # 75002252, VWR # 20300-084) of the centrifuge (Heraeus Megafuge 1.0; Heraeus # 75003491, VWR # 20300-016).

The loaded sample cylinders are gently shaken to evenly distribute the sample across the mesh surface and then placed upright in a pan containing saline solution. The cylinders should be positioned to ensure free flow of saline through the mesh bottom. Cylinders should not be placed against each other or against the wall of the pan, or sealed against the pan bottom. The sample material is allowed to swell, without confining pressure and in excess saline, for a time that corresponds to 80% of the CCRC saturation or equilibrium time for the specific material under study.

Cylinders are immediately removed from the solution. Each cylinder is placed (mesh side down) onto a cylinder stand and the resulting assembly is loaded into the rotor basket such that the two sample assemblies are in balancing positions in the centrifuge rotor.

The samples are centrifuged for 3 minutes (± 10 s) after achieving the rotor velocity required to generate a centrifugal acceleration of $250 \pm 5g$ at the bottom of the cylinder stand. The openings in the cylinder stands allow any solution expelled from the absorbent by the applied centrifugal forces to flow from the sample to the bottom of the rotor bucket where it is contained. The sample cylinders are promptly removed after the rotor comes to rest and weighed to the nearest 0.01 g.

The cylinder centrifuge retention capacity expressed as grams of saline solution absorbed per gram of sample material is calculated for each replicate as follows:

$$CCRC = \frac{m_{CS} - (m_{Cb} + m_s)}{m_s} \left[\frac{g}{g} \right]$$

where:

m_{CS} : is the mass of the cylinder with sample after centrifugation [g]
 m_{Cb} : is the mass of the dry cylinder without sample [g]
 m_s : is the mass of the sample without saline solution [g]

The CCRC referred to herein is the average of the duplicate samples reported to the nearest 0.01 g/g.

The saturation time is determined from a plot of CCRC values versus increasing swell time (60 minute increments). As used here, saturation time is defined as the swell time required to reach the saturation or equilibrium CCRC value. The saturation value is determined by sequentially calculating the standard deviation (SD) of the CCRC values of three consecutive points on the curve (the first SD calculated corresponds to time points 1-3, the second SD to time points 2-4, the third SD to time points 3-5, and so on). The saturation value is defined as the largest of the three consecutive CCRC values having a standard deviation less than 2.

Saline Flow Conductivity (SFC)

A measure of permeability and an indication of porosity is provided by the saline flow conductivity of the gel bed as described in U.S. Patent No. 5,562,646, (Goldman et al.) issued Oct. 8, 1996 (whereby however a 0.9% NaCl solution is used instead of Jayco solution).

Extractables or Extractable Polymers value

Another important characteristic of particularly preferred water-swellaable materials and the water-swellaable polymers useful herein is the level of extractable polymer material or extractables present therein. Evaluation and explanation of which levels of extractable polymer is still acceptable is disclosed and explained in detail in US 4,654,039. As a general rule the extractable amount should be as low as possible and the lower it is the less undesired reaction the extractable material can cause. Preferred are levels of extractables of less than 10% by weight, or even less than 5% or even less than 3% (1 hour test values).

Method to determine the Free Swell Rate of water-swellaable materials herein

This method serves to determine the swell rate of the water-swellaable materials herein in a 0.9% saline solution, without stirring or confining pressure. The amount of time taken to absorb a certain amount of fluid is recorded and this is reported in gram of fluid (0.9% saline) absorbed per gram of water-swellaable material per second, e.g. g/g/sec.

The saline solution is prepared by adding 9.0 gram of NaCl into 1000ml distilled, deionized water, and this is stirred until all NaCl is dissolved.

The sample material (1.0 g +/- 0.001 g) is weighed and placed evenly over the bottom of a 25ml beaker. A 20.0 ml aliquot of the saline solution (also at 23 °C) is promptly poured into the beaker. A timer is started immediately after the saline solution is delivered and stopped when the final portion of the fluid phase coalesces with the swelling sample.

This is readily indicated by the loss of light reflection from the bulk saline surface, particularly at the interface with the beaker walls. The elapsed time, t_s , in seconds is recorded. The free swell rate, in g liquid/g sample material/sec, is calculated as: $FSR = 20/t_s$. The test is run in triplicate and the average is used for the free swell rate of the sample material.

Determination of the coating caliper and coating caliper uniformity

Wet-extensible coatings on water-swellaable polymers or materials as used herein can typically be investigated by standard scanning electron microscopy, preferably environmental scanning electron microscopy (ESEM) as known to those skilled in the art. In the following method the ESEM evaluation is also used to determine the average coating caliper and the coating caliper uniformity of the coated water-swellaable polymers/ materials via cross-section of the materials.

Equipment model: ESEM XL 30 FEG (Field Emission Gun)

ESEM setting : high vacuum mode with gold covered samples to obtain also images at low magnification (35X) and ESEM dry mode with LFD (large Field Detector which detects ~80% Gasous Secondary Electrons + 20% Secondary Electrons) and bullet without PLA (Pressure Limiting Aperture) to obtain images of the latex shells as they are (no gold coverage required).

Filament Tension: 3KV in high vacuum mode and 12 KV in ESEM dry mode.

Pressure in Chamber on the ESEM dry mode: from 0.3 Torr to 1 Torr on gelatinous samples and from 0.8 to 1 Torr for other samples.

Samples of coated water-swellaable material or polymers or of uncoated polymers can be observed after about 1 hour at ambient conditions (20C, 80% relative humidity) using the standard ESEM conditions/ equipment.

Then, the same samples can be observed in high vacuum mode. Then the samepls can be cut via a cross-sectional cut with a teflon blade (Teflon blades are available from the AGAR scientific catalogue (ASSING) with reference code T5332), and observed again under vacuum mode.

The coatings have different morphology than the uncoated water-swellaable polymers and the coatings are clearly visible in the ESEM images, in particular when observing the cross-sectional views.

The average coating caliper is determined then by analyzing at least 5 particles of the water-swellaable material or coated water-swellaable polymer and determining 5 average calipers, an average per particle (by analyzing the cross-section of each particle and measuring the caliper of the coating in at least 3 different areas) and taking then the average of these 5 average calipers.

The uniformity of the coating is determined by determining the minimum and maximum caliper of the coating via ESEM of the cross-sectional cuts of at least 5 different particles and determining the average (over 5) minimum and average maximum caliper and the ratio thereof.

If the coating is not clearly visible in ESEM, then staining techniques known to the skilled in the art that are specific for the coating applied may be used such as enhancing the contrast with osmium tetroxide, potassium permanganate and the like, e.g. prior to using the ESEM method.

What is claimed is:

- 1 A process for making a water-swellaable material, comprising coated water-swellaable polymers, the process comprising the steps of:
 - a) obtaining water-swellaable polymers; and
 - b) simultaneously or subsequently to step a), applying at least 1% by weight of the resulting water-swellaable material, of a coating agent to at least part of said water-swellaable polymers to obtain the water-swellaable material comprising coated water-swellaable polymers,

whereby said coating agent in step b) comprises a material that is has a tensile stress at break in the wet state of at least 1MPa.

2. A process for making a water-swellaable material, comprising coated water-swellaable polymers, the process comprising the steps of:
 - a) obtaining water-swellaable polymers; and
 - b) simultaneously or subsequently to step a), applying at least 1% by weight of the resulting water-swellaable material, of a coating agent to at least part of said water-swellaable polymers; and
 - c) annealing and/ or curing the resulting coated water-swellaable polymers of step b), to obtain the water-swellaable material comprising coated water-swellaable polymers,

whereby said coating agent in step b) comprises a material that is wet- extensible and has a tensile stress at break in the wet state of at least 1MPa.

3. A process as in claim 1 or 2 for making a particulate water-swellaable material, whereby the water-swellaable polymers of step a) are in particulate form.
4. A process as in any preceding claim, wherein the wet-extensible material and the coating agent have a wet-elongation of at least 400%, preferably at least 500%, more preferably 800%.
5. A process according to any preceding claim, wherein the wet-extensible material and the coating agent have a tensile stress at break in the wet state of at least 3 MPa and more preferably at least 5 MPa.

6. A process according to any preceding claim, wherein the wet-extensible material and/ or the coating agent has, in the wet state, a wet secant elastic modulus at 400% elongation ($SM_{wet400\%}$) of at least 0.5 MPa, preferably at least 0.75 MPa, more preferably at least about 2MPa and most preferably at least about 3MPa.
7. A process according to any preceding claim whereby the coating agent in step b) is applied in fluid form, being in the form of a solution, a dispersion, or a hotmelt.
8. A process according to claim 7, whereby said annealing step is present and involves submitting the resulting coated water-swellaable polymers of step b) to a heat treatment of at least 70°C, or even at least 80°C.
9. A process according to any proceeding claim comprising said curing step, which involves submitting the coated water-swellaable polymers or said annealed coated water-swellaable polymers to a heat treatment step at a temperature of at least 140°C, preferably for at least 2 hours.
10. A process according to any preceding claim, whereby the water-swellaable polymers have a CCRC value of at least 30 g/g, preferably at least 50 g/g.
11. A process according to any preceding claim whereby the coating agent and/ or the wet-extensible material is breathable.
12. A process according to any preceding claim whereby the water-swellaable polymers of step a) are liquid-containing and at least partially swollen, comprising said liquid at a level of from 0.5 g/g to about 20 g/g (gram of liquid per weight of the water-swellaable polymers), preferably from 1g/g to about 10g/g by weight of said liquid.
13. A process as in any preceding claim, whereby said coating agent has a first glass transition temperature T_g of less than 0°C.
14. A water-swellaable material comprising coated water-swellaable polymers, obtainable by the process of any of the preceding claims.

15. A water-swellaable material as in claim 14, whereby said coating agent is hydrophilic.
16. A water-swellaable material as in claim 14 or 15, whereby the coating agent forms a continuous shell around at least some of said water-swellaable polymers, said shell having an average caliper of 1 μ m to 50 μ m, more preferably 1 μ m to 20 μ m.
17. A water-swellaable material of claim 16, whereby said shell is uniform with the ratio of smallest to largest caliper from 1:1 to 1:3, preferably from 1:1 to 1:2.

INTERNATIONAL SEARCH REPORT

US2004/025640

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61L15/00 A61L15/60 A61L15/42 C08J9/00

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 7 A61L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96/14885 A (REZAI EBRAHIM ; HSUEH KESYIN (JP); SHIMIZU MOTOHIRO (JP); PROCTER & GA) 23 May 1996 (1996-05-23) page 4, line 4 - line 34 page 28, line 13 - page 29, line 14 -----	1,3-17
X	WO 03/043670 A (BASF AG ; AZAD MICHAEL M (US); HERFERT NORBERT (US); ROBINSON JIM (US)) 30 May 2003 (2003-05-30) page 40, line 14 - page 41, line 13 page 16, line 9 - line 24 page 32, line 29 - page 33, line 40 -----	1,3-17
X	US 6 534 572 B1 (AHMED SHARF U ET AL) 18 March 2003 (2003-03-18) column 13, line 63 - column 14, line 16 column 14, line 34 - line 41 ----- -/--	1-17

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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 document 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

16 November 2004

Date of mailing of the international search report

23/11/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bochelen, D

INTERNATIONAL SEARCH REPORT

US2004/025640

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 392 908 A (DEHNEL ROGER B) 12 July 1983 (1983-07-12) column 3, line 12 - line 44; examples 1,3,4 -----	1-17
X	US 5 849 816 A (PEARLSTEIN LEONARD ET AL) 15 December 1998 (1998-12-15) column 9, line 25 - line 47 -----	1,3-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

/US2004/025640

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9614885	A	23-05-1996	AT 204487 T AU 3971095 A CA 2205039 A1 DE 69522338 D1 DE 69522338 T2 EP 0790839 A1 ES 2159649 T3 JP 10509362 T WO 9614885 A1 US 5859074 A ZA 9509384 A	15-09-2001 06-06-1996 23-05-1996 27-09-2001 07-02-2002 27-08-1997 16-10-2001 14-09-1998 23-05-1996 12-01-1999 11-06-1996
WO 03043670	A	30-05-2003	WO 03043670 A1 EP 1448242 A1	30-05-2003 25-08-2004
US 6534572	B1	18-03-2003	AU 3891899 A BR 9910261 A CN 1308654 T EP 1084194 A1 JP 2002526560 T WO 9957201 A1 US 6458877 B1	23-11-1999 02-01-2001 15-08-2001 21-03-2001 20-08-2002 11-11-1999 01-10-2002
US 4392908	A	12-07-1983	AT 3240 T AU 537089 B2 AU 6650181 A BR 8100387 A CA 1184446 A1 DE 3160233 D1 EP 0033235 A2 ES 8203234 A1 JP 1364998 C JP 56118736 A JP 61033614 B ZA 8100410 A	15-05-1983 07-06-1984 30-07-1981 11-08-1981 26-03-1985 16-06-1983 05-08-1981 01-07-1982 09-02-1987 17-09-1981 02-08-1986 25-08-1982
US 5849816	A	15-12-1998	US 5549590 A CA 2256098 A1 EP 0880367 A1 WO 9727884 A1 AU 2966395 A BR 9508490 A EP 0697217 A1 IL 114709 A JP 2979047 B2 JP 9503954 T WO 9604024 A1 CA 2172847 A1 US 5539019 A ZA 9506359 A	27-08-1996 07-08-1997 02-12-1998 07-08-1997 04-03-1996 03-11-1998 21-02-1996 16-07-2000 15-11-1999 22-04-1997 15-02-1996 15-02-1996 23-07-1996 11-06-1996