Title: PROCESS FOR THE PRODUCTION OF WATER-AbsORBENT POLYMER PARTICLES COMPRISING SUBSEQUENT HYDROGEL COMMUNITING STEPS

Abstract: The invention generally relates to a process for the preparation of water-absorbent polymer particles, comprising the process steps of (i) preparing an aqueous monomer solution comprising at least one partially neutralized, monoethylenically unsaturated monomer bearing carboxylic acid groups (a) and at least one crosslinker (a3); (ii) optionally adding fine particles of a water-absorbent polymer to the aqueous monomer solution; (iii) adding a polymerization initiator or a at least one component of a polymerization initiator system that comprises two or more components to the aqueous monomer solution; (iv) optionally decreasing the oxygen content of the aqueous monomer solution; (v) charging the aqueous monomer solution into a polymerization reactor; (vi) polymerizing the monomers in the aqueous monomer solution in the polymerization reactor, thereby obtaining a polymer gel; (vii) discharging the polymer gel out of the polymerization reactor, and subjecting a) the polymer gel to a first comminuting step, thereby obtaining at least two polymer gel strands, and b) the at least two polymer gel strands to a further comminuting step; (viii) drying the polymer gel particles; (ix) grinding the dried polymer gel particles thereby obtaining particulate water-absorbent polymer particles; (x) sizing the ground water-absorbent polymer particles; and (xi) optionally treating the surface of the ground and sized water-absorbent polymer particles.
PROCESS FOR THE PRODUCTION OF WATER-ABSORBENT POLYMER PARTICLES COMPRISING SUBSEQUENT HYDROGEL COMMINUTING STEPS

[Technical Field]

The invention relates to a process for the preparation of water-absorbent polymer particles; to a water-absorbent polymer particle obtainable by such a process; to a plurality of water-absorbent polymer particles; to a composite material comprising such a water-absorbent polymer particle or such a plurality of water-absorbent polymer particles; to a process for the production of a composite material; to a composite material obtainable by such a process; to a use of the water-absorbent polymer particle or a plurality of water-absorbent polymer particles; to a device for the preparation of water-absorbent polymer particles; and to a process for the preparation of water-absorbent polymer particles using such a device.

[Background Art]

Superabsorbers are water-insoluble, crosslinked polymers which are able to absorb large amounts of aqueous fluids, especially body fluids, more especially urine or blood, with swelling and the formation of hydrogels, and to retain such fluids under a certain pressure. By virtue of those characteristic properties, such polymers are chiefly used for incorporation into sanitary articles, such as, for example, baby's nappies/diapers, incontinence products or sanitary towels.

The preparation of superabsorbers is generally carried out by free-radical polymerization of acid-group-carrying monomers in the presence of crosslinkers, it being possible for polymers having different absorber properties to be prepared by the choice of the monomer composition, the crosslinkers and the polymerization conditions and of the processing conditions for the hydrogel obtained after the polymerization (for details see, for example, Modern Superabsorbent Polymer Technology, FL Buchholz, GT Graham, Wiley-VCH, 1998).

The polymer gel, also called hydrogel, obtained after the polymerization is usually comminuted, dried and classified in order to obtain a particulate superabsorber with a well defined particles size distribution. In a further process step these superabsorbent particles are often surface crosslinked in order to improve the absorption behavior. For this purpose the particles are mixed with an aqueous solution containing a surface crosslinking agent and optionally further additives and the thus obtained mixture is heat treated in order to promote the crosslinking reaction.

[Disclosure]

[Technical Problem]

According to processes for the preparation of water-absorbent polymer particles disclosed in the prior art the polymer gel is comminuted prior to drying. Therein, the comminuting is performed by a single device as a single-step comminution. This leads to a high loads on the comminuting tools of the comminuting device and hence to a rather low operational lifetime of said comminuting tools. Moreover, comminuting result is unsatisfactory in terms of a uniform and gentle comminution of the polymer gel. Moreover, often a comminuting device comprising a cutting knife of a complex shape is applied. Such a cutting knife is expensive, requires a rather large amount of maintenance, and is not easy to exchange.

[Technical Solution]

Generally, it is an object of the present invention to at least partly overcome a disadvantage arising from the prior art in the context of the production of water-absorbent polymer particles.

A further object is to provide a process for the preparation of water-absorbent polymer particles, wherein complex shapes of cutting edges for comminuting the polymer gel are avoided as far as possible. It is a further object of the invention to provide a process for the preparation of water-absorbent polymer particles, wherein an amount of maintenance required for comminuting device, or costs of a comminuting device, or both are reduced. It is a further object of the invention to provide a process for the preparation of water-absorbent polymer particles, wherein large or non-planar or both cutting edges for comminuting the polymer gel are avoided as far as possible. It is a further object of the invention to provide a process for the preparation of water-absorbent polymer particles, wherein the comminuting devices used are long term stable. It is a further object of the invention to provide a process for the preparation of water-absorbent polymer particles, wherein a part of a comminuting device which comprises a cutting edge is easily exchangeable. It is yet a further object of the invention to pro-
vide a process for the preparation of water-absorbent polymer particles, wherein the polymer gel is gently comminuted. It is a further object of the present invention to provide a process for the production of water-absorbent polymer particles, wherein the process shows a balanced combination of: an increased operational lifetime of a comminuting device, a low number of comminuting steps, a decreased drying time of the polymer gel. A further object is to provide water-absorbent polymer particles which have been produced by a less expensive process. It is a further object of the present invention to provide a water-absorbent polymer particle or a plurality of water-absorbent polymer particles produced by a process having at least one, preferably a balanced combination of at least two, of the above advantages, wherein the water-absorbent polymer particle shows no reduction of quality. It is a further object of the present invention to provide a composite material comprising a water-absorbent polymer particle produced by a process having at least one of the above advantages, wherein the composite material shows no reduction of quality. It is a further object of the present invention to provide a device for producing water-absorbent polymer particles by a process having at least one of the above advantages.

A contribution to the solution of at least one of the above objects is given by the independent claims. The dependent claims provide preferred embodiments of the present invention which also serve solving at least one of the above mentioned objects.

According to an embodiment, a process for the preparation of water-absorbent polymer particles includes the process steps of:

(i) preparing an aqueous monomer solution comprising at least one partially neutralized, monoethylenically unsaturated monomer bearing carboxylic acid groups (al) and at least one crosslinker (a3);

(ii) optionally adding fine particles of a water-absorbent polymer to the aqueous monomer solution;

(iii) adding a polymerization initiator or a at least one component of a polymerization initiator system that comprises two or more components to the aqueous monomer solution;

(iv) optionally decreasing the oxygen content of the aqueous monomer solution;

(v) charging the aqueous monomer solution into a polymerization reactor (904);

(vi) polymerizing the monomers in the aqueous monomer solution in the polymerization reactor (904), thereby obtaining a polymer gel (401);

(vii) discharging the polymer gel (401) out of the polymerization reactor (904), and subjecting
a) the polymer gel (401) to a first comminuting step in a first comminuting device (402), thereby obtaining at least two polymer gel strands (403) each having a strand width (406), and

b) the at least two polymer gel strands (403) to a further comminuting step in a further comminuting device (404), thereby obtaining polymer gel particles (405) having a diameter (408) or a width (407) or both which is less than the strand width (406);

(viii) drying the polymer gel particles (405);

(ix) grinding the dried polymer gel particles thereby obtaining particulate water-absorbent polymer particles;

(x) sizing the grinded water-absorbent polymer particles; and

(xi) optionally treating the surface of the grinded and sized water-absorbent polymer particles.

According to another embodiment, a device for the preparation of water-absorbent polymer particles in a process stream includes:

a) a first container (901), designed to take an aqueous monomer solution, comprising at least one partially neutralized, monoethylenically unsaturated monomer bearing carboxylic acid groups (al);

b) a further container (902), designed to take at least one crosslinker (oc3);

c) a mixing device (903), wherein the mixing device (903) is

i) located down-stream to the first container (901) and the further container (902),

ii) designed to mix the monomer solution and the at least one crosslinker (a3);

d) a polymerization reactor (904), wherein the polymerization reactor (904) is

i) located down-stream to the first container (901) and the further container (902),

ii) designed to comprise the aqueous monomer solution and the at least one crosslinker (a3) during polymerizing the monomers in the aqueous monomer solution, thereby obtaining a polymer gel (401);

e) a first comminuting device (402), wherein the first comminuting device (402) is

i) located down-stream to the polymerization reactor (904),
ii) designed to subject the polymer gel (401) to a first comminuting step, thereby obtaining at least two polymer gel strands (403) each having a strand width (406);

f) a further comminuting device (404), wherein the further comminuting device (404) is
   i) located down-stream to the first comminuting device (402),
   ii) designed to subject the at least two polymer gel strands (403) to a further comminuting step, thereby obtaining polymer gel particles (405) having a diameter (408) or a width (407) or both which is less than the strand width (406);

g) a belt dryer (905), wherein the belt dryer (905) is
   i) located down-stream to the further comminuting device (404),
   ii) designed to dry the polymer gel particles (405),

h) a grinding device (906), wherein the grinding device (906) is
   i) located down-stream to the belt dryer (905),
   ii) designed to grind the dried polymer gel, thereby obtaining water-absorbent polymer particles;

j) a sizing device (907), wherein the sizing device (907) is
   i) located down-stream to the grinding device (906),
   ii) designed to size the grinded water-absorbent polymer particles.

[Advantageous Effects]

Complex shapes of cutting edges for comminuting the polymer gel may be avoided as far as possible and an amount of maintenance required for comminuting device, or costs of a comminuting device, or both maybe reduced. Large or non-planar or both cutting edges for comminuting the polymer gel may be avoided as far as possible and the comminuting devices used may be long term stable. A part of a comminuting device which comprises a cutting edge may be easily exchangeable. The polymer gel may be gently comminuted. The process may show a balanced combination of: an increased operational lifetime of a comminuting device, a low number of comminuting steps, a decreased drying time of the polymer gel.

[Description of Drawings!]

Figure 1 is a flow chart diagram depicting the steps of a process according to the invention;
Figure 2 is a flow chart diagram depicting the steps of another process according to the invention;
Figure 3 is a flow chart diagram depicting the steps of another process according to the invention;
Figure 4 is a scheme of a sequence of comminuting steps according to the invention;
Figure 5 is a scheme of another sequence of comminuting steps according to the invention;
Figure 6 is a scheme of another sequence of comminuting steps according to the invention;
Figure 7 is a scheme of a first comminuting device according to the invention;
Figure 8a is a scheme of a further comminuting device according to the invention in an external view;
Figure 8b is a scheme of inner parts the further comminuting device of figure 8a) in an exploded view; and
Figure 9 is a block diagram of a device for the preparation of water-absorbent polymer particles according to the invention.

100 process according to the invention
101 step (i)
102 step (ii)
103 step (iii)
104 step (iv)
105 step (v)
106 step (vi)
107 step (vii)
108 step (viii)
109 step (ix)
110 step (x)
111 step (xi)
401 polymer gel
402 first comminuting device
403 polymer gel strands
A contribution to the solution of at least one of these objects is made by a process for the preparation of water-absorbent polymer particles, comprising the process steps of

(i) preparing an aqueous monomer solution comprising at least one partially neutralized, monoethylenically unsaturated monomer bearing carboxylic acid groups (al) and at least one crosslinker (a3);

(ii) optionally adding fine particles of a water-absorbent polymer to the aqueous monomer solution;

(iii) adding a polymerization initiator or a at least one component of a polymerization initiator system that comprises two or more components to the aqueous monomer solution;
(iv) optionally decreasing the oxygen content of the aqueous monomer solution;
(v) charging the aqueous monomer solution into a polymerization reactor;
(vi) polymerizing the monomers in the aqueous monomer solution in the polymerization reactor, thereby obtaining a polymer gel;
(vii) discharging the polymer gel out of the polymerization reactor, and subjecting the polymer gel to a first comminuting step in a first comminuting device, thereby obtaining at least two, preferably at least three, more preferably at least four, more preferably at least five, more preferably at least 6, more preferably at least 7, more preferably at least 8, more preferably at least 9, more preferably at least 10, most preferably at least 15, polymer gel strands each having a strand width, and
(b) the at least two, preferably the at least three, more preferably the at least four, more preferably the at least five, more preferably the at least 6, more preferably the at least 7, more preferably the at least 8, more preferably the at least 9, more preferably the at least 10, most preferably the at least 15, polymer gel strands to a further comminuting step in a further comminuting device, thereby obtaining polymer gel particles having a diameter or a width or both which is less than the strand width;
(viii) drying the polymer gel particles;
(ix) grinding the dried polymer gel particles thereby obtaining particulate water-absorbent polymer particles;
(x) sizing the grinded water-absorbent polymer particles; and
(xi) optionally treating the surface of the grinded and sized water-absorbent polymer particles.

Therein, subsequent steps of the process according to the invention may be performed simultaneously or may overlap in time or both. This holds particularly for the steps (i) to (iv), especially particularly for the steps (iii) and (iv).

The process according to the present invention is preferably a continuous process in which the aqueous monomer solution is continuously provided and is continuously fed into the polymerization reactor. The hydrogel obtained is continuously discharged out of the polymerization reactor and is continuously comminuted, dried, grinded and classified in the subsequent process steps. This continuous process may, however, be interrupted in order to, for example,
substitute certain parts of the process equipment, like the belt material of the conveyor belt if a conveyor belt is used as the polymerization reactor,

- clean certain parts of the process equipment, especially for the purpose of removing polymer deposits in tanks or pipes, or

- start a new process when water-absorbent polymer particles with other absorption characteristics have to be prepared.

Water-absorbent polymer particles which are preferred according to the invention are particles that have an average particle size in accordance with WSP 220.2 (test method of „Word Strategic Partners” EDANA and INDA) in the range of from 10 to 3,000 µm, preferably 20 to 2,000 µm and particularly preferably 150 to 850 µm. In this context, it is particularly preferable for the content of water-absorbent polymer particles having a particle size in a range of from 300 to 600 µm to be at least 30 wt.-%, particularly preferably at least 40 wt.-% and most preferably at least 50 wt.-%, based on the total weight of the water-absorbent polymer particles.

In process step (i) of the process according to the present invention an aqueous monomer solution containing partially neutralized, monoethylenically unsaturated monomers bearing carboxylic acid groups (al) and at least one crosslinker (α3) is prepared.

Preferred monoethylenically unsaturated monomers bearing carboxylic acid groups (al) are those cited in DE 102 23 060 A1 as preferred monomers (al), whereby acrylic acid is particularly preferred.

It is preferred according to the present invention that the water-absorbent polymer produced by the process according to the invention comprises monomers bearing carboxylic acid groups to at least 50 wt.-%, preferably to at least 70 wt.-% and further preferably to at least 90 wt.-%, based on the dry weight. It is particularly preferred according to the invention, that the water-absorbent polymer produced by the process according to the invention is formed from at least 50 wt.-%, preferably at least 70 wt.-% of acrylic acid, which is preferably neutralized to at least 20 mol-%, particularly preferably to at least 50 mol-%. The concentration of the partially neutralized, monoethylenically unsaturated monomers bearing carboxylic acid groups (al) in the aqueous monomer solution that is provided in process step (i) is preferably in the range of from 10 to 60 wt.-%, preferably from 30 to 55 wt.-% and most preferably from 40 to 50 wt.-%, based on the total weight of the aqueous monomer solution.

The aqueous monomer solution may also comprise monoethylenically unsaturated monomers (a2) which are copolymerizable with (al). Preferred monomers (a2) are those
monomers which are cited in DE 102 23 060 A1 as preferred monomers (a2), whereby acrylamide is particularly preferred.

Preferred crosslinkers (α3) according to the present invention are compounds which have at least two ethylenically unsaturated groups in one molecule (crosslinker class I), compounds which have at least two functional groups which can react with functional groups of the monomers (al) or (a2) in a condensation reaction (= condensation crosslinkers), in an addition reaction or a ring-opening reaction (cross-linker class II), compounds which have at least one ethylenically unsaturated group and at least one functional group which can react with functional groups of the monomers (al) or (a2) in a condensation reaction, an addition reaction or a ring-opening reaction (crosslinker class III), or polyvalent metal cations (crosslinker class IV). Thus with the compounds of crosslinker class I a crosslinking of the polymer is achieved by radical polymerization of the ethylenically unsaturated groups of the crosslinker molecules with the monoethylenically unsaturated monomers (al) or (a2), while with the compounds of crosslinker class II and the polyvalent metal cations of crosslinker class IV a crosslinking of the polymer is achieved respectively via condensation reaction of the functional groups (crosslinker class II) or via electrostatic interaction of the polyvalent metal cation (crosslinker class IV) with the functional groups of the monomer (al) or (a2). With compounds of crosslinker class III a cross-linking of the polymers is achieved correspondingly by radical polymerization of the ethylenically unsaturated groups as well as by condensation reaction between the functional groups of the crosslinkers and the functional groups of the monomers (al) or (a2).

Preferred crosslinkers (α3) are all those compounds which are cited in DE 102 23 060 A1 as crosslinkers (α3) of the crosslinker classes I, II, III and IV, whereby
- as compounds of crosslinker class I, N, N'-methylene bisacrylamide, polyethyleneglycol di(meth)acrylates, triallylmethylammonium chloride, tetraallylammonium chloride and allylnonaethylene glycol acrylate produced with 9 mol ethylene oxide per mol acrylic acid are particularly preferred, wherein N, N'-methylene bisacrylamide is even more preferred, and
- as compounds of crosslinker class IV, Al₂(30₄)₃ and its hydrates are particularly preferred.

Preferred water-absorbent polymers produced by the process according to the invention are polymers which are crosslinked by crosslinkers of the following crosslinker classes or by crosslinkers of the following combinations of crosslinker classes respectively: I, II, III, IV, I II, I III, I IV, I II III, I II IV, I III IV, I II III IV, I II IV or I II IV.
Further preferred water-absorbent polymers produced by the process according to the invention are polymers which are crosslinked by any of the crosslinkers disclosed in DE 102 23 060 A1 as crosslinkers of crosslinker classes I, whereby N,N'-methylene bis-acylamide, polyethyleneglycol di(meth)acrylates, triallyl-methylammonium chloride, tetraallylammonium chloride and allylnonaethylene-glycol acrylate produced from 9 mol ethylene oxide per mol acrylic acid are particularly preferred as crosslinkers of crosslinker class I, wherein N, sI'-methylene bisacrylamide is even more preferred.

The aqueous monomer solution may further comprise water-soluble polymers (a4). Preferred water-soluble polymers (a4) include partly or completely saponified polyvinyl alcohol, polyvinylpyrrolidone, starch or starch derivatives, polyglycols or polyacrylic acid. The molecular weight of these polymers is not critical, as long as they are water-soluble. Preferred water-soluble polymers (a4) are starch or starch derivatives or polyvinyl alcohol. The water-soluble polymers (a4), preferably synthetic, such as polyvinyl alcohol, can not only serve as a graft base for the monomers to be polymerized. It is also conceivable for these water-soluble polymers to be mixed with the polymer gel or the already dried water-absorbent polymer.

The aqueous monomer solution can furthermore also comprise auxiliary substances (a5), these auxiliary substances including, in particular, complexing agents, such as, for example, EDTA.

The relative amount of monomers (a1) and (a2) and of crosslinking agents (a3) and water-soluble polymers (a4) and auxiliary substances (a5) in the aqueous monomer solution is preferably chosen such that the water-absorbent polymer structure obtained after drying the comminuted polymer gel is based

- to the extent of 20 to 99.999 wt.-%, preferably to the extent of 55 to 98.99 wt.-% and particularly preferably to the extent of 70 to 98.79 wt.-% on monomers (a1),
- to the extent of 0 to 80 wt.-%, particularly preferably to the extent of 0 to 44.99 wt.-% and particularly preferably to the extent of 0.1 to 44.89 wt.-% on the monomers (a2),
- to the extent of 0 to 5 wt.-%, particularly preferably to the extent of 0.001 to 3 wt.-% and particularly preferably to the extent of 0.01 to 2.5 wt.-% on the crosslinking agents (a3),
- to the extent of 0 to 30 wt.-%, particularly preferably to the extent of 0 to 5 wt.-% and particularly preferably to the extent of 0.1 to 5 wt.-% on the water-soluble polymers (a4),
- to the extent of 0 to 20 wt.-%, particularly preferably to the extent of 0 to 10 wt.-% and particularly preferably to the extent of 0.1 to 8 wt.-% on the auxiliary substances (a5), and
- to the extent of 0.5 to 25 wt.-%, particularly preferably to the extent of 1 to 10 wt.-% and particularly preferably to the extent of 3 to 7 wt.-% on water (a6)
the sum of the amounts by weight (al) to (a6) being 100 wt.-%.

Optimum values for the concentration in particular of the monomers, crosslinking agents and water-soluble polymers in the monomer solution can be determined by simple pre-
liminary experiments or from the prior art, in particular from the publications US 4,286,082, DE 27 06 135 Al, US 4,076,663, DE 35 03 458 Al, DE 40 20 780 Cl, DE 42 44 548 Al, DE 43 33 056 Al and DE 44 18 818 Al.

In process step (ii) fine particles of a water-absorbent polymer may optionally be added to the aqueous monomer solution. Independent of optional step (ii) fine water-
absorbent polymer particles may be added to the aqueous monomer solution at one selected
from the group consisting of after step (iii), after step (iv), and before step (v), or a combina-
tion of at least two thereof.

Water-absorbent fine particles are preferably water-absorbent polymer particles the composition of which corresponds to the composition of the above described water-absorbent polymer particles, wherein it is preferred that at least 90 wt.-% of the water-absorbent fine particles, preferably at least 95 wt.-% of the water-absorbent fine particles and most preferred
at least 99 wt.-% of the water-absorbent fine particles have a particle size of less than 200 \( \mu \text{m} \), preferably less than 150 \( \mu \text{m} \) and particular preferably less than 100 \( \mu \text{m} \).

In a preferred embodiment of the process according to the present invention the water-
absorbent fine particles which may optionally be added to the aqueous monomer solution in process step (ii) are water-absorbent fine particles which are obtained in process step (x) of the process according to the present invention and which are thus recycled.

The fine particles can be added to the aqueous monomer solution by means of any mixing device the person skilled of the art would consider as appropriate for this purpose. In a preferred embodiment of the present invention, which is especially useful if the process is performed continuously as described above, the fine particles are added to the aqueous monomer solution in a mixing device in which a first stream of the fine particles and a second stream of the aqueous monomer solution are directed continuously, but from different direc-
tions, onto a rotating mixing device. Such a kind of mixing setup can be realised in a so called "Rotor Stator Mixer" which comprises in its mixing area a preferably cylindrically shaped, non-rotating stator, in the centre of which a likewise preferably cylindrically shaped rotor is rotating. The walls of the rotor as well as the walls of the stator are usually provided with notches, for example notches in the form of slots, through which the mixture of fine particles and aqueous monomer solution can be sucked through and thus can be subjected to high shear forces.
In this context it is particularly preferred that the first stream of the fine particles and the second stream of the aqueous monomer solution form an angle $\delta$ in the range from 60 to 120°, more preferred in the range from 75 to 105°, even more preferably in the range from 85 to 95° and most preferred form an angle of about 90°. It is also preferred that the stream of the mixture of fine particles and aqueous monomer solution that leaves the mixer and the first stream of fine particles that enters the mixer form an angle $\varepsilon$ in the range from 60 to 120°, preferably in the range from 75 to 105°, even more preferred in the range from 85 to 95° and most preferred form an angle of about 90°.

Such a kind of mixing set up can, for example, be realized by means of mixing devices which are disclosed in DE-A-25 20 788 and DE-A-26 17 612, the content of which is incorporated herein by reference. Concrete examples of mixing devices which can be used to add the fine particles to the aqueous monomer solution in process step (ii) of the present invention are the mixing devices which can be obtained by the IKA® Werke GmbH & Co. KG, Staufen, Germany, under designations MHD 2000/4, MHD 2000/05, MHD 2000/10, MDH 2000/20, MHD 2000/30 und MHD 2000/50, wherein the mixing device MHD 2000/20 is particularly preferred. Further mixing devices which can be used are those offered by ystral GmbH, Bal-brechten-Dottingen, Germany, for example under designation „Conti TDS“, or by Kinematika AG, Luttau, Switzerland, for example under the trademark Megatron®.

The amount of fine particles that may be added to the aqueous monomer solution in process step (ii) is preferably in the range from 0.1 to 15 wt.-%, even more preferred in the range from 0.5 to 10 wt.-% and most preferred in the range from 3 to 8 wt.-%, based on the weight of the aqueous monomer solution.

In process step (iii) of the process according to the present invention a polymerization initiator or at least one component of a polymerization initiator system that comprises two or more components is added to the aqueous monomer solution.

As polymerization initiators for initiation of the polymerization all initiators forming radicals under the polymerization conditions can be used, which are commonly used in the production of superabsorbers. Among these belong thermal catalysts, redox catalysts and photo-initiators, whose activation occurs by energetic irradiation. The polymerization initiators may be dissolved or dispersed in the aqueous monomer solution. The use of water-soluble catalysts is preferred.

As thermal initiators may be used all compounds known to the person skilled in the art that decompose under the effect of an increased temperature to form radicals. Particularly preferred are thermal polymerisation initiators with a half life of less than 10 seconds, more
preferably less than 5 seconds at less than 180°C, more preferably at less than 140°C.
Peroxides, hydroperoxides, hydrogen peroxide, persulfates and azo compounds are
particularly preferred thermal polymerization initiators. In some cases it is advantageous to
use mixtures of various thermal polymerization initiators. Among such mixtures, those
consisting of hydrogen peroxide and sodium or potassium peroxodisulfate are preferred,
which may be used in any desired quantitative ratio. Suitable organic peroxides are preferably
acetylacetone peroxide, methyl ethyl ketone peroxide, benzoyl peroxide, lauroyl peroxide,
acetyl peroxide, capryl peroxide, isopropyl peroxidicarbonate, 2-ethylhexyle
peroxidicarbonate, tert.-butyl hydroperoxide, cumene hydroperoxide, and peroxides of tert.-
amyl perpivalate, tert.-butyl perpivalate, tert.-butyl perneohexonate, tert.-butyl isobutyrate,
tert.-butyl per-2-ethylhexenoate, tert.-butyl perisononanoate, tert.-butyl permaleate, tert.-butyl
perbenzoate, tert.-butyl-3,5,5-trimethylhexanoate and amyl perneodecanoate. Furthermore,
the following thermal polymerisation initiators are preferred: azo compounds such as azo-bis-
isobutyronitril, azo-bis-dimethylvaleronitril, azo-bis-ami-dinopropane dihydrochloride, 2,2'-
azobis-(N,N-dimethylene)isobutryramidine di-hydrochloride, 2-(carbamoylazo)isobutyronitrile
and 4,4'-azobis-(4-cyano-valeric acid). The aforementioned compounds are used in
conventional amounts, preferably in a range from 0.01 to 5 mol-%, more preferably 0.1 to 2
mol-%, respectively based on the amount of the monomers to be polymerized.

Redox catalysts comprise two or more components, usually one or more of the peroxy
compounds listed above, and at least one reducing component, preferably ascorbic acid,
glucose, sorbose, mannose, ammonium or alkali metal hydrogen sulfite, sulfate, thiosulfate,
hyposulfite or sulfide, metal salts such as iron II ions or silver ions or sodium hydroxymethyl
sulfoxylate. Preferably ascorbic acid or sodium pyrosulfite is used as reducing component of
the redox catalyst. 1 x 10^6 to 1 mol-% of the reducing component of the redox catalyst and
1 x 10^5 to 5 mol-% of the oxidizing component of the redox catalyst are used, in each case
referred to the amount of monomers used in the polymerization. Instead of the oxidizing
component of the redox catalyst, or as a complement thereto, one or more, preferably watersoluble azo compounds may be used.

The polymerization is preferably initiated by action of energetic radiation, so-called
photo-initiators are generally used as initiator. These can comprise for example so-called a-
splitters, H-abstraction systems or also azides. Examples of such initiators are benzophenone
derivatives such as Michlers ketone, phenanthrene derivatives, fluorine derivatives, anthra-
quinone derivatives, thioxanthone derivatives, cumarin derivatives, benzoinether and deriva-
tives thereof, azo compounds such as the above-mentioned radical formers, substituted hexaa-
rylbisimidazoles or acylphosphine oxides. Examples of azides are: 2-(N,N-dimethylamino)ethyl-4-azidocinnamate, 2-(N,N-dimethylamino)ethyl-4-azidonaphthylketone, 2-(N,N-di-methylamino)ethyl-4-azidobenzoate, 5-azido-1-naphthyl-2’-(N,N-dimethylamino)ethylsulfone, N-(4-sulfonylazidophenyl)maleimide, N-acetyl-4-sulfonyl-azidoaniline, 4-sulfonylazidoaniline, 4-azidoaniline, 4-azidophenacyl bromide, p-azidobenzoic acid, 2,6-bis(p-azidobenzylidene)cyclohexanone and 2,6-bis(p-azidobenzylidene)-4-methylcyclohexanone. A further group of photo-initiators are di-alkoxy ketals such as 2,2-dimethoxy-1,2-diphenylethan-1-one. The photo-initiators, when used, are generally employed in quantities from 0.0001 to 5 wt.-% based on the monomers to be polymerized.

According to a further embodiment of the process according to the invention it is preferred that in process step (iii) the initiator comprises the following components

iii. a peroxodisulfate; and

iii. an organic initiator molecule comprising at least three oxygen atoms or at least three nitrogen atoms;

wherein the initiator comprises the peroxodisulfate and the organic initiator molecule in a molar ratio in the range of from 20:1 to 50:1. In one aspect of this embodiment it is preferred that the concentration of the initiator component iii. is in the range from 0.05 to 2 wt.-%, based on the amount of monomers to be polymerized. In another aspect of this embodiment it is preferred that the organic initiator molecule is selected from the group consisting of 2,2-dimethoxy-1,2-diphenylethan-1-one, 2,2-azobis-(2-amidinopropane)dihydrochloride, 2,2-azobis-(cyano valeric acid) or a combination of at least two thereof. In a further aspect of this embodiment it is preferred that the peroxodisulfate is of the general formula $M_2S_2O_8$, with $M$ being selected from the group consisting of $\text{NH}_4$, Li, Na, K or at least two thereof. The above described components are in particular suitable for UV initiation of the polymerization in step (vi) of the process of the present invention. Employing this composition further yields low residual monomer and reduced yellowing in the water-absorbent polymer particle, obtainable by the process according to the present invention.

In this context it should also be noted that step (iii), adding the polymerization initiator, may be realized before step (iv), simultaneously to step (iv), or overlapping in time with step (iv), i.e. when the oxygen content of the aqueous monomer solution is decreased. If a polymerization initiator system is used that comprises two or more components, one or more of the components of such a polymerization initiator system may, for example, be added before process step (iv), whereas the remaining component or the remaining components which are necessary to complete the activity of the polymerisation initiator system, are added
after process step (iv), perhaps even after process step (v). Independent of optional step (iv),
decreasing the oxygen content of the aqueous monomer solution may also be performed
before process step (iii) according to the invention.

In process step (iv) of the process according to the present invention the oxygen con-
tent of the aqueous monomer solution is optionally decreased. Independent of optional step
(iv), decreasing the oxygen content of the aqueous monomer solution may also be performed
before, during or after process step (ii) according to the invention. Preferably, the oxygen con-
tent of the aqueous monomer solution is decreased after the fine particles have been added in
process step (ii).

Whenever the oxygen content of the aqueous monomer solution is decreased, this may
be realized by bringing the aqueous monomer solution into contact with an inert gas, such as
nitrogen. The phase of the inert gas being in contact with the aqueous monomer solution is
free of oxygen and is thus characterized by a very low oxygen partial pressure. As a conse¬
quency oxygen converts from the aqueous monomer solution into the phase of the inert gas
until the oxygen partial pressures in the phase of the inert gas and the aqueous monomer solu¬
tion are equal. Bringing the aqueous monomer phase into contact with a phase of an inert gas
can be accomplished, for example, by introducing bubbles of the inert gas into the monomer
solution in co-current, countercurrent or intermediate angles of entry. Good mixing can be
achieved, for example, with nozzles, static or dynamic mixers or bubble columns. The oxygen
content of the monomer solution before the polymerization is preferably lowered to less than
1 ppm by weight, more preferably to less than 0.5 ppm by weight, based on the monomer so¬
lution.

In process step (v) of the process according to the present invention the aqueous
monomer solution is charged into a polymerization reactor, preferably onto a conveyor belt,
especially preferred at an upstream position of the conveyor belt and in process step (vi) the
monomers in the aqueous monomer solution are polymerized in the polymerization reactor,
thereby obtaining a polymer gel. If polymerization is performed on a conveyor belt as part of
the polymerization reactor, a polymer gel sheet is obtained in a downstream portion of the
conveyor belt, which, before drying, is comminuted in the first comminuting step and the
further comminuting step in order to obtain polymer gel particles.

As the polymerization reactor every reactor can be used which the person skilled in
the art would regard as appropriate for the continuous or batchwise polymerization of
monomers like acrylic acid in aqueous solutions. An example of a suitable polymerization
reactor is a kneading reactor. In a kneader the polymer gel formed in the polymerization of the
aqueous monomer solution may be comminuted continuously by, for example, contrarotatory stirrer shafts, as described in WO 2001/38402. Such a comminuting in the polymerization reactor may be performed prior to the comminuting in the first comminuting device.

Another example of a preferred polymerization reactor is a conveyor belt. As a conveyor belt that is useful for the process according to the present invention any conveyor belt can be used which the person skilled in the art considers to be useful as a support material onto which the above described aqueous monomer solution can be charged and subsequently polymerized to form a hydrogel.

The conveyor belt usually comprises an endless moving conveyor belt passing over supporting elements and at least two guide rollers, of which at least one is driven and one is configured so as to be adjustable. Optionally, a winding and feed system for a release sheet that may be used in sections on the upper surface of the conveyor belt is provided. The system includes a supply and metering system for the reaction components, and optional irradiating means arranged in the direction of movement of the conveyor belt after the supply and metering system, together with cooling and heating devices, and a removal system for the polymer gel strand that is arranged in the vicinity of the guide roller for the return run of the conveyor belt. In order to provide for the completion of polymerization with the highest possible space-time yield, according to the present invention, in the vicinity of the upper run of the conveyor belt on both sides of the horizontal supporting elements, starting in the area of the supply and metering systems, there are upwardly extending supporting elements, the longitudinal axes of which intersect at a point that is beneath the upper run, and which shape the conveyor belt that is supported by them so that it become suitably trough-shaped. Thus, according to the present invention, the conveyor belt is supported in the vicinity of the supply system for the reaction components by a plurality of trough-shaped supporting and bearing elements that form a deep trough-like or dish-like configuration for the reaction components that are introduced. The desired trough-like shape is determined by the shape and arrangement of the supporting elements along the length of the path of the upper run. In the area where the reaction components are introduced, the supporting elements should be relatively close to each other, whereas in the subsequent area, after the polymerization has been initiated, the supporting elements can be arranged somewhat further apart. Both the angle of inclination of the supporting elements and the cross-section of the supporting elements can be varied in order to flatten out the initially deep trough towards the end of the polymerization section and once again bring it to an extended state. In a further embodiment of the invention, each supporting element is preferably formed by a cylindrical or spherical roller that is rotatable
about its longitudinal axis. By varying both the cross-section of the roller as well as the configuration of the roller it is easy to achieve the desired cross-sectional shape of the trough. In order to ensure proper formation of the trough by the conveyor belt, both when it makes the transition from a flat to a trough-like shape and when it is once again returned to the flat shape, a conveyor belt that is flexible in both the longitudinal and the transverse directions is preferred.

The belt can be made of various materials, although these preferably have to meet the requirements of good tensile strength and flexibility, good fatigue strength under repeating bending stresses, good deformability and chemical resistance to the individual reaction components under the conditions of the polymerization. These demands are usually not met by a single material. Therefore, a multi-layer material is commonly used as belt of the present invention. The mechanical requirements can be satisfied by a carcass of, for example, fabric inserts of natural and/or synthetic fibers or glass fibers or steel cords. The chemical resistance can be achieved by a cover of, for example, polyethylene, polypropylene, polyisobutylene, halogenated polyolefins such as polyvinyl chloride or polytetrafluoroethylene, polyamides, natural or synthetic rubbers, polyester resins or epoxy resins. The preferred cover material is silicone rubber.

In process step (vii) of the process according to the present invention the polymer gel obtained in the polymerization reactor is comminuted, thereby obtaining polymer gel particles. Preferred polymer gel particles are one selected from the group consisting of polymer gel strands, polymer gel flakes, and polymer gel nuggets, or a combination of at least two thereof. Prior to the comminuting in the first comminuting device according to the invention a comminuting in the polymerization reactor, such as a kneading reactor, may be performed. The first comminuting device is preferably a separate device which is not identical to the polymerization reactor. Hence, the polymer gel may be comminuted prior to discharging out of the polymerization reactor. The comminuting of the polymer gel in the first comminuting device is performed after discharging the polymer gel out of the polymerization reactor. If the polymerization reactor is a conveyor belt, the polymer gel which is preferably a polymer gel sheet is discharged from the conveyor belt as a continuous sheet that is of a soft semi-solid consistency and is then passed on for further processing such as comminuting.

Comminution of the polymer gel strand is preferably performed in at least two steps: - by the first comminuting step in the first comminuting device at least two polymer gel strands each having the strand width are obtained. The first comminuting device preferably comprises a plurality of rotating discs, preferably rotating toothed wheels. Preferably, the
polymer gel is comminuted in the first comminuting device by contact to rotating discs, preferably rotating toothed wheels. A preferred first comminuting device comprises a first plurality of rotating discs and a further plurality of rotating discs, wherein the rotatings discs of the first plurality rotate in counter direction to the direction of rotation of the rotating discs of the further plurality. Preferably, the polymer gel is fed between the first plurality of rotating discs and the further plurality of rotating discs for comminution in the first comminuting step.

- by the further comminuting step in the further comminuting device polymer gel particles having a diameter or a width or both which is less than the strand width are obtained. Preferably, each polymer gel particle has a diameter or a width or both which is less than the strand width of the strand from which the polymer gel particle has been obtained in the first comminuting step. A preferred further comminuting device is a "wolf" (grinding) unit, preferably a mincer, preferably having a screw and a first hole plate, whereby the screw conveys against the first hole plate. Therein, holes of the first hole plate preferably comprise planar cutting edges. Preferably, the first hole plate rotates, preferably with respect to a further hole plate, preferably comprising a higher number of holes than the first hole plate.

An optimal surface-volume ratio is achieved hereby, which has an advantageous effect on the drying behaviour in process step (viii). A polymer gel, preferably a polymer gel sheet, which has been comminuted in this way is particularly suited to belt drying. The two-step comminution offers a better "airability" because of the air channels located between the granulate kernels.

The polymer gel particles obtained in the further comminuting step may be polymer gel strands having a width which is less than the strand width. The polymer gel particles obtained in the further comminuting step may also be nuggets or flakes or both. A diameter of a polymer gel particle is a length of a longest straight line, wherein the longest straight line connects two points which are located on a surface of the polymer gel particle, and crosses a geometric centre of the polymer gel particle. The strand width of a polymer gel strand is preferably a length over which the polymer gel strand extends in a direction which is perpendicular to the length of the polymer gel strand. A preferable strand width of a polymer gel strand is perpendicular to the length of the polymer gel strand and a direction along which the polymer gel strand extends over a length which is a thickness of the polymer gel sheet from which the polymer gel strand was obtained in the first comminuting step.

In process step (viii) of the process according to the present invention the polymer gel particles are dried.
The drying of the polymer gel particles can be effected in any dryer or oven the person skilled in the art considers as appropriate for drying the above described polymer gel particles. Rotary tube furnaces, fluidised bed dryers, plate dryers, paddle dryers and infrared dryers may be mentioned by way of example.

Especially preferred are belt dryers. A belt dryer is a convective system of drying, for the particularly gentle treatment of through-airable products. The product to be dried is placed onto an endless conveyor belt which lets gas through, and is subjected to the flow of a heated gas stream, preferably air. The drying gas is recirculated in order that it may become very highly saturated in the course of repeated passage through the product layer. A certain fraction of the drying gas, preferably not less than 10%, more preferably not less than 15% and most preferably not less than 20% and preferably up to 50%, more preferably up to 40% and most preferably up to 30% of the gas quantity per pass, leaves the dryer as a highly saturated vapor and carries off the water quantity evaporated from the product. The temperature of the heated gas stream is preferably not less than 50°C, more preferably not less than 100°C and most preferably not less than 150°C and preferably up to 250°C, more preferably up to 220°C and most preferably up to 200°C.

The size and design of the dryer depends on the product to be processed, the manufacturing capacity and the drying duty. A belt dryer can be embodied as a single-belt, multi-belt, multi-stage or multistory system. The present invention is preferably practiced using a belt dryer having at least one belt. One-belt dryers are very particularly preferred. To ensure optimum performance of the belt-drying operation, the drying properties of the water-absorbent polymers are individually determined as a function of the processing parameters chosen. The hole size and mesh size of the belt is conformed to the product. Similarly, certain surface enhancements, such as electropolishing or Teflonizing, are possible.

The polymer gel particles to be dried are preferably applied to the belt of the belt dryer by means of a swivel belt. The feed height, i.e. the vertical distance between the swivel belt and the belt of the belt dryer, is preferably not less than 10 cm, more preferably not less than 20 cm and most preferably not less than 30 cm and preferably up to 200 cm, more preferably up to 120 cm and most preferably up to 40 cm. The thickness on the belt dryer of the polymer gel particles to be dried is preferably not less than 2 cm, more preferably not less than 5 cm and most preferably not less than 8 cm and preferably not more than 20 cm, more preferably not more than 15 cm and most preferably not more than 12 cm. The belt speed of the belt dryer is preferably not less than 0.005 m/s, more preferably not less than 0.01 m/s and most
preferably not less than 0.015 m/s and preferably up to 0.05 m/s, more preferably up to 0.03 m/s and most preferably up to 0.025 m/s.

Furthermore, it is preferable according to the invention that the polymer gel is dried to a water content in the range of from 0.5 to 25 wt.-%, preferably from 1 to 10 wt.-% and particularly preferably from 3 to 7 wt.-%, based on the dried polymer gel particles.

In process step (ix) of the process according to the present invention the dried polymer gel particles are ground thereby obtaining particulate water-absorbent polymer particles.

For grinding of the dried polymer gel particles any device can be used the person skilled in the art considers as appropriate for grinding the above described dried polymer particles. As an example for a suitable grinding device a single- or multistage roll mill, preferably a two- or three-stage roll mill, a pin mill, a hammer mill or a vibratory mill may be mentioned.

In process step (x) of the process according to the present invention the ground water-absorbent polymer particles are sized, preferably using appropriate sieves. In this context it is particularly preferred that after sizing the water-absorbent polymer particles the content of polymer particles having a particle size of less than 150 µm is less than 10 wt.-%, preferably less than 8 wt.-% and particularly less than 6 wt.-% and that the content of polymer particles having a particle size of more than 850 µm is also less than 10 wt.-%, preferably less than 8 wt.-% and particularly preferably less than 6 wt.-%. It is also preferred that after sizing the water-absorbent polymer particles at least 50 wt.-%, more preferred at least 40 wt.-% and most preferred at least 30 wt.-% of the water-absorbent polymer particles have a particle size in a range of from 300 to 600 µm.

In process step (xi) of the process according to the present invention the surfaces of the ground and sized water-absorbent polymer particles are optionally treated. As measures to treat the surface of water-absorbent polymer particles any measure can be used the person skilled in the art considers as appropriate for such a purpose. Examples of surface treatments include, for example, surface crosslinking, the treatment of the surface with water-soluble salts, such as aluminium sulfate or aluminium lactate, the treatment of the surface with inorganic particles, such as silicon dioxide, and the like. Preferably, the components used to treat the surface of the polymer particles (cross-linker, water soluble salts) are added in the form of aqueous solutions to the water-absorbent polymer particles. After the particles have been mixed with the aqueous solutions, they are heated to a temperature in the range from 150 to 230°C, preferably 160 to 200°C in order to promote the surface-crosslinking reaction.

In an embodiment of the invention the strand width of the at least two polymer gel strands in step (vii) is in the range of from 10 to 100 mm, preferably from 10 to 90 mm, pref-
erably from 15 to 80 mm, more preferably from 20 to 70 mm, more preferably from 25 to 50 mm, most preferably from 30 to 50 mm.

In an embodiment of the invention the diameter or the width or both of the polymer gel particles in step (vii) is in the range of from 5 to 20 mm, preferably from 7 to 18 mm, more preferably from 9 to 16 mm, more preferably from 10 to 15 mm, most preferably from 12 to 14 mm.

In an embodiment of the invention the first comminuting device comprises at least one more, preferably at least two more, more preferably at least 5 more, more preferably at least 10 more, most preferably at least 20 more, rotating components than the further comminuting device. A preferred rotating component of the first comminuting device comes into contact with the polymer gel in the first comminuting step. A preferred rotating component of the further comminuting device comes into contact with at least one of the polymer gel strands or the polymer gel particles or both in the further comminuting step. A preferred rotating component is a rotating disc or a rotating shaft or both. Preferably, the first comminuting device comprises at least one more, preferably at least two more, more preferably at least 5 more, more preferably at least 10 more, most preferably at least 20 more, rotating disc and at least one more rotating shaft than the further comminuting device.

In an embodiment of the invention a plurality of water-absorbent particles is added to the at least two polymer gel strands or the polymer gel particles or both after the first comminuting step, preferably in the further comminuting step or in the further comminuting device, or both.

In an embodiment of the invention the water-absorbent particles to be added to the at least two polymer gel strands or the polymer gel particles or both have a particle diameter of less than 150 \(\mu m\), preferably less than 140 \(\mu m\), more preferably less than 130 \(\mu m\), more preferably less than 120 \(\mu m\), more preferably less than 110 \(\mu m\), most preferably less than 100 \(\mu m\).

In an embodiment of the invention an anti-sticking agent is added to the polymer gel or the at least two polymer gel strands or both in the first comminuting device, or to the at least two polymer gel strands or the polymer gel particles or both in the further comminuting device, or both. A preferred antisticking agent is a liquid, preferably an emulsion. Preferably the antisticking agent is added by spraying or dripping or both.

In an embodiment of the invention the antisticking agent comprises one selected from the group consisting of a solvent, a polyalkylsiloxane, and a surfactant, or a combination of at least two thereof. A preferred solvent is water. A preferred polyalkylsiloxane is polydimethylsiloxane. A preferred surfactant is one selected from the group consisting of a sugar ester, a
glycerine ester, a sorbitan fatty acid ester, and a sorbitan etoxylated fatty acid ester, or a combination of at least two thereof.

In an embodiment of the invention the surfactant is a compound according to the general formula R-(-O-CH2-CH2-)n-OX, wherein R is selected from C₄ to C₂₀, n is an integer in the range of from 10 to 10,000, preferably from 50 to 5,000, more preferably from 100 to 500, and X is H or M, wherein M is a metal ion. A particularly preferred compound according to said general formula is polyethylene glycol trimethylsilyl ether.

In an embodiment of the invention the antisticking agent comprises

a) the solvent in an amount in the range of from 95 to 99 wt.-%, preferably from 95.5 to 98.5 wt.-%, more preferably from 96.5 to 97.5 wt.-%,

b) the polyalkysiloxane in an amount in the range of from 0.5 to 5 wt.-%, preferably from 1 to 4 wt.-%, more preferably from 2.4 to 3.2 wt.-%, and

c) the surfactant in an amount in the range of from 0.01 to 1 wt.-%, preferably from 0.05 to 0.7 wt.-%, more preferably from 0.1 to 0.3 wt.-%,

each based on the total weight of the antisticking agent and the amounts in wt.-% adding up to a total of 100 wt.-%.

In an embodiment of the invention the first comminuting device comprises no knife. A knife is a cutting device which comprises a cutting edge. A preferred cutting edge is a blade.

In an embodiment of the invention the further comminuting device comprises a knife, comprising at least one planar cutting edge, preferably at least 2 planar cutting edges, more preferably at least 3 planar cutting edges, more preferably at least 4 planar cutting edges, most preferably at least planar cutting edges. A preferred planar cutting edge is circular. Another preferred cutting edge is an edge of a hole. A preferred hole is a hole of a rotating hole plate of a mincer.

In an embodiment of the invention the further comminuting device comprises a knife, not comprising a non-planar cutting edge.

In an embodiment of the invention in process step (vii) prior to the further comminuting step the at least two polymer gel strands are subjected to an intermediate comminuting step in an intermediate comminuting device, whereby a length of the at least two polymer gel strands is decreased. A preferred intermediate comminuting device comprises a knife, comprising a planar cutting edge. A preferred planar cutting edge rotates. Another preferred intermediate comminuting device comprises two planar cutting edges, which incline an angle in the range of from 1 to 20°, preferably from 2 to 15°, most preferably from 5 to 10°. Preferably,
the two planar cutting edges rotate against each other. Preferably the intermediate comminuting device comminutes the at least two polymer gel strands by a scissor-like cutting action of the two planar cutting edges. Preferably the at least two polymer gel strands which are introduced to the intermediate comminuting device are semi-endless and spaghetti-like, and the intermediate comminuting device decreases the length of the at least two polymer gel strands to a length in the range of from 5 to 50 mm.

In an embodiment of the invention the first comminuting device comminutes the polymer gel by contact to at least two, preferably at least three, more preferably at least four, more preferably at least five, more preferably at least six, more preferably at least seven, more preferably at least eight, more preferably at least nine, more preferably at least ten, more preferably at least fifteen, most preferably at least twenty, toothed wheels.

In an embodiment of the invention the further comminuting device conveys the at least two polymer gel strands by a screw.

In an embodiment of the invention the polymer gel being discharged in process step (vii) comprises water in the range of from 40 to 60 wt.-%, preferably from 50 to 60 wt.-%, more preferably from 53 to 56 wt.-%, based on the polymer gel.

In an embodiment of the invention the polymer gel being discharged in process step (vii) is a polymer gel sheet; wherein the polymer gel sheet is characterized by a thickness in the range of from 10 to 200 mm, preferably from 10 to 100 mm, more preferably from 15 to 75 mm, most preferably from 15 to 50 mm.

In an embodiment of the invention the polymer gel being discharged in process step (vii) is a polymer gel sheet; wherein the polymer gel sheet is characterized by a width in the range of from 30 to 300 cm, preferably from 50 to 250 cm, more preferably from 60 to 200 cm, most preferably from 80 to 100 cm.

In an embodiment of the invention the polymerization in step (vi) is performed in presence of a blowing agent. The blowing agent may be added to the aqueous monomer solution in one selected from the group consisting of step (i), step (ii), step (iii), step (iv), step (v), and step (vi), or in a combination of at least two thereof. Preferably, the blowing agent is added to the monomer solution in step (i). The blowing agent should be added prior or immediately after the polymerization in step (vi) is initiated. Particularly preferably, the blowing agent is added to the monomer solution after or simultaneously to adding the initiator or a component of an initiator system. Preferably the blowing agent is added to the monomer solution in an amount in the range of from 500 to 4000 ppm by weight, preferably from 1000 to
3500 ppm by weight, more preferably from 1500 to 3200 ppm by weight, most preferably from 2000 to 3000 ppm by weight, based on the total weight of the monomer solution.

A blowing agent is a substance which is capable of producing a cellular structure or pores or both via a foaming process during polymerization of the monomers. The foaming process is preferably endothermic. A preferred endothermic foaming process is started by heat from an exothermic polymerisation or crosslinking or both reaction. A preferred blowing agent is a physical blowing agent or a chemical blowing agent or both. A preferred physical blowing agent is one selected from the group consisting of a CFC, a HCFC, a hydrocarbon, and C0₂, or a combination of at least two thereof. A preferred C0₂ is liquid C0₂. A preferred hydrocarbon is one selected from the group consisting of pentane, isopentane, and cyclopentane, or a combination of at least two thereof. A preferred chemical blowing agent is one selected from the group consisting of a carbonate blowing agent, a nitrite, a peroxide, calcined soda, an oxalic acid derivative, an aromatic azo compound, a hydrazine, an azide, a N,N'-Dinitrosoamide, and an organic blowing agent, or a combination of at least two thereof.

A very particularly preferred blowing agent is a carbonate blowing agent. Carbonate blowing agents which may be used according to the invention are disclosed in US 5, 118, 719 A, and are incorporated herein by reference. A preferred carbonate blowing agent is a carbonate containing salt, or a bicarbonate containing salt, or both. Another preferred carbonate blowing agent comprises one selected from the group consisting of C0₂ as a gas, C0₂ as a solid, ethylene carbonate, sodium carbonate, potassium carbonate, ammonium carbonate, magnesium carbonate, or magnesium hydroxide carbonate, calcium carbonate, barium carbonate, a bicarbonate, a hydrate of these, other cations, and naturally occurring carbonates, or a combination of at least two thereof. A preferred naturally occurring carbonate is dolomite. The above mentioned carbonate blowing agents release C0₂ when being heated while dissolved or dispersed in the monomer solution. A particularly preferred carbonate blowing agent is MgC0₃, which may also be represented by the formula (MgC0₃)₄.Mg(OH)₂.5H₂O. Another preferred carbonate blowing agent is agent is (NH₄)₂C0₃. The MgC0₃ and (NH₄)₂C0₃ may also be used in mixtures. Preferred carbonate blowing agents are carbonate salts of multivalent cations, such as Mg, Ca, Zn, and the like. Examples of such carbonate blowing agents are Na₂C0₃, K₂C0₃, (NH₄)₂C0₃, MgC0₃, CaC0₃, NaHC0₃, KHCO₃, NH₄HC0₃, Mg(HC0₃)₂, Ca(HC0₃)₂, ZnC0₃, and BaC0₃. Although certain of the multivalent transition metal cations may be used, some of them, such as ferric cation, can cause color staining and may be subject to reduction oxidation reactions or hydrolysis equilibria in water. This may lead to difficulties in quality control of the final polymeric product. Also, other mul-
tivalent cations, such as Ni, Ba, Cd, Hg would be unacceptable because of potential toxic or skin sensitizing effects.

A preferred nitrite is ammonium nitrite. A preferred peroxide is hydrogen peroxide. A preferred aromatic azo compound is one selected from the group consisting of a triazene, arylazosulfones, arylazotriarylmethanes, a hydrazo compound, a diazoether, and diazoamino benzene, or a combination of at least two thereof. A preferred hydrazine is phenylhydrazine. A preferred azide is a carbonyl azide or a sulfonyl azide or both. A preferred N,N'-Dinitrosoamide is N,N'-diethyl-N,N'-dinitrosoterephthalamide.

A contribution to solving at least one of the above objects is provided by a device for the preparation of water-absorbent polymer particles in a process stream, comprising

a) a first container, designed to take an aqueous monomer solution, comprising at least one partially neutralized, monoethylenically unsaturated monomer bearing carboxylic acid groups (a1);

b) a further container, designed to take at least one crosslinker (a3);

c) a mixing device, wherein the mixing device is

i) located down-stream to the first container and the further container,

ii) designed to mix the monomer solution and the at least one crosslinker (a3);

d) a polymerization reactor, wherein the polymerization reactor is

i) located down-stream to the first container and the further container,

ii) designed to comprise the aqueous monomer solution and the at least one crosslinker (a3) during polymerizing the monomers in the aqueous monomer solution, thereby obtaining a polymer gel;

e) a first comminuting device, wherein the first comminuting device is

i) located down-stream to the polymerization reactor,

ii) designed to subject the polymer gel to a first comminuting step, thereby obtaining at least two polymer gel strands each having a strand width;

f) a further comminuting device, wherein the further comminuting device is

i) located down-stream to the first comminuting device,
ii) designed to subject the at least two polymer gel strands to a further comminuting step, thereby obtaining polymer gel particles having a diameter or a width or both which is less than the strand width;

g) a belt dryer, wherein the belt dryer is

5 i) located down-stream to the further comminuting device,
   ii) designed to dry the polymer gel particles,

h) a grinding device, wherein the grinding device is

10 i) located down-stream to the belt dryer,
   ii) designed to grind the dried polymer gel, thereby obtaining water-absorbent polymer particles;

j) a sizing device, wherein the sizing device is

15 i) located down-stream to the grinding device,
   ii) designed to size the grinded water-absorbent polymer particles.

Therein, the mixing device may be identical to the polymerization reactor. Moreover, a comminuting different from the comminuting in the first comminuting device or the comminuting in the further comminuting device or both may be performed in the polymerization reactor. A preferred first comminuting device is a first comminuting device according to the process according to the invention. A preferred further comminuting device is a further comminuting device according to the process according to the invention. Preferred components or devices or both of the device according to the invention are designed according to the process according to the invention.

In an embodiment of the invention the device further comprises an intermediate comminuting device, wherein the intermediate comminuting device is

25 a) located down-stream to the first comminuting device and upstream to the further comminuting device,
   b) designed to subject the at least two polymer gel strands to an intermediate comminuting step, thereby decreasing a length of the at least two polymer gel strands.

A preferred intermediate comminuting device is the intermediate comminuting device according to the process according to the invention.

A contribution to the solution of at least one of the above objects is provided by a process for the preparation of water-absorbent polymer particles in the device
according to the invention. Preferably, the process comprises the process steps (i) to (xi) according to the invention.

A contribution to the solution of at least one of the above objects is provided by a water-absorbent polymer particle, obtainable by the process according to the invention. A further aspect of the present invention pertains to a plurality of surface-crosslinked water-absorbent polymer particles, comprising

a) a chelating agent, in particular EDTA, in an amount in the range of from 500 to 3,000 ppm by weight, preferably from 1,000 to 2,000 ppm by weight;

b) a polyalkylene glycol, in particular polyethylene glycol, in an amount in the range of from 500 to 3,000 ppm by weight, preferably from 1,000 to 2,000 ppm by weight; and

c) a SiO₂ in an amount in the range of from 500 to 3,000 ppm by weight, preferably from 1,000 to 2,000 ppm by weight;

each based on the weight of the plurality of surface-crosslinked water-absorbent polymer particles. According to a further aspect of this embodiment, the plurality of surface-crosslinked water-absorbent polymer particles further comprises Ag-zeolite, preferably in an amount in the range from 0.0001 to 1 wt.-part, more preferably in the range from 0.001 to 0.5 wt.-part and most preferred in the range of 0.002 to 0.01 wt.-part, each based on the total weight of the plurality of surface-crosslinked water-absorbent polymer particles.

A contribution to the solution of at least one of the above objects is provided by a plurality of water-absorbent polymer particles, comprising a polyalkylsiloxane, or a compound according to a general formula R-(-O-CH₂-CH₂)ₙ-OX, or both; wherein in the general formula R is C₄ to C₂₀, n is an integer in the range of from 10 to 10,000, preferably from 50 to 5,000, more preferably from 100 to 500, and X is H or M; wherein M is a metal ion. A particularly preferred compound according to said general formula is polyethylene glycol trimethylisomyl ether. A preferred polyalkylsiloxane is polydimethylsiloxane.

In an embodiment of the invention the plurality of water-absorbent polymer particles comprises

a) the polyalkylsiloxane in an amount in the range of from 0.01 to 1 wt.-%, preferably from 0.02 to 0.9 wt.-%, more preferably from 0.03 to 0.8 wt.-%, more preferably from 0.04 to 0.7 wt.-%, more preferably from 0.05 to 0.6 wt.-%, more preferably from 0.05 to 0.5 wt.-%, more preferably from 0.05 to 0.4 wt.-%, more
preferably from 0.05 to 0.3 wt.-%, more preferably from 0.05 to 0.2 wt.-%, more preferably from 0.06 to 0.15 wt.-%, most preferably from 0.07 to 0.11 wt.-%, or

b) the compound according to the general formula R-(O-CH₂)n-OX in an amount in the range of from 0.001 to 0.1 wt.-%, preferably from 0.002 to 0.09 wt.-%, more preferably from 0.003 to 0.08 wt.-%, more preferably from 0.002 to 0.07 wt.-%, more preferably from 0.002 to 0.06 wt.-%, more preferably from 0.002 to 0.05 wt.-%, more preferably from 0.002 to 0.04 wt.-%, more preferably from 0.002 to 0.03 wt.-%, more preferably from 0.002 to 0.02 wt.-%, more preferably from 0.002 to 0.01 wt.-%, most preferably from 0.001 to 0.009 wt.-%, or

c) both,

each based on the total weight of the plurality of water-absorbent polymer particles.

A contribution to the solution of at least one of the above objects is provided by a composite material comprising the water-absorbent polymer particle according to the invention, or the plurality of water-absorbent particles according to the invention.

In an embodiment of the invention the composite material according to the invention comprises one selected from the group consisting of a foam, a shaped article, a fibre, a foil, a film, a cable, a sealing material, a liquid-absorbing hygiene article, a carrier for plant and fungal growth-regulating agents, a packaging material, a soil additive, and a building material, or a combination of at least two thereof. A preferred cable is a blue water cable. A preferred liquid-absorbing hygiene article is one selected from the group consisting of a diaper, a tampon, and a sanitary towel, or a combination of at least two thereof. A preferred diaper is a baby's diaper or a diaper for incontinent adults or both.

A contribution to the solution of at least one of the above objects is provided by a process for the production of a composite material, wherein the water-absorbent polymer particle according to the invention or the plurality of water-absorbent polymer particles according to the invention, and a substrate, and optionally an auxiliary substance are brought into contact with one another.

A contribution to the solution of at least one of the above objects is provided by a composite material obtainable by a process according to the invention.

A contribution to the solution of at least one of the above objects is provided by a use of the water-absorbent polymer particle according to the invention, or the plurality of water-absorbent polymer particles according to the invention in a foam, a shaped article, a fibre, a
foil, a film, a cable, a sealing material, a liquid-absorbing hygiene article, a carrier for plant
and fungal growth-regulating agents, a packaging material, a soil additive, for controlled re-
lease of an active compound, or in a building material.

Test Methods

The following test methods are used in the invention. In absence of a test method, the
ISO test method for the feature to be measured being closest to the earliest filing date of the
present application applies. If no ISO test method is available, the EDANA test method being
closest to the earliest filing date of the present application applies. In absence of distinct mea-
suring conditions, standard ambient temperature and pressure (SATP) as a temperature of
298.15 K (25 °C, 77 °F) and an absolute pressure of 100 kPa (14.504 psi, 0.986 atm) apply.

water content

The water content after drying is determined according to the Karl Fischer method.

Examples

The present invention is now explained in more detail by examples and drawings
given by way of example which do not limit it.

A) Preparation of a partially neutralized acrylic acid monomer solution

0.4299 wt.-parts of water are mixed in an adequate container with 0.27 wt.-parts of
acrylic acid and 0.0001 wt.-parts of mono methyl ether hydroquinone (MEHQ). 0.2 wt.-parts
of an aqueous 48 wt.-% sodium hydroxide solution are added to the mixture. A sodium-
acrylate monomer solution with a neutralization ratio of 70 mol-% is achieved.

Optionally the sodium-acrylate monomer solution is degased with nitrogen.

B) Polymerization of the monomer solution

1 wt.-part of the monomer solution prepared in step A) is mixed with 0.001 wt.-parts
of trimethylol propane triacrylate as crosslinker, 0.001 wt.-parts of sodium peroxodisulfate as
first initiator component, 0.000034 wt.-parts of 2,2-dimethoxy-1,2-diphenylethan-1-one (Ci-
ba® Irgacure® 651 by Ciba Specialty Chemicals Inc., Basel, Switzerland) as a second initiator
component, up to 0.1 wt.-parts of acrylic acid particles (with a particle size of less than
150 µm) in a container to achieve a mixed solution. If according to table 1 below a blowing
agent is added, 0.1 wt.-part, based on the total amount of the mixed solution, of sodium carbonate are added to the mixed solution.

A sufficient amount of the mixed solution is subjected to further treatment in order to obtain a polymer gel and further downstream water-absorbent polymer particles and further downstream surface-crosslinked water-absorbent polymer particles as well as further downstream a water-absorbent product which is post treated. Details of the further treatment are given below.

Subsequently, the mixed solution is placed on the belt of a conveyor belt reactor and the polymerization is initiated by UV radiation. The conveyor belt has a length of at least 20 m and a width of 0.8 m. The conveyor belt is formed as a trough to keep the solution on the belt while polymerized. The dimensions of the conveyor belt and the conveying speed of the conveyor belt are selected in a way that a poly-acrylic acid gel is formed at a downstream end of the belt. At the end of this step a water-absorbent polymer gel is achieved. The polymer gel has a water content of about 52 wt.-%, based on the total weight of the polymer gel.

C) Comminuting and drying of the polymer gel

The polymer gel forms a polymer gel strand which is discharged from the conveyor belt and comminuted in the steps:

- The polymer gel is cut into a plurality of gel strands by a crusher as shown in figure 7. The gel strips have a length in the range from 10 to 20 cm and a width in the range of from 30 to 50 mm, then

- a mincer according to figure 8a) and 8b) is used to shred the strands into gel particles having a width in the range from 12 to 14 mm,

wherein the above given comminuting devices according to the invention are used in the examples 1 to 3. Additionally, an intermediate comminuting device is used in example 4. Different comminuting devices are used in the comparative examples.

The comminuted gel is dried in a belt dryer at a temperature of 180 °C to a water content of 5 wt.-% based on the dried polymer gel. The belt of the belt drier provides orifices, where hot air is pressed into the polymer gel via nozzles. Additionally hot air is blown from above the belt onto the gel.

D) Milling and sizing

The dried polymer gel is ground in three steps. First the dried polymer gel is fed through a Herbold Granulator HGM 60/145 (HERBOLD Meckesheim GmbH) and the achieved parts of the dried polymer gel have a size of less than 7 mm and are then kept for 2.5 hours in a container to equalize the humidity content of the polymer gel parts. The dried po-
lymer gel parts are then milled in a roller mill of Bauermeister Type 350.1 x 1800 (3-stage crusher) (Bauermeister Zerkleinerungstechnik GmbH) to obtain water-absorbent polymer particles having a particle size of less than 1 mm.

The water absorbent polymer particles are sieved with a tumbler sieves having several screens. The mesh sizes of the screens change from 20, 30, 40, 50, 60 to 100 U.S.-mesh. At least 50 wt.-% of the obtained water-absorbent polymer particles have a particles size in the range of from 300 to 600 μm. Less than 5 wt.-% of the water-absorbent polymer particles of the examples according to the invention are smaller than 150 μm, less than 5 wt.-% of the water-absorbent polymer particles of the examples according to the invention are have a particle size of more than 850 μm. The obtained water-absorbent polymer particles are named precursor I.

E) Silicon dioxide treatment

In a treatment step the precursor I is mixed in a disc mixer with about 0.01 wt.-part (+-10 %) of silicon dioxide (SiO₂), based on the total weight of the precursor I plus SiO₂. The silicon dioxide is used in form of Sipernat ® 22 obtainable from Evonik Industries AG, Essen, Germany. When mixing the precursor I with the SiO₂, the precursor still has a temperature of more than 80 °C to 100 °C, preferably of 100 °C. A precursor II is achieved.

F) Surface crosslinking

In a further step 1 wt.-part of the precursor II is mixed with 0.003 wt.-part (+-10 %) of a surface crosslinker, based on the total weight of the mixture of precursor II and crosslinker. The surface crosslinker is composed of 19 wt.-% water, 40 wt.-% ethylene glycol diglycidyl ether, 1 wt.-% Na₂SC>₃, 40 wt.-% polyethylene glycol with a molecular weight of 400 g/mol, each based on the total amount of the crosslinker. The ingredients of the crosslinker are mixed in a line static mixer. The crosslinker is mixed in a ringlayer mixer CoriMix ® CM 350 (Gebruder Lodige Maschinenbau GmbH, Paderborn, Germany) with precursor II. The mixture is heated to a temperature in the range of from 130 to 160 °C. The mixture is then dried in a paddle dryer Andritz Gouda Paddle Dryer, preferably of type GPWD12W120, by Andritz AG, Graz, Austria for 45 minutes at a temperature in the range of from 130 to 160 °C. Surface-cross-linked absorbent polymer particles are obtained.

In a cooling device in the form of a fluid bed, the temperature of the surface-cross-linked absorbent polymer particles is decreased to below 60 °C, obtaining cooled surface-cross-linked absorbent polymer particles referred as to precursor III.
G) Post treatment

1 wt.-part of precursor III is then subjected to mixing with 0.005 wt.-part Ag-zeolite. Subsequently, the mixture is sieved. The sieve is selected to separate agglomerates of the cooled surface-cross-linked absorbent polymer particle having a particle size of more than 850 µm. At least 50 wt.-% of the surface-crosslinked absorbent polymer particles have a particles size in the range of from 300 to 600 µm. Less than 5 wt.-% of the surface-crosslinked absorbent polymer particles of the examples according to the invention are smaller than 150 µm, less than 5 wt.-% of the surface-crosslinked absorbent polymer particles of the examples according to the invention are have a particle size of more than 850 µm. Post treated crosslinked water-absorbent polymer particles are obtained.

The following scale is used to compare the results of measuring the parameters given in the tables 1 and 2 for the examples and the comparative examples. In the order given in the following the measurement results are getting better from left to right: – , − , + , ++ , +++ , ++++. 

<table>
<thead>
<tr>
<th>Example</th>
<th>Lifetime of device 1</th>
<th>Lifetime of device 2</th>
<th>Lifetime of device 3</th>
<th>Blowing agent</th>
<th>Antisticking agent</th>
<th>Drying time / kg polymer gel particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>+</td>
<td>/</td>
<td>+</td>
<td>none</td>
<td>none</td>
<td>+</td>
</tr>
<tr>
<td>Example 2</td>
<td>+</td>
<td>/</td>
<td>+</td>
<td>sodium carbonate</td>
<td>none</td>
<td>++</td>
</tr>
<tr>
<td>Example 3</td>
<td>+</td>
<td>/</td>
<td>+</td>
<td>sodium carbonate</td>
<td>diluted EG-601</td>
<td>+++</td>
</tr>
<tr>
<td>Example 4</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>sodium carbonate</td>
<td>diluted EG-601</td>
<td>++++</td>
</tr>
<tr>
<td>Comparative Example 1</td>
<td>-</td>
<td>/</td>
<td>/</td>
<td>none</td>
<td>none</td>
<td>--</td>
</tr>
<tr>
<td>Comparative Example 2</td>
<td>-</td>
<td>/</td>
<td>/</td>
<td>sodium carbonate</td>
<td>none</td>
<td>-</td>
</tr>
<tr>
<td>Comparative Example 3</td>
<td>-</td>
<td>/</td>
<td>/</td>
<td>sodium carbonate</td>
<td>diluted EG-601</td>
<td>+</td>
</tr>
</tbody>
</table>

Table 1: Lifetimes of comminuting devices, blowing agent and antisticking agent applied and resulting drying time of polymer gel particles.
In the examples 1, 2 and 3 according to the invention the following comminuting devices are used. Device 1 is the crusher in figure 7, and device 3 is the mincer in figures 8a) and 8b). No intermediate device 2 is used. In the example 4 according to the invention the following comminuting devices are used. Device 1 is the crusher in figure 7, device 2 is a shredder comprising two planar cutting edges which rotate against each other and incline an angle of about 10°. The shredder comminutes the polymer gel strands obtained from the crusher by a scissor-like action of the cutting edges. Device 3 is the mincer in figures 8a) and 8b). In the comparative examples 1 to 3 only a device 1 is used for comminuting. Said device 1 is the mincer in figures 8a) and 8b).

As can be seen by comparing the results of example 1 and the comparative example 1, a sequence of comminuting steps applying the crusher and the mincer results in a longer operational lifetime of the mincer (in example 1 as device 3, in comparative example 1 as device 1). The operational lifetime is the operational time after which a comminuting tool of the corresponding comminuting device has to be exchanged or serviced as it shows a damage or a deterioration. Moreover, the drying time, hence the time required to dry the comminuting polymer gel to a water content of 5 wt.-% based on the dried polymer gel as described above, is less in example 1 than in the comparative example 1.

Moreover, table 1 shows that the drying time is less if a blowing agent, here sodium carbonate, is applied. Additionally, adding an antisticking agent to the device 1 while comminuting the polymer gel in the device 1 reduces the drying time further. The antisticking agent is obtained from a polydimethyl siloxane emulsion (EG-601 by Eugene Industry, 166, Nongso-ri, Juchon-myon, Gimhae-si, Gyengnam, Korea) by diluting the emulsion with water to a water content of 97 wt.-% based on the weight of the diluted emulsion.

In example 4 according to the invention an intermediate comminuting device (device 2) is used as described above. As shown with respect to example 3, this leads to a longer operational lifetime of the mincer (device 3) and to a further reduction of the drying time.

Figure 1 shows a flow chart diagram depicting the steps 101 to 111 of a process 100 for the preparation of water-absorbent polymer particles according to the invention. In a first step 101 an aqueous monomer solution comprising at least one partially neutralized, monoe-thylenically unsaturated monomer bearing carboxylic acid groups (al) and at least one cross-linker (a3) is provided. Preferably, the aqueous monomer solution is an aqueous solution of partially neutralized acrylic acid, further comprising crosslinkers. In a second step 102 fine particles of a water-absorbent polymer are added to the aqueous monomer solution. In a third step 103 a polymerization initiator or at least one component of a polymerization initiator
system that comprises two or more components is added to the aqueous monomer solution. In a fourth step 104 the oxygen content of the aqueous monomer solution is decreased by bubbling nitrogen into the aqueous monomer solution. In a fifth step 105 the monomer solution is charged onto a belt of a polymerization belt reactor as a polymerization reactor 904. The belt is an endless conveyor belt. In a sixth step 106 the aqueous monomer solution is polymerized to a polymer gel 401. The polymer gel 401 is a polymer gel sheet. In a seventh step 107 the polymer gel 401 is discharged from the belt. Subsequently, the polymer gel 401 is subjected to a first comminuting step in a first comminuting device 402, thereby obtaining at least two polymer gel strands 403 each having a strand width 406. Subsequently the at least two polymer gel strands 403 are subjected to a further comminuting step in a further comminuting device 404, thereby obtaining polymer gel particles 405 having a diameter 408 or a width 407 or both which is less than the strand width 406. In an eighth step 108 the polymer gel particles 405 are charged onto a belt of a belt dryer 905 and subsequently dried at a temperature of about 120 to 150°C. The dried polymer gel particles are discharged from the belt dryer 905 and subsequently in a ninth step 109 grinded to obtain water-absorbent polymer particles. In a tenth step 110 the water-absorbent polymer particles are sized to obtain water-absorbent polymer particles having a well defined particle size distribution. In an eleventh step 111 the surface of the water-absorbent polymer particles is treated in terms of a surface crosslinking.

Figure 2 shows a flow chart diagram depicting the steps 101 to 111 of a process 100 for the preparation of water-absorbent polymer particles according to the invention. The process 100 shown in figure 2 is the same as the process 100 in figure 1, wherein the third process step 103 and the fourth process step 104 overlap in time. While the polymerization initiator is added to the aqueous monomer solution, nitrogen is bubbled into the aqueous monomer solution in order to decrease its oxygen content.

Figure 3 shows a flow chart diagram depicting the steps 101, 103, 105 to 110 of a process 100 for the preparation of water-absorbent polymer particles according to the invention. The process 100 shown in figure 3 is the same as the process 100 in figure 1, wherein the second step 102, the fourth step 104, and the eleventh step 111 are not part of the process 100 according to figure 3.

Figure 4 shows a scheme of a sequence of comminuting steps of step (vii) 107 of the process 100 according to the invention. A polymer gel 401, which is a polymer gel sheet obtained by polymerization on a belt of a polymerization belt reactor as a polymerization reactor 904, is fed into a first comminuting device 402 and thus subjected to a first comminuting step, thereby obtaining two polymer gel strands 403 each having a strand width 406. The two
polymer gel strands 406 are fed into a further comminuting device 404 and thus subjected to a further comminuting step, thereby obtaining polymer gel particles 405 having a width 407 which is less than the strand width 406. The polymer gel particles 405 are strand-shaped.

Figure 5 shows a scheme of another sequence of comminuting steps of step (vii) 107 of the process 100 according to the invention. A polymer gel 401, which is a polymer gel sheet obtained by polymerization on a belt of a polymerization belt reactor as a polymerization reactor 904, is fed into a first comminuting device 402 and thus subjected to a first comminuting step, thereby obtaining three polymer gel strands 403 each having a strand width 406. The three polymer gel strands 403 are fed into a further comminuting device 404 and thus subjected to a further comminuting step, thereby obtaining polymer gel particles 405 having a width 407 which is less than the strand width 406. The polymer gel particles 405 are nugget-shaped.

Figure 6 shows a scheme of another sequence of comminuting steps of step (vii) 107 of the process 100 according to the invention. A polymer gel 401, which is a polymer gel sheet obtained by polymerization on a belt of a polymerization belt reactor as a polymerization reactor 904, is fed into a first comminuting device 402 and thus subjected to a first comminuting step, thereby obtaining three polymer gel strands 403 each having a strand width 406. The three polymer gel strands 403 are fed into a further comminuting device 404 and thus subjected to a further comminuting step, thereby obtaining polymer gel particles 405 having a diameter 408 which is less than the strand width 406. The polymer gel particles 405 are about spherical.

Figure 7 shows a scheme of a first comminuting device 402 according to the invention. The first comminuting device 402 comprises a plurality of toothed wheels 702. A first portion of the toothed wheels 702 rotates around a first axis of rotation 701 and a further portion of the toothed wheels 702 rotates around a further axis of rotation 701. The toothed wheels 402 of the first portion rotate in counter direction and towards the toothed wheels 402 of the further portion. A polymer gel 401 being fed between the rotating toothed wheels 402 is comminuting by the comminuting device 402 and at least two polymer gel strands 403 each having a strand width 406 of about 45 mm are obtained.

Figure 8a) shows a scheme of a further comminuting device 404 according to the invention in an external view. The further comminuting device 404 is a mincer ("meat grinder") comprising a static hole plate 801, a rotating screw 802, and a feed unit 803 for feeding a polymer gel 401 into the mincer. The polymer gel strands 403 obtained in the first comminuting
device 402 of figure 7 may be fed into the further comminuting device 404 by means of the feed unit 803.

Figure 8b) shows a scheme of inner parts the further comminuting device 404 of figure 8a) in an exploded view. The further comminuting device 404 comprises a screw 802 which rotates together with a rotating hole plate 804. Thereby, the screw 802 conveys the polymer gel strands 403 towards the static hole plate 801 and through holes of the static hole plate 801. As the rotating hole plate 804 rotates with respect to the static hole plate 801 circular cutting edges 805 of holes of the rotating hole plate 804 comminute the polymer gel strands to obtain polymer gel particles 405 (not shown). If the polymer gel strands 403 obtained in the first comminuting device 402 of figure 7 are comminuted in the further comminuting device 404, polymer gel particles 405 being nugget-shaped and having a width 407 of 10 mm are obtained.

Figure 9 shows a block diagram of a device 900 for the preparation of water-absorbent polymer particles according to the invention. The arrows show a direction of a process stream 908 of the preparation of water-absorbent polymer particles. The device 900 comprises a first container 901, a further container 902, downstream a mixing device 903, downstream a polymerization reactor 904, downstream a first comminuting device 402, downstream a further comminuting device 404, downstream a belt dryer 905, downstream a grinding device 906, and downstream a sizing device 907, each according to the process 100 according to the invention.
[CLAIMS]

[Claim 1]

A process (100) for the preparation of water-absorbent polymer particles, comprising the process steps of

(i) preparing an aqueous monomer solution comprising at least one partially neutralized, monoethylenically unsaturated monomer bearing carboxylic acid groups (al) and at least one crosslinker (a3);

(ii) optionally adding fine particles of a water-absorbent polymer to the aqueous monomer solution;

(iii) adding a polymerization initiator or a at least one component of a polymerization initiator system that comprises two or more components to the aqueous monomer solution;

(iv) optionally decreasing the oxygen content of the aqueous monomer solution;

(v) charging the aqueous monomer solution into a polymerization reactor (904);

(vi) polymerizing the monomers in the aqueous monomer solution in the polymerization reactor (904), thereby obtaining a polymer gel (401);

(vii) discharging the polymer gel (401) out of the polymerization reactor (904), and subjecting

c) the polymer gel (401) to a first comminuting step in a first comminuting device (402), thereby obtaining at least two polymer gel strands (403) each having a strand width (406), and

d) the at least two polymer gel strands (403) to a further comminuting step in a further comminuting device (404), thereby obtaining polymer gel particles (405) having a diameter (408) or a width (407) or both which is less than the strand width (406);

(viii) drying the polymer gel particles (405);

(ix) grinding the dried polymer gel particles thereby obtaining particulate water-absorbent polymer particles;

(x) sizing the grinded water-absorbent polymer particles; and

(xi) optionally treating the surface of the grinded and sized water-absorbent polymer particles.

[Claim 2]
The process (100) according to claim 1, wherein the strand width (406) of the at least two polymer gel strands (403) in step (vii) is in the range of from 10 to 100 mm.

[Claim 3]

The process (100) according to claim 1 or 2, wherein the diameter (408) or the width (407) or both of the polymer gel particles (405) in step (vii) is in the range of from 5 to 20 mm.

[Claim 4]

The process (100) according to any of the preceding claims, wherein the first comminuting device (402) comprises at least one more rotating component than the further comminuting device (404).

[Claim 5]

The process (100) according to any of the preceding claims, wherein a plurality of water-absorbent particles is added to the at least two polymer gel strands (403) or the polymer gel particles (405) or both after the first comminuting step.

[Claim 6]

The process (100) according to claim 5, wherein the water-absorbent particles to be added to the at least two polymer gel strands (403) or the polymer gel particles (405) or both have a particle diameter of less than 150 μη.

[Claim 7]

The process (100) according to any of the preceding claims, wherein an antisticking agent is added to the polymer gel (401) or the at least two polymer gel strands (403) or both in the first comminuting device (402), or to the at least two polymer gel strands (403) or the polymer gel particles (405) or both in the further comminuting device (404), or both.

[Claim 8]

The process (100) according to claim 7, wherein the antisticking agent comprises one selected from the group consisting of a solvent, a polyalkylsiloxane, and a surfactant, or a combination of at least two thereof.

[Claim 9]
The process (100) according to claim 8, wherein the surfactant is a compound according to the general formula \( R-(-\text{O}-\text{CH}_2\text{-CH}_2-)_n\text{-OX} \),
wherein \( R \) is selected from \( \text{C}_4 \) to \( \text{C}_{20} \), \( n \) is an integer in the range of from 10 to 10,000,
and \( X \) is H or M,
wherein M is a metal ion.

[Claim 10]

The process (100) according to claim 8 or 9, wherein the antisticking agent comprises

a) the solvent in an amount in the range of from 95 to 99 wt.-%,
b) the polyalkylsiloxane in an amount in the range of from 0.5 to 5 wt.-%, and
c) the surfactant in an amount in the range of from 0.01 to 1 wt.-%,
each based on the total weight of the antisticking agent and the amounts in wt.-% adding up to a total of 100 wt.-%.

[Claim 11]

The process (100) according to any of the preceding claims, wherein the first comminuting device (402) comprises no knife.

[Claim 12]

The process (100) according to any of the preceding claims, wherein the further comminuting device (404) comprises a knife, comprising at least one planar cutting edge (805).

[Claim 13]

The process (100) according to any of the preceding claims, wherein the further comminuting device (404) comprises a knife, not comprising a non-planar cutting edge.

[Claim 14]

The process (100) according to any of the preceding claims, wherein in process step (vii) prior to the further comminuting step the at least two polymer gel strands (403) are subjected to an intermediate comminuting step in an intermediate comminuting device, whereby a length of the at least two polymer gel strands (403) is decreased.

[Claim 15]
The process (100) according to any of the preceding claims, wherein the first comminuting device (402) comminutes the polymer gel (401) by contact to at least two toothed wheels (702).

[Claim 16]

The process (100) according to any of the preceding claims, wherein the further comminuting device (404) conveys the at least two polymer gel strands (403) by a screw (802).

[Claim 17]

The process (100) according to any of the preceding claims, wherein the polymer gel (401) being discharged in process step (vii) comprises water in the range of from 40 to 60 wt.-%, based on the polymer gel (401).

[Claim 18]

The process (100) according to any of the preceding claims, wherein the polymer gel (401) being discharged in process step (vii) is a polymer gel sheet; wherein the polymer gel sheet is characterized by a thickness in the range of from 10 to 200 mm.

[Claim 19]

The process (100) according to any of the preceding claims, wherein the polymer gel (401) being discharged in process step (vii) is a polymer gel sheet; wherein the polymer gel sheet is characterized by a width in the range of from 30 to 300 cm.

[Claim 20]

The process (100) according to any of the preceding claims, wherein the polymerization in step (vi) is performed in presence of a blowing agent.

[Claim 21]

A device (900) for the preparation of water-absorbent polymer particles in a process stream (908), comprising

a) a first container (901), designed to take an aqueous monomer solution, comprising at least one partially neutralized, monoethylenically unsaturated monomer bearing carboxylic acid groups (al);

b) a further container (902), designed to take at least one crosslinker (a3);
c) a mixing device (903), wherein the mixing device (903) is
   i) located down-stream to the first container (901) and the further container (902),
   ii) designed to mix the monomer solution and the at least one crosslinker (a3);

d) a polymerization reactor (904), wherein the polymerization reactor (904) is
   i) located down-stream to the first container (901) and the further container (902),
   ii) designed to comprise the aqueous monomer solution and the at least one crosslinker (a3) during polymerizing the monomers in the aqueous monomer solution, thereby obtaining a polymer gel (401);

e) a first comminuting device (402), wherein the first comminuting device (402) is
   i) located down-stream to the polymerization reactor (904),
   ii) designed to subject the polymer gel (401) to a first comminuting step, thereby obtaining at least two polymer gel strands (403) each having a strand width (406);

f) a further comminuting device (404), wherein the further comminuting device (404) is
   i) located down-stream to the first comminuting device (402),
   ii) designed to subject the at least two polymer gel strands (403) to a further comminuting step, thereby obtaining polymer gel particles (405) having a diameter (408) or a width (407) or both which is less than the strand width (406);

g) a belt dryer (905), wherein the belt dryer (905) is
   i) located down-stream to the further comminuting device (404),
   ii) designed to dry the polymer gel particles (405),

h) a grinding device (906), wherein the grinding device (906) is
   i) located down-stream to the belt dryer (905),
   ii) designed to grind the dried polymer gel, thereby obtaining water-absorbent polymer particles;

j) a sizing device (907), wherein the sizing device (907) is
   i) located down-stream to the grinding device (906),
   ii) designed to size the grinded water-absorbent polymer particles.
[Claim 22]
The device (900) according to claim 21, wherein the device (900) further comprises an intermediate comminuting device, wherein the intermediate comminuting device is
5 a) located down-stream to the first comminuting device (402) and upstream to the further comminuting device (404),
b) designed to subject the at least two polymer gel strands (403) to an intermediate comminuting step, thereby decreasing a length of the at least two polymer gel strands (403).

[Claim 23]
A process for the preparation of water-absorbent polymer particles in the device according to claim 21 or 22.

[Claim 24]
A water-absorbent polymer particle, obtainable by the process (100) according to any of claims 1 to 20, or 23.

[Claim 25]
A plurality of water-absorbent polymer particles, comprising a polyalkylsiloxane, or a compound according to a general formula R-(0-CH₂-CH₂⁻)ₙ-OX, or both; wherein in the general formula R is C₄ to C₂₀, n is an integer in the range of from 10 to 10,000, and X is H or M;
20 wherein M is a metal ion.

[Claim 26]
The plurality of water-absorbent polymer particles according to claim 25, wherein the plurality of water-absorbent polymer particles comprises
25 a) the polyalkylsiloxane in an amount in the range of from 0.01 to 1 wt.-%, or
b) the compound according to the general formula R-(0-CH₂-CH₂⁻)ₙ-OX in an amount in the range of from 0.001 to 0.1 wt.-%, or
c) both,
each based on the total weight of the plurality of water-absorbent polymer particles.

[Claim 27]
A composite material comprising the water-absorbent polymer particle according to claim 24, or the plurality of water-absorbent polymer particles according to claim 25 or 26.

[Claim 28]

The composite material according to claim 27, comprising one selected from the group consisting of a foam, a shaped article, a fibre, a foil, a film, a cable, a sealing material, a liquid-absorbing hygiene article, a carrier for plant and fungal growth-regulating agents, a packaging material, a soil additive, and a building material, or a combination of at least two thereof.

[Claim 29]

A process for the production of a composite material, wherein the water-absorbent polymer particle according to claim 24 or the plurality of water-absorbent polymer particles according to claim 25 or 26, and a substrate, and optionally an auxiliary substance are brought into contact with one another.

[Claim 30]

A composite material obtainable by a process according to claim 29.

[Claim 31]

A use of the water-absorbent polymer particle according to claim 24, or the plurality of water-absorbent polymer particles according to claim 25 or 26 in a foam, a shaped article, a fibre, a foil, a film, a cable, a sealing material, a liquid-absorbing hygiene article, a carrier for plant and fungal growth-regulating agents, a packaging material, a soil additive, for controlled release of an active compound, or in a building material.
A. CLASSIFICATION OF SUBJECT MATTER

- C08F 2/01 (2006.01)
- C08F 2/10 (2006.01)
- C08F 20/06 (2006.01)
- A61L 15/60 (2006.01)
- A61L 15/24 (2006.01)
- C08J 3/24 (2006.01)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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 practicable, search terms used)

- SPATEN (ALL English language databases), WPI, EPODOC, Espacenet, Google Patents, Google Scholar and Keywords: water-absorbent, superabsorbent, hydrogel, continuous polymerisation, multi-step comminuting, surfactant, anti-stick, polyalkylsiloxane, acrylic acid and like terms.
- EPODOC, WPI: Applicant name (SONGWON) search.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category*</th>
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<th>Relevant to claim No.</th>
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Documents are listed in the continuation of Box C

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- * Special categories of cited documents:
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Date of the actual completion of the international search: 6 August 2014

Date of mailing of the international search report: 06 August 2014

Name and mailing address of the ISA/AU:

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<td>US 2007/0041796 A1 (HUE et al.) 22 February 2007 Abstract; para. [0036-0054], [0072-0078], [0088-0090], [0122-0133], [0166], [0181], [0194-0197], [0207-0213], [0219], [0231], [0238], [0278-0290], [0326], [0354-0365]; Example 8; Figs. 3-7</td>
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<td>US 2005/0046069 A1 (SASABE et al.) 03 March 2005 Abstract, para. [0004], [0020], [0030], [0052], [0084-0089], [0103], [0111-0113], [0151-0172], [0193-0213]; Examples 1-8; Figs. 1-6</td>
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<td>WO 2004/007598 A1 (BASF AKTIENGESELLSCHAFT) 22 January 2004 Page 2, line 25 - page 3, line 2; page 10, lines 37-46; Example 2</td>
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End of Annex