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(54) **Title**: A PROCESS FOR PRODUCING SURFACE-POSTCROSSLINKED WATER-ABSORBENT POLYMER PARTICLES BY POLYMERIZING DROPLETS OF A MONOMER SOLUTION

(57) **Abstract**: The present invention relates to a process for producing surface-postcrosslinked water-absorbent polymer particles comprising polymerizing droplets of a monomer solution, wherein water-absorbent polymer particles having an average particle diameter from 150 to 400 μηη, an amount of water-absorbent polymer particles having a particle size of less than 100 μηη of less than 5% by weight and an amount of water-absorbent polymer particles having a particle size of more than 500 μηη of less than 5% by weight are coated with at least one surface-postcrosslinker and thermal surface-postcrosslinked.

A process for producing surface-postcrosslinked water-absorbent polymer particles by polymerizing droplets of a monomer solution

Description

The present invention relates to a process for producing surface-postcrosslinked water-absorbent polymer particles comprising polymerizing droplets of a monomer solution, wherein water-absorbent polymer particles having an average particle diameter from 150 to 400 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 5% by weight and an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 5% by weight are coated with at least one surface-postcrosslinker and thermal surface-postcrosslinked.

The preparation of water-absorbent polymer particles is described in the monograph "Modern Superabsorbent Polymer Technology", F.L. Buchholz and A.T. Graham, Wiley-VCH, 1998, on pages 71 to 103 (ISBN 978-0471194118).

To improve the use properties, for example, absorption under pressure AUL and absorption under high pressure (AUHL), water-absorbing polymer particles are generally surface-postcrosslinked. This increases the level of crosslinking of the particle surface, which can at least partly decouple the absorption under high pressure (AUHL) and the centrifuge retention capacity (CRC). Crosslinkers suitable for that purpose are compounds which can form covalent bonds to at least two carboxylate groups of the water-absorbing polymer particles.

The higher level of crosslinking of the particle surface reduces the swelling capacity. Thus, the centrifuge retention capacity (CRC) decreases with the particle size of the surface-postcrosslinked water-absorbent polymer particles (see the monograph "Modern Superabsorbent Polymer Technology", pages 190 to 193).

Being products which absorb aqueous solutions, water-absorbent polymer particles are used to produce diapers, tampons, sanitary napkins and other hygiene articles, but also as water-retaining agents in market gardening. Water-absorbent polymer particles are also referred to as "superabsorbent polymers" or "superabsorbents".

The preparation of water-absorbent polymer particles by polymerizing droplets of a monomer solution in a surrounding heated gas phase is described, for example, in WO 2008/009580 A1, WO 2008/052971 A1, WO2011/026876 A1, WO 2011/117263 A1, WO 2014/079694 A1, WO 2014/079710 A1, and the prior PCT application PCT/EP2015/050532.

The preparation of water-absorbent polymer particles by polymerizing droplets of a monomer solution in a surrounding hydrophobic solvent is described, for example, in

WO 2006/014031 A1, WO 2008/068208 A1, and the prior PCT application PCT/EP2014/072390.

Polymerization of monomer solution droplets ("dropletization polymerization") affords water-absorbent polymer particles of high roundness. The the roundness of the polymer particles and can be determined with the PartAn® 3001 L Particle Analysator (Microtrac Europe GmbH; Meerbusch; Germany).

It was an object of the present invention to provide water-absorbent polymer particles having improved properties, i.e. a high centrifuge retention capacity (CRC), a high absorption under no load (AUNL), a high absorption under load (AUL), and a high absorption under high load (AUHL).

The object is achieved by a process for producing surface-postcrosslinked water-absorbent polymer particles comprising polymerizing droplets of a monomer solution, comprising

a) at least one ethylenically unsaturated monomer which bears acid groups and may be at least partly neutralized,
b) optionally one or more crosslinker,
c) at least one initiator,
d) optionally one or more ethylenically unsaturated monomers copolymerizable with the monomers mentioned under a),
e) optionally one or more water-soluble polymers, and
f) water,

in a surrounding heated gas phase or in a surrounding hydrophobic solvent, coating the water-absorbent polymer particles with at least one surface-postcrosslinker and thermal surface-postcrosslinking of the coated water-absorbent polymer particles, wherein the water-absorbent polymer particles are optionally classified prior to the coating, the water-absorbent polymer particles have an average particle diameter (d_{50}) from 150 to 400 µm prior to the coating and after the optional classification, the amount of water-absorbent polymer particles having a particle size of less than 100 µm prior to the coating and after the optional classification is less than 5% by weight and the amount of water-absorbent polymer particles having a particle size of more than 500 µm prior to the coating and after the optional classification is less than 5% by weight.

The present invention is based on the finding that surface-postcrosslinked water-absorbent polymer particles that are based on water-absorbent polymer particles produced by polymerizing droplets of a monomer solution have a maximum of the absorption under high load (AUHL) at relative small particle diameters.

Detailed description of the invention

Preparation of the water-absorbent polymer particles

The water-absorbent polymer particles are prepared by a process, comprising the steps forming water-absorbent polymer particles by polymerizing a monomer solution, comprising

a) at least one ethylenically unsaturated monomer which bears acid groups and may be at least partly neutralized,
b) optionally one or more crosslinker,
c) at least one initiator,
d) optionally one or more ethylenically unsaturated monomers copolymerizable with the monomers mentioned under a),
e) optionally one or more water-soluble polymers, and
f) water,

in a surrounding heated gas phase or in a surrounding hydrophobic solvent, coating the water-absorbent polymer particles with at least one surface-postcrosslinker and thermal surface-postcrosslinking of the coated water-absorbent polymer particles, wherein the water-absorbent polymer particles are optionally classified prior to the coating, the water-absorbent polymer particles have an average particle diameter (d_{50}) from 150 to 400 µm, preferably from 170 to 379 µm, more preferably from 190 to 350 µm, most preferably from 200 to 330 µm, prior to the coating and after the optional classification, the amount of water-absorbent polymer particles having a particle size of less than 100 µm prior to the coating and after the optional classification is less than 5% by weight, preferably less than 2% by weight, more preferably less than 1% by weight, most preferably less than 0.5% by weight, and the amount of water-absorbent polymer particles having a particle size of more than 500 µm prior to the coating and after the optional classification is less than 5% by weight, preferably less than 2% by weight, more preferably less than 1% by weight, most preferably less than 0.5% by weight.

Preferred are water-absorbent polymer particles prior to the coating and after the optional classification having an average particle diameter (d_{50}) from 170 to 379 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 2% by weight, and an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 2% by weight.

More preferred are water-absorbent polymer particles prior to the coating and after the optional classification having an average particle diameter (d_{50}) from 190 to 350 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 1% by weight, and an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 1% by weight.

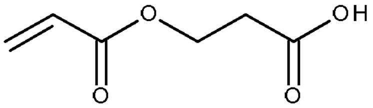
Most preferred are water-absorbent polymer particles prior to the coating and after the optional classification having an average particle diameter (d_{50}) from 200 to 330 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 0.5% by weight, an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 0.5% by weight.

The average particle diameter of the water-absorbent polymer particles to be coated and thermal surface-postcrosslinked can be adjusted by adjusting the droplet size of the monomer solution to be polymerized or by classifying of the water-absorbent polymer particles prior to the coating.

The water-absorbent polymer particles are typically insoluble but swellable in water.

The monomers a) are preferably water-soluble, i.e. the solubility in water at 23°C is typically at least 1 g/100 g of water, preferably at least 5 g/100 g of water, more preferably at least 25 g/100 g of water, most preferably at least 35 g/100 g of water.

Suitable monomers a) are, for example, ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, and itaconic acid. Particularly preferred monomers are acrylic acid and methacrylic acid. Very particular preference is given to acrylic acid having a concentration of diacrylic acid from 0 to 2% by weight, more preferably 0.0001 to 1% by weight, most preferably from 0.0002 to 0.5% by weight. Diacrylic acid is formed during the storage of acrylic acid via Michael addition and is given by following chemical structure:



Further suitable monomers a) are, for example, ethylenically unsaturated sulfonic acids such as vinylsulfonic acid, styrenesulfonic acid and 2-acrylamido-2-methylpropanesulfonic acid (AMPS).

Impurities may have a strong impact on the polymerization. Preference is given to especially purified monomers a). Useful purification methods are disclosed in WO 2002/055469 A1, WO 2003/078378 A1 and WO 2004/035514 A1. A suitable monomer a) is according to WO 2004/035514 A1 purified acrylic acid having 99.8460% by weight of acrylic acid, 0.0950% by weight of acetic acid, 0.0332% by weight of water, 0.0203 by weight of propionic acid, 0.0001% by weight of furfurals, 0.0001% by weight of maleic anhydride, 0.0003% by weight of diacrylic acid and 0.0050% by weight of hydroquinone monomethyl ether.

The content of acrylic acid and/or salts thereof in the total amount of monomers a) is preferably at least 50 mol%, more preferably at least 90 mol%, most preferably at least 95 mol%.

The acid groups of the monomers a) are typically partly neutralized, preferably to an extent of from 25 to 85 mol%, preferentially to an extent of from 50 to 80 mol%, more preferably from 60 to 75 mol%, for which the customary neutralizing agents can be used, preferably alkali metal hydroxides, alkali metal oxides, alkali metal carbonates or alkali metal hydrogen carbonates, and mixtures thereof. Instead of alkali metal salts, it is also possible to use ammonia or organic amines, for example, triethanolamine. It is also possible to use oxides, carbonates, hydrogen-carbonates and hydroxides of magnesium, calcium, strontium, zinc or aluminum as powders, slurries or solutions and mixtures of any of the above neutralization agents. An example for a mixture is a solution of sodiumaluminate. Sodium and potassium are particularly preferred as alkali metals, but very particular preference is given to sodium hydroxide, sodium carbonate or sodium hydrogen carbonate, and mixtures thereof. Typically, the neutralization is achieved by mixing in the neutralizing agent as an aqueous solution, as a melt or preferably also as a solid. For example, sodium hydroxide with water content significantly below 50% by weight may be present as a waxy material having a melting point above 23°C. In this case, metered addition as piece material or melt at elevated temperature is possible.

Optionally, it is possible to add to the monomer solution, or to starting materials thereof, one or more chelating agents for masking metal ions, for example iron, for the purpose of stabilization. Suitable chelating agents are, for example, alkali metal citrates, citric acid, alkali metal tatrates, alkali metal lactates and glycolates, pentasodium triphosphate, ethylenediamine tetraacetate, nitrilotriacetic acid, and all chelating agents known under the Trilon® name, for example Trilon® C (pentasodium diethylenetriaminepentaacetate), Trilon® D (trisodium (hydroxyethyl)-ethylenediaminetriacetate), and Trilon® M (methylglycinediacetic acid).

The monomers a) comprise typically polymerization inhibitors, preferably hydroquinone monoethers, as inhibitor for storage.

The monomer solution comprises preferably up to 250 ppm by weight, more preferably not more than 130 ppm by weight, most preferably not more than 70 ppm by weight, preferably not less than 10 ppm by weight, more preferably not less than 30 ppm by weight and especially about 50 ppm by weight of hydroquinone monoether, based in each case on acrylic acid, with acrylic acid salts being counted as acrylic acid. For example, the monomer solution can be prepared using acrylic acid having appropriate hydroquinone monoether content. The hydroquinone monoethers may, however, also be removed from the monomer solution by absorption, for example on activated carbon.

Preferred hydroquinone monoethers are hydroquinone monomethyl ether (MEHQ) and/or alpha-tocopherol (vitamin E).

Suitable crosslinkers b) are compounds having at least two groups suitable for crosslinking. Such groups are, for example, ethylenically unsaturated groups which can be polymerized by a free-radical mechanism into the polymer chain and functional groups which can form covalent bonds with the acid groups of monomer a). In addition, polyvalent metal ions which can form coordinate bond with at least two acid groups of monomer a) are also suitable crosslinkers b).

The crosslinkers b) are preferably compounds having at least two free-radically polymerizable groups which can be polymerized by a free-radical mechanism into the polymer network. Suitable crosslinkers b) are, for example, ethylene glycol dimethacrylate, diethylene glycol diacrylate, polyethylene glycol diacrylate, allyl methacrylate, trimethylolpropane triacrylate, triallylamine, tetraallylammonium chloride, tetraallyloxyethane, as described in EP 0 530 438 A1, di- and triacrylates, as described in EP 0 547 847 A1, EP 0 559 476 A1, EP 0 632 068 A1, WO 93/21237 A1, WO 2003/104299 A1, WO 2003/104300 A1, WO 2003/104301 A1 and in DE 103 31 450 A1, mixed acrylates which, as well as acrylate groups, comprise further ethylenically unsaturated groups, as described in DE 103 314 56 A1 and DE 103 55 401 A1, or crosslinker mixtures, as described, for example, in DE 195 43 368 A1, DE 196 46 484 A1, WO 90/15830 A1 and WO 2002/32962 A2.

Suitable crosslinkers b) are in particular pentaerythritol triallyl ether, tetraallyloxyethane, polyethyleneglycole diallylethers (based on polyethylene glycole having a molecular weight between 400 and 20000 g/mol), N,N’-methylenebisacrylamide, 15-tuply ethoxylated trimethylolpropane, polyethylene glycol diacrylate, trimethylolpropane triacrylate and triallylamine.

Very particularly preferred crosslinkers b) are the polyethoxylated and/or -propoxylated glycerols which have been esterified with acrylic acid or methacrylic acid to give di- or triacrylates, as described, for example in WO 2003/104301 A1. Di- and/or triacrylates of 3- to 18-tuply ethoxylated glycerol are particularly advantageous. Very particular preference is given to di- or triacrylates of 1- to 5-tuply ethoxylated and/or propoxylated glycerol. Most preferred are the triacrylates of 3- to 5-tuply ethoxylated and/or propoxylated glycerol and especially the triacrylate of 3-tuply ethoxylated glycerol.

The amount of crosslinker b) is preferably from 0.0001 to 0.6% by weight, more preferably from 0.0015 to 0.2% by weight, most preferably from 0.01 to 0.06% by weight, based in each case on monomer a). On increasing the amount of crosslinker b) the centrifuge retention capacity (CRC) decreases and the absorption under a pressure of 21.0 g/cm² (AUL) passes through a maximum.

The initiators c) used may be all compounds which disintegrate into free radicals under the polymerization conditions, for example peroxides, hydroperoxides, hydrogen peroxide, persulfates, azo compounds and redox initiators. Preference is given to the use of water-soluble initiators. In some cases, it is advantageous to use mixtures of various initiators, for example mixtures of hydrogen peroxide and sodium or potassium peroxodisulfate. Mixtures of hydrogen peroxide and sodium peroxodisulfate can be used in any proportion. The initiators c) should be water-soluble.

Particularly preferred initiators c) are azo initiators such as 2,2´-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride, 2,2´-azobis[2-(5-methyl-2-imidazolin-2-yl)propane] dihydrochloride, 2,2´-azobis(2-amidinopropane)dihydrochloride, 4,4´-azobis(4-cyanopentanoic acid), 4,4´-azobis(4-cyanopentanoic acid) sodium salt, 2,2´-azobis[2-methyl-N-(2-hydroxyethyl)-propionamide and 2,2´-azobis[2-(5-methyl-2-imidazolin-2-yl)propane] dihydrochloride, and photoinitiators such as 2-hydroxy-2-methylpropiophenone and 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one, redox initiators such as sodium persulfate/hydroxymethylsulfinic acid, ammonium peroxodisulfate/hydroxymethylsulfinic acid, hydrogen peroxide/hydroxymethylsulfinic acid, sodium persulfate/ascorbic acid, ammonium peroxodisulfate/ascorbic acid and hydrogen peroxide/ascorbic acid, photoinitiators such as 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one, and mixtures thereof. The reducing component used is, however, preferably a mixture of the sodium salt of 2-hydroxy-2-sulfinatoacetic acid, the disodium salt of 2-hydroxy-2-sulfonatoacetic acid and sodium bisulfite. Such mixtures are obtainable as Brüggolite® FF6 and Brüggolite® FF7 (Brüggemann Chemicals; Heilbronn; Germany). Of course it is also possible within the scope of the present invention to use the purified salts or acids of 2-hydroxy-2-sulfinatoacetic acid and 2-hydroxy-2-sulfonatoacetic acid – the latter being available as sodium salt under the trade name Blancolen® HP (Brüggemann Chemicals; Heilbronn; Germany).

In a preferred embodiment of the present invention a combination of at least one persulfate c_1) and at least one azo initiator c_2) is used as initiator c).

The amount of persulfate c_1) to be used is preferably from 0,01 to 0.25% by weight, more preferably from 0.05 to 0.2% by weight, most preferably from 0.1 to 0.15% by weight, each based on monomer a). If the amount of persulfate is too low, a sufficient low level of residual monomers cannot be achieved. If the amount of persulfate is too high, the water-absorbent polymer particles do not have a sufficient whiteness and may suffer degradation upon heating.

The amount of azo initiator c_2) to be used is preferably from 0,1 to 2% by weight, more preferably from 0.15 to 1% by weight, most preferably from 0.2 to 0.5% by weight, each based on monomer a). If the amount of azo initiator is too low, a high centrifuge retention capacity (CRC) cannot be achieved. If the amount of azo initiator is too high, the process becomes too expensive.

In a more preferred embodiment of the present invention a combination of at least one persulfate c_1), a reducing component, and at least one azo initiator c_2) is used as initiator c).

The amount of reducing component to be used is preferably from 0.0002 to 1% by weight, more preferably from 0.0001 to 0.8% by weight, more preferably from 0.0005 to 0.6% by weight, most preferably from 0.001 to 0.4% by weight, each based on monomer a).

Examples of ethylenically unsaturated monomers d) which are copolymerizable with the monomers a) are acrylamide, methacrylamide, hydroxyethyl acrylate, hydroxyethyl methacrylate, butanediol monoacrylate, butanediol monomethacrylate dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl acrylate, diethylaminopropyl methacrylate, polyethyleneoxid modified acrylates and methacrylates, for example Visomer® MPEG 750 MAW and Visomer® MPEG 2005 MAW (Evonik Industries AG, Essen, Germany), and N-vinylpyrrolidone.

Useful water-soluble polymers e) include polyvinyl alcohol, modified polyvinyl alcohol comprising acidic side groups for example Poval® K (Kuraray Europe GmbH; Frankfurt; Germany), polyvinylpyrrolidone, alginates, starch, starch derivatives, modified cellulose such as methylcellulose, carboxymethylcellulose or hydroxyethylcellulose, gelatin, polyglycols or polyacrylic acids, polyesters and polyamides, polylactic acid, polyvinylamine, polyallylamine, water soluble copolymers of acrylic acid and maleic acid available as Sokalan® (BASF SE; Ludwigshafen; Germany), preferably starch, starch derivatives and modified cellulose.

Additives for colour stability and additives for reducing residual monomers can also be added to the monomer solution.

The preferred amount of the additive for colour stability in the monomer solution is at least of 0.001%, preferably from 0.005% to 5% by weight, more preferably from 0.01 to 3% by weight, most preferably from 0.02 to 2% by weight, each based on monomer a).

Additives for colour stability are, for example, the following acids and/or their alkali metal salts (preferably Na and K-salts) are available and may be used within the scope of the present invention to impart colour stability to the finished product: 1-hydroxyethane-1,1-diphosphonic acid, amino-tris(methylene phosphonic acid), ethylenediamine-tetra(methylene phosphonic acid), diethylenetriamine-penta(methylene phosphonic acid), hexamethylene diamine-tetra(methylenephosphonic acid), hydroxyethyl-amino-di(methylene phosphonic acid), 2-phosphonobutane-1,2,4-tricarboxylic acid, bis(hexamethylenetriamine penta(methylene phosphonic acid)), 2-hydroxy-2-sulfonatoacetic acid and sodium bisulfite , sodium dihydrogenphospate, sodium hypophospite, trisodium salt of methylglycinediacetic acid, diethylenetriamine-pentaacetic acid.

More preferred is 2-hydroxy-2-sulfonatoacetic acid, which is available under the trade name Blancolen® HP and 1-Hydroxyethane 1,1-diphosphonic acid di sodium salt under the trade name Cublen® K 2012, trisodium salt of methylglycinediacetic acid is available under the trade name Trilon® M, diethylenetriaminepentaacetic acid is available under the trade name Trilon® C, sodium dihydrogenphospate, sodium hypophospite.

Most preferred is 2-hydroxy-2-sulfonatoacetic acid that is used in an amount of preferred from 0.005 to 1.0% by weight, more preferred 0.01 to 0.5% by weight, most preferred 0.1 to 0.3% by weight, each based on monomer a).

Additives for reducing residual monomers are described in EP 0 605 215 A1, for example nitrogen-containing compounds, sulfurous acid and salts thereof, hydrogen sulfite and salts thereof, phosphorous acid and salts thereof, pyrosulforous acid and salts thereof, hypophosphorous acid and salts thereof, and thiosulfuric acid and salts thereof, and can be also added in the surface-postcrosslinking step and/or in the coating step. More preferred are sodium and/or potassium bisulfite. Most preferred is the use of sodium bisulfite in the surface-postcrosslinking step. Sodium bisulfite is used in an amount of preferably 0.0001 to 1.0% by weight, more preferred 0.005 to 0.5% by weight, most preferred 0.025 to 0.1% by weight.

For optimal action, the preferred polymerization inhibitors require dissolved oxygen. Therefore, the monomer solution can be freed of dissolved oxygen before the polymerization by inertization, i.e. flowing through with an inert gas, preferably nitrogen. It is also possible to reduce the concentration of dissolved oxygen by adding a reducing agent. The oxygen content of the monomer solution is preferably lowered before the polymerization to less than 1 ppm by weight, more preferably to less than 0.5 ppm by weight.

The water content of the monomer solution is preferably less than 65% by weight, preferentially less than 62% by weight, more preferably less than 60% by weight, most preferably less than 58% by weight.

The monomer solution has, at 20°C, a dynamic viscosity of preferably from 0.002 to 0.02 Pa·s, more preferably from 0.004 to 0.015 Pa·s, most preferably from 0.005 to 0.01 Pa·s. The mean droplet diameter in the droplet generation rises with rising dynamic viscosity.

The monomer solution has, at 20°C, a density of preferably from 1 to 1.3 g/cm^3, more preferably from 1.05 to 1.25 g/cm^3, most preferably from 1.1 to 1.2 g/cm^3.

The monomer solution has, at 20°C, a surface tension of from 0.02 to 0.06 N/m, more preferably from 0.03 to 0.05 N/m, most preferably from 0.035 to 0.045 N/m. The mean droplet diameter in the droplet generation rises with rising surface tension.

Polymerization

The water-absorbent polymer particles are produced by polymerizing droplets of the monomer in a surrounding heated gas phase, for example using a system described in WO 2008/040715 A2, WO 2008/052971 A1, WO 2008/069639 A1 and WO 2008/086976 A1, or in a surrounding hydrophobic solvent, for example using a system described in WO 2008/068208 A1 and WO 2008/084031 A1.

The droplets are preferably generated by means of a droplet plate. A droplet plate is a plate having a multitude of bores, the liquid entering the bores from the top. The droplet plate or the liquid can be oscillated, which generates a chain of ideally monodisperse droplets at each bore on the underside of the droplet plate. In a preferred embodiment, the droplet plate is not agitated.

Within the scope of the present invention it is also possible to use two or more droplet plates with different bore diameters so that a range of desired particle sizes can be produced. It is preferable that each droplet plate carries only one bore diameter, however mixed bore diameters in one plate are also possible.

The number and size of the bores are selected according to the desired capacity and droplet size. The droplet diameter is typically 1.9 times the diameter of the bore. What is important here is that the liquid to be dropletized does not pass through the bore too rapidly and the pressure drop over the bore is not too great. Otherwise, the liquid is not dropletized, but rather the liquid jet is broken up (sprayed) owing to the high kinetic energy. In a preferred embodiment of the present invention the pressure drop is from 4 to 5 bar. The Reynolds number based on the throughput per bore and the bore diameter is preferably less than 2000, preferentially less than 1600, more preferably less than 1400 and most preferably less than 1200.

The underside of the droplet plate has at least in part a contact angle preferably of at least 60°, more preferably at least 75° and most preferably at least 90° with regard to water.

The contact angle is a measure of the wetting behavior of a liquid, in particular water, with regard to a surface, and can be determined using conventional methods, for example in accordance with ASTM D 5725. A low contact angle denotes good wetting, and a high contact angle denotes poor wetting.

It is also possible for the droplet plate to consist of a material having a lower contact angle with regard to water, for example a steel having the German construction material code number of 1.4571, and be coated with a material having a larger contact angle with regard to water.

Useful coatings include for example fluorous polymers, such as perfluoroalkoxyethylene, polytetrafluoroethylene, ethylene-chlorotrifluoroethylene copolymers, ethylene-tetrafluoroethylene copolymers and fluorinated polyethylene.

The coatings can be applied to the substrate as a dispersion, in which case the solvent is subsequently evaporated off and the coating is heat treated. For polytetrafluoroethylene this is described for example in US-3,243,321.

Further coating processes are to be found under the headword “Thin Films” in the electronic version of “Ullmann’s Encyclopedia of Industrial Chemistry” (Updated Sixth Edition, 2000 Electronic Release).

The coatings can further be incorporated in a nickel layer in the course of a chemical nickelization.

It is the poor wettability of the droplet plate that leads to the production of monodisperse droplets of narrow droplet size distribution.

The droplet plate has preferably at least 5, more preferably at least 25, most preferably at least 50 and preferably up to 2000, more preferably up to 1500 bores, most preferably up to 1000. The diameter of the bores is adjusted to the desired droplet size.

The spacing of the bores is usually from 2 to 50 mm, preferably from 3 to 40 mm, more preferably from 4 to 30 mm, most preferably from 5 to 25 mm. Smaller spacings of the bores may cause agglomeration of the polymerizing droplets.

The diameter of the bores size area is 1900 to 22300 µm², more preferably from 7800 to 20100 µm², most preferably from 11300 to 17700 µm². Circular bores are preferred with a bore size from 50 to 170 µm, more preferably from 100 to 160 µm, most preferably from 120 to 150 µm.

For optimizing the average particle diameter, droplet plates with different bore diameters can be used. The variation can be done by different bores on one plate or by using different plates, where the each plate has a different bore diameter. The average particle size distribution can be monomodal, bimodal or multimodal. Most preferably it is monomodal or bimodal.

The temperature of the monomer solution as it passes through the bore is preferably from 5 to 80°C, more preferably from 10 to 70°C, most preferably from 30 to 60°C.

A carrier gas flows through the reaction zone. The carrier gas may be conducted through the reaction zone in cocurrent to the free-falling droplets of the monomer solution, i.e. from the top downward. After one pass, the gas is preferably recycled at least partly, preferably to an extent of at least 50%, more preferably to an extent of at least 75%, into the reaction zone as cycle gas. Typically, a portion of the carrier gas is discharged after each pass, preferably up to 10%, more preferably up to 3% and most preferably up to 1%.

The oxygen content of the carrier gas is preferably from 0.1 to 25% by volume, more preferably from 1 to 10% by volume, most preferably from 2 to 7% by weight. In the scope of the present invention it is also possible to use a carrier gas which is free of oxygen.

As well as oxygen, the carrier gas preferably comprises nitrogen. The nitrogen content of the gas is preferably at least 80% by volume, more preferably at least 90% by volume, most preferably at least 95% by volume. Other possible carrier gases may be selected from carbon dioxide, argon, xenon, krypton, neon, helium, sulfurhexafluoride. Any mixture of carrier gases may be used. It is also possible to use air as carrier gas. The carrier gas may also become loaded with water and/or acrylic acid vapors.

The gas velocity is preferably adjusted such that the flow in the reaction zone (5) is directed, for example no convection currents opposed to the general flow direction are present, and is preferably from 0.1 to 2.5 m/s, more preferably from 0.3 to 1.5 m/s, even more preferably from 0.5 to 1.2 m/s, most preferably from 0.7 to 0.9 m/s.

The gas entrance temperature, i.e. the temperature with which the gas enters the reaction zone, is preferably from 160 to 200°C, more preferably from 165 to 195°C, even more preferably from 170 to 190°C, most preferably from 175 to 185°C.

The steam content of the gas that enters the reaction zone is preferably from 0.01 to 0.15 kg per kg dry gas, more from 0.02 to 0.12 kg per kg dry gas, most from 0.03 to 0.10 kg per kg dry gas.

The gas entrance temperature is controlled in such a way that the gas exit temperature, i.e. the temperature with which the gas leaves the reaction zone, is less than 150°C, preferably from 90 to 140°C, more preferably from 100 to 130°C, even more preferably from 105 to 125°C, most preferably from 110 to 120°C.

The water-absorbent polymer particles can be divided into three categories: water-absorbent polymer particles of Type 1 are particles with one cavity, water-absorbent polymer particles of Type 2 are particles with more than one cavity, and water-absorbent polymer particles of Type 3 are solid particles with no visible cavity.

The morphology of the water-absorbent polymer particles can be controlled by the reaction conditions during polymerization. Water-absorbent polymer particles having a high amount of particles with one cavity (Type 1) can be prepared by using low gas velocities and high gas exit temperatures. Water-absorbent polymer particles having a high amount of particles with more than one cavity (Type 2) can be prepared by using high gas velocities and low gas exit temperatures.

Water-absorbent polymer particles having more than one cavity (Type 2) show an improved mechanical stability.

The reaction can be carried out under elevated pressure or under reduced pressure, preferably from 1 to 100mbar below ambient pressure, more preferably from 1.5 to 50mbar below ambient pressure, most preferably from 2 to 10mbar below ambient pressure.

The reaction off-gas, i.e. the gas leaving the reaction zone, may be cooled in a heat exchanger. This condenses water and unconverted monomer a). The reaction off-gas can then be reheated at least partly and recycled into the reaction zone as cycle gas. A portion of the reaction off-gas can be discharged and replaced by fresh gas, in which case water and unconverted monomers a) present in the reaction off-gas can be removed and recycled.

Particular preference is given to a thermally integrated system, i.e. a portion of the waste heat in the cooling of the off-gas is used to heat the cycle gas.

The reactors can be trace-heated. In this case, the trace heating is adjusted such that the wall temperature is at least 5°C above the internal surface temperature and condensation on the surfaces is reliably prevented.

Thermal posttreatment

The formed water-absorbent polymer particles are thermal posttreated in a fluidized bed. In a preferred embodiment of the present invention an internal fluidized bed is used. An internal fluidized bed means that the product of the dropletization polymerization is accumulated in a fluidized bed below the reaction zone.

The residual monomers can be removed during the thermal posttreatment. What is important here is that the water-absorbent polymer particles are not too dry. In the case of excessively dry particles, the residual monomers decrease only insignificantly. A too high water content increases the caking tendency of the water-absorbent polymer particles.

In the fluidized state, the kinetic energy of the polymer particles is greater than the cohesion or adhesion potential between the polymer particles.

The fluidized state can be achieved by a fluidized bed. In this bed, there is upward flow toward the water-absorbing polymer particles, so that the particles form a fluidized bed. The height of the fluidized bed is adjusted by gas rate and gas velocity, i.e. via the pressure drop of the fluidized bed (kinetic energy of the gas).

The velocity of the gas stream in the fluidized bed is preferably from 0.3 to 2.5 m/s, more preferably from 0.4 to 2.0 m/s, most preferably from 0.5 to 1.5 m/s.

The pressure drop over the bottom of the internal fluidized bed is preferably from 1 to 100mbar, more preferably from 3 to 50mbar, most preferably from 5 to 25mbar.

The moisture content of the water-absorbent polymer particles at the end of the thermal posttreatment is preferably from 1 to 20% by weight, more preferably from 2 to 15% by weight, even more preferably from 3 to 12% by weight, most preferably 6 to 9% by weight.

The temperature of the water-absorbent polymer particles during the thermal posttreatment is from 20 to 140°C, preferably from 40 to 110°C, more preferably from 50 to 105°C, most preferably from 60 to 100°C.

The average residence time in the internal fluidized bed is from 10 to 300 minutes, preferably from 60 to 270 minutes, more preferably from 40 to 250 minutes, most preferably from 120 to 240 minutes.

In one embodiment of the present invention the thermal posttreatment is completely or at least partially done in an external fluidized bed. The operating conditions of the external fluidized bed are within the scope for the internal fluidized bed as described above.

The level of residual monomers can be further reduced by an additional thermal posttreatment in a mixer with rotating mixing tools as described in WO 2011/117215 A1.

The morphology of the water-absorbent polymer particles can also be controlled by the reaction conditions during thermal posttreatment. Water-absorbent polymer particles having a high amount of particles with one cavity (Type 1) can be prepared by using high product temperatures and short residence times. Water-absorbent polymer particles having a high amount of particles with more than one cavity (Type 2) can be prepared by using low product temperatures and long residence times.

The present invention is based upon the fact that the thermal posttreatment has a strong impact on the morphology of the formed water-absorbent polymer particles. Water-absorbent polymer particles having superior properties can be produced by adjusting the conditions of the thermal posttreatment.

Surface-postcrosslinking

In the present invention the water-absorbent polymer particles are surface-postcrosslinked for further improvement of the properties.

Surface-postcrosslinkers are compounds which comprise groups which can form at least two covalent bonds with the carboxylate groups of the polymer particles. Suitable compounds are, for example, polyfunctional amines, polyfunctional amidoamines, polyfunctional epoxides, as described in EP 0 083 022 A2, EP 0 543 303 A1 and EP 0 937 736 A2, di- or polyfunctional alcohols as described in DE 33 14 019 A1, DE 35 23 617 A1 and EP 0 450 922 A2, or β-hydroxyalkylamides, as described in DE 102 04 938 A1 and US 6,239,230. Also ethyleneoxide, aziridine, glycidol, oxetane and its derivatives may be used.

Polyvinylamine, polyamidoamines and polyvinylalcohole are examples of multifunctional polymeric surface-postcrosslinkers.

In addition, DE 40 20 780 C1 describes alkylene carbonates, DE 198 07 502 A1 describes 1,3-oxazolidin-2-one and its derivatives such as 2-hydroxyethyl-1,3-oxazolidin-2-one, DE 198 07 992 C1 describes bis- and poly-1,3-oxazolidin-2-ones, EP 0 999 238 A1 describes bis- and poly-1,3-oxazolidines, DE 198 54 573 A1 describes 2-oxotetrahydro-1,3-oxazine and its derivatives, DE 198 54 574 A1 describes N-acyl-1,3-oxazolidin-2-ones, DE 102 04 937 A1 describes cyclic ureas, DE 103 34 584 A1 describes bicyclic amide acetals, EP 1 199 327 A2 describes oxetanes and cyclic ureas, and WO 2003/31482 A1 describes morpholine-2,3-dione and its derivatives, as suitable surface-postcrosslinkers.

In addition, it is also possible to use surface-postcrosslinkers which comprise additional polymerizable ethylenically unsaturated groups, as described in DE 37 13 601 A1.

In a preferred embodiment of the present invention the at least one surface-postcrosslinker is selected from alkylene carbonates, 1,3-oxazolidin-2-ones, bis- and poly-1,3-oxazolidin-2-ones, bis- and poly-1,3-oxazolidines, 2-oxotetrahydro-1,3-oxazines, N-acyl-1,3-oxazolidin-2-ones, N-hydroxyethyl-1,3-oxazolidin-2-ones, cyclic ureas, bicyclic amide acetals, oxetanes, and morpholine-2,3-diones. Suitable surface-postcrosslinkers are ethylene carbonate, 3-methyl-1,3-oxazolidin-2-one, 3-methyl-3-oxethanmethanol, 1,3-oxazolidin-2-one, 3-(2-hydroxyethyl)-1,3-oxazolidin-2-one, 1,3-dioxan-2-one or a mixture thereof.

It is also possible to use any suitable mixture of surface-postcrosslinkers. It is particularly favorable to use mixtures of 1,3-dioxolan-2-on (ethylene carbonate) and 1,3-oxazolidin-2-ones. Such mixtures are obtainable by mixing and partly reacting of 1,3-dioxolan-2-on (ethylene carbonate) with the corresponding 2-amino-alcohol (e.g. 2-aminoethanol) and may comprise ethylene glycol from the reaction.

In a more preferred embodiment of the present invention at least one alkylene carbonate is used as surface-postcrosslinker. Suitable alkylene carbonates are 1,3-dioxolan-2-on (ethylene carbonate), 4-methyl-1,3-dioxolan-2-on (propylene carbonate), 4,5-dimethyl-1,3-dioxolan-2-on, 4,4-dimethyl-1,3-dioxolan-2-on, 4-ethyl-1,3-dioxolan-2-on, 4-hydroxymethyl-1,3-dioxolan-2-on (glycerine carbonate), 1,3-dioxane-2-on (trimethylene carbonate), 4-methyl-1,3-dioxane-2-on, 4,6-dimethyl-1,3-dioxane-2-on and 1,3-dioxepan-2-on, preferably 1,3-dioxolan-2-on (ethylene carbonate) and 1,3-dioxane-2-on (trimethylene carbonate), most preferably1,3-dioxolan-2-on (ethylene carbonate).

In a most preferred embodiment of the present invention a mixture of ethylene carbonate and diglycidyl ethers, for example mono-, di- and polyethylene glycol diglycidyl ether, is used as surface-postcrosslinker.

The amount of surface-postcrosslinker is preferably from 0.01 to 10% by weight, more preferably from 0.5 to 7.5% by weight, most preferably from 1 to 5% by weight, based in each case on the polymer.

The content of residual monomers in the water-absorbent polymer particles prior to the coating with the surface-postcrosslinker is in the range from 0.03 to 15% by weight, preferably from 0.05 to 12%by weight, more preferably from 0.1 to 10% by weight, even more preferably from 0.15 to 7.5% by weight, most preferably from 0.2 to 5% by weight, even most preferably from 0.25 to 2.5% by weight.

The moisture content of the water-absorbent polymer particles prior to the thermal surface-postcrosslinking is preferably from 1 to 20% by weight, more preferably from 2 to 15% by weight, most preferably from 3 to 10% by weight.

In a preferred embodiment of the present invention, polyvalent cations are applied to the particle surface in addition to the surface-postcrosslinkers before, during or after the thermal surface-postcrosslinking.

The polyvalent cations usable in the process according to the invention are, for example, divalent cations such as the cations of zinc, magnesium, calcium, iron and strontium, trivalent cations such as the cations of aluminum, iron, chromium, rare earths and manganese, tetravalent cations such as the cations of titanium and zirconium, and mixtures thereof. Possible counterions are chloride, bromide, sulfate, hydrogensulfate, carbonate, hydrogencarbonate, nitrate, hydroxide, phosphate, hydrogenphosphate, dihydrogenphosphate and carboxylate, such as acetate, glycolate, tartrate, formiate, propionate, 3-hydroxypropionate, lactamide and lactate, and mixtures thereof. Aluminum sulfate, aluminum acetate, and aluminum lactate are preferred. Apart from metal salts, it is also possible to use polyamines and/or polymeric amines as polyvalent cations. A single metal salt can be used as well as any mixture of the metal salts and/or the polyamines above.

Preferred polyvalent cations and corresponding anions are disclosed in WO 2012/045705 A1 and are expressly incorporated herein by reference. Preferred polyvinylamines are disclosed in WO 2004/024816 A1 and are expressly incorporated herein by reference.

The amount of polyvalent cation used is, for example, from 0.001 to 1.5% by weight, preferably from 0.005 to 1% by weight, more preferably from 0.02 to 0.8% by weight, based in each case on the polymer.

The addition of the polyvalent metal cation can take place prior, after, or cocurrently with the surface-postcrosslinking. Depending on the formulation and operating conditions employed it is possible to obtain a homogeneous surface coating and distribution of the polyvalent cation or an inhomogenous typically spotty coating. Both types of coatings and any mixes between them are useful within the scope of the present invention.

The surface-postcrosslinking is typically performed in such a way that a solution of the surface-postcrosslinker is sprayed onto the hydrogel or the dry polymer particles. After the spraying, the polymer particles coated with the surface-postcrosslinker are dried thermally and cooled.

The spraying of a solution of the surface-postcrosslinker is preferably performed in mixers with moving mixing tools, such as screw mixers, disk mixers and paddle mixers. Suitable mixers are, for example, vertical Schugi Flexomix® mixers (Hosokawa Micron BV; Doetinchem; the Netherlands), Turbolizers® mixers (Hosokawa Micron BV; Doetinchem; the Netherlands), horizontal Pflugschar® plowshare mixers (Gebr. Lödige Maschinenbau GmbH; Paderborn; Germany), Vrieco-Nauta Continuous Mixers (Hosokawa Micron BV; Doetinchem; the Netherlands), Processall Mixmill Mixers (Processall Incorporated; Cincinnati; US) and Ruberg continuous flow mixers (Gebrüder Ruberg GmbH & Co KG, Nieheim, Germany). Ruberg continuous flow mixers and horizontal Pflugschar® plowshare mixers are preferred. The surface-postcrosslinker solution can also be sprayed into a fluidized bed.

The solution of the surface-postcrosslinker can also be sprayed on the water-absorbent polymer particles during the thermal posttreatment. In such case the surface-postcrosslinker can be added as one portion or in several portions along the axis of thermal posttreatment mixer. In one embodiment it is preferred to add the surface-postcrosslinker at the end of the thermal post-treatment step. As a particular advantage of adding the solution of the surface-postcrosslinker during the thermal posttreatment step it may be possible to eliminate or reduce the technical effort for a separate surface-postcrosslinker addition mixer.

The surface-postcrosslinkers are typically used as an aqueous solution. The addition of nonaqueous solvent can be used to adjust the penetration depth of the surface-postcrosslinker into the polymer particles.

The thermal surface-postcrosslinking is preferably carried out in contact dryers, more preferably paddle dryers, most preferably disk dryers. Suitable driers are, for example, Hosokawa Bepex® horizontal paddle driers (Hosokawa Micron GmbH; Leingarten; Germany), Hosokawa Bepex® disk driers (Hosokawa Micron GmbH; Leingarten; Germany), Holo-Flite® dryers (Metso Minerals Industries Inc.; Danville; U.S.A.) and Nara paddle driers (NARA Machinery Europe; Frechen; Germany). Nara paddle driers and, in the case of low process temperatures (<160°C) for example, when using polyfunctional epoxides, Holo-Flite® dryers are preferred. Moreover, it is also possible to use fluidized bed dryers. In the latter case the reaction times may be shorter compared to other embodiments.

When a horizontal dryer is used then it is often advantageous to set the dryer up with an inclined angle of a few degrees vs. the earth surface in order to impart proper product flow through the dryer. The angle can be fixed or may be adjustable and is typically between 0 to 10 degrees, preferably 1 to 6 degrees, most preferably 2 to 4 degrees.

In one embodiment of the present invention a contact dryer is used that has two different heating zones in one apparatus. For example Nara paddle driers are available with just one heated zone or alternatively with two heated zones. The advantage of using a two or more heated zone dryer is that different phases of the thermal post-treatment and/or of the post-surface-crosslinking can be combined.

In one preferred embodiment of the present invention a contact dryer with a hot first heating zone is used which is followed by a temperature holding zone in the same dryer. This set up allows a quick rise of the product temperature and evaporation of surplus liquid in the first heating zone, whereas the rest of the dryer is just holding the product temperature stable to complete the reaction.

In another preferred embodiment of the present invention a contact dryer with a warm first heating zone is used which is then followed by a hot heating zone. In the first warm zone the thermal post-treatment is affected or completed whereas the surface-postcrosslinking takes place in the subsequential hot zone.

In a typical embodiment a paddle heater with just one temperature zone is employed.

A person skilled in the art will depending on the desired finished product properties and the available base poylmer qualities from the polymerization step choose any one of these set ups.

The thermal surface-postcrosslinking can be effected in the mixer itself, by heating the jacket, blowing in warm air or steam. Equally suitable is a downstream dryer, for example a shelf dryer, a rotary tube oven or a heatable screw. It is particularly advantageous to mix and dry in a fluidized bed dryer.

Preferred thermal surface-postcrosslinking temperatures are in the range from 100 to 180°C, preferably from 120 to 170°C, more preferably from 130 to 165°C, most preferably from 140 to 160°C. The preferred residence time at this temperature in the reaction mixer or dryer is preferably at least 5 minutes, more preferably at least 20 minutes, most preferably at least 40 minutes, and typically at most 120 minutes.

It is preferable to cool the polymer particles after thermal surface-postcrosslinking. The cooling is preferably carried out in contact coolers, more preferably paddle coolers, most preferably disk coolers. Suitable coolers are, for example, Hosokawa Bepex® horizontal paddle coolers (Hosokawa Micron GmbH; Leingarten; Germany), Hosokawa Bepex® disk coolers (Hosokawa Micron GmbH; Leingarten; Germany), Holo-Flite® coolers (Metso Minerals Industries Inc.; Danville; U.S.A.) and Nara paddle coolers (NARA Machinery Europe; Frechen; Germany). Moreover, it is also possible to use fluidized bed coolers.

In the cooler the polymer particles are cooled to temperatures of in the range from 20 to 150°C, preferably from 40 to 120°C, more preferably from 60 to 100°C, most preferably from 70 to 90°C. Cooling using warm water is preferred, especially when contact coolers are used.

Coating

To improve the properties, the water-absorbent polymer particles can be coated and/or optionally moistened. The internal fluidized bed, the external fluidized bed and/or the external mixer used for the thermal posttreatment and/or a separate coater (mixer) can be used for coating of the water-absorbent polymer particles. Further, the cooler and/or a separate coater (mixer) can be used for coating/moistening of the surface-postcrosslinked water-absorbent polymer particles. Suitable coatings for controlling the acquisition behavior and improving the permeability (SFC or GBP) are, for example, inorganic inert substances, such as water-insoluble metal salts, organic polymers, cationic polymers, anionic polymers and polyvalent metal cations. Suitable coatings for improving the color stability are, for example reducing agents, chelating agents and anti-oxidants. Suitable coatings for dust binding are, for example, polyols. Suitable coatings against the undesired caking tendency of the polymer particles are, for example, fumed silica, such as Aerosil® 200, and surfactants, such as Span® 20. Preferred coatings are aluminium dihydroxy monoacetate, aluminium sulfate, aluminium lactate, aluminium 3-hydroxypropionate, zirconium acetate, citric acid or its water soluble salts, di- and mono-phosphoric acid or their water soluble salts, Blancolen®, Brüggolite® FF7, Cublen® , Plantacare® 818 UP and Span® 20.

If salts of the above acids are used instead of the free acids then the preferred salts are alkali-metal, earth alkali metal, aluminum, zirconium, titanium, zinc and ammonium salts.

Under the trade name Cublen® (Zschimmer & Schwarz Mohsdorf GmbH & Co KG; Burgstädt; Germany)the following acids and/or their alkali metal salts (preferably Na and K-salts) are available and may be used within the scope of the present invention for example to impart color-stability to the finished product:

1-hydroxyethane-1,1-diphosphonic acid, amino-tris(methylene phosphonic acid), ethylenediamine-tetra(methylene phosphonic acid), diethylenetriamine-penta(methylene phosphonic acid), hexamethylene diamine-tetra(methylenephosphonic acid), hydroxyethyl-amino-di(methylene phosphonic acid), 2-phosphonobutane-1,2,4-tricarboxylic acid, bis(hexamethylenetriamine penta(methylene phosphonic acid)).

Most preferably 1-hydroxyethane-1,1-diphosphonic acid or its salts with sodium, potassium, or ammonium are employed. Any mixture of the above Cublenes® can be used.

Alternatively, any of the chelating agents described before for use in the polymerization can be coated onto the finished product.

Suitable inorganic inert substances are silicates such as montmorillonite, kaolinite and talc, zeolites, activated carbons, polysilicic acids, magnesium carbonate, calcium carbonate, calcium phosphate, barium sulfate, aluminum oxide, titanium dioxide and iron(II) oxide. Preference is given to using polysilicic acids, which are divided between precipitated silicas and fumed silicas according to their mode of preparation. The two variants are commercially available under the names Silica FK, Sipernat®, Wessalon® (precipitated silicas) and Aerosil® (fumed silicas) respectively. The inorganic inert substances may be used as dispersion in an aqueous or water-miscible dispersant or in substance.

When the water-absorbent polymer particles are coated with inorganic inert substances, the amount of inorganic inert substances used, based on the water-absorbent polymer particles, is preferably from 0.05 to 5% by weight, more preferably from 0.1 to 1.5% by weight, most preferably from 0.3 to 1% by weight.

Suitable organic polymers are polyalkyl methacrylates or thermoplastics such as polyvinyl chloride, waxes based on polyethylene, polypropylene, polyamides or polytetrafluoro-ethylene. Other examples are styrene-isoprene-styrene block-copolymers or styrene-butadiene-styrene block-copolymers. Another example are silanole-group bearing polyvinylalcoholes available under the trade name Poval® R (Kuraray Europe GmbH; Frankfurt; Germany).

Suitable cationic polymers are polyalkylenepolyamines, cationic derivatives of polyacrylamides, polyethyleneimines and polyquaternary amines.

Polyquaternary amines are, for example, condensation products of hexamethylenediamine, dimethylamine and epichlorohydrin, condensation products of dimethylamine and epichlorohydrin, copolymers of hydroxyethylcellulose and diallyldimethylammonium chloride, copolymers of acrylamide and α-methacryloyloxyethyltrimethylammonium chloride, condensation products of hydroxyethylcellulose, epichlorohydrin and trimethylamine, homopolymers of diallyldimethylammonium chloride and addition products of epichlorohydrin to amidoamines. In addition, polyquaternary amines can be obtained by reacting dimethyl sulfate with polymers such as polyethyleneimines, copolymers of vinylpyrrolidone and dimethylaminoethyl methacrylate or copolymers of ethyl methacrylate and diethylaminoethyl methacrylate. The polyquaternary amines are available within a wide molecular weight range.

However, it is also possible to generate the cationic polymers on the particle surface, either through reagents which can form a network with themselves, such as addition products of epichlorohydrin to polyamidoamines, or through the application of cationic polymers which can react with an added crosslinker, such as polyamines or polyimines in combination with polyepoxides, polyfunctional esters, polyfunctional acids or polyfunctional (meth)acrylates.

It is possible to use all polyfunctional amines having primary or secondary amino groups, such as polyethyleneimine, polyallylamine and polylysine. The liquid sprayed by the process according to the invention preferably comprises at least one polyamine, for example polyvinylamine or a partially hydrolyzed polyvinylformamide.

The cationic polymers may be used as a solution in an aqueous or water-miscible solvent, as dispersion in an aqueous or water-miscible dispersant or in substance.

When the water-absorbent polymer particles are coated with a cationic polymer, the use amount of cationic polymer based on the water-absorbent polymer particles is usually not less than 0.001% by weight, typically not less than 0.01% by weight, preferably from 0.1 to 15% by weight, more preferably from 0.5 to 10% by weight, most preferably from 1 to 5% by weight.

Suitable anionic polymers are polyacrylates (in acidic form or partially neutralized as salt), co-polymers of acrylic acid and maleic acid available under the trade name Sokalan® (BASF SE; Ludwigshafen; Germany), and polyvinylalcohols with built in ionic charges available under the trade name Poval® K (Kuraray Europe GmbH; Frankfurt; Germany).

Suitable polyvalent metal cations are Mg^{2+}, Ca^{2+}, Al^{3+}, Sc^{3+}, Ti^{4+}, Mn^{2+}, $Fe^{2+/3+}$, Co^{2+}, Ni^{2+}, $Cu^{+/2+}$, Zn^{2+}, Y^{3+}, Zr^{4+}, Ag^{+}, La^{3+}, Ce^{4+}, Hf^{4+} and $Au^{+/3+}$; preferred metal cations are Mg^{2+}, Ca^{2+}, Al^{3+}, Ti^{4+}, Zr^{4+} and La^{3+}; particularly preferred metal cations are Al^{3+}, Ti^{4+} and Zr^{4+}. The metal cations may be used either alone or in a mixture with one another. Suitable metal salts of the metal cations mentioned are all of those which have a sufficient solubility in the solvent to be used. Particularly suitable metal salts have weakly complexing anions, such as chloride, hydroxide, carbonate, acetate, formiate, propionate, nitrate and sulfate. The metal salts are preferably used as a solution or as a stable aqueous colloidal dispersion. The solvents used for the metal salts may be water, alcohols, ethylenecarbonate, propylenecarbonate, dimethylformamide, dimethyl sulfoxide and mixtures thereof. Particular preference is given to water and water/alcohol mixtures, such as water/methanol, water/isopropanol, water/1,3-propanediole, water/1,2-propandiole/1,4-butanediole or water/propylene glycol.

When the water-absorbent polymer particles are coated with a polyvalent metal cation, the amount of polyvalent metal cation used, based on the water-absorbent polymer particles, is preferably from 0.05 to 5% by weight, more preferably from 0.1 to 1.5% by weight, most preferably from 0.3 to 1% by weight.

Suitable reducing agents are, for example, sodium sulfite, sodium hydrogensulfite (sodium bisulfite), sodium dithionite, sulfinic acids and salts thereof, ascorbic acid, sodium hypophosphite, sodium phosphite, and phosphinic acids and salts thereof. Preference is given, however, to salts of hypophosphorous acid, for example sodium hypophosphite, salts of sulfinic acids, for example the disodium salt of 2-hydroxy-2-sulfinatoacetic acid, and addition products of aldehydes, for example the disodium salt of 2-hydroxy-2-sulfonatoacetic acid. The reducing agent used can be, however, a mixture of the sodium salt of 2-hydroxy-2-sulfinatoacetic acid, the disodium salt of 2-hydroxy-2-sulfonatoacetic acid and sodium bisulfite. Such mixtures are obtainable as Brüggolite® FF6 and Brüggolite® FF7 (Brüggemann Chemicals; Heilbronn; Germany). Also useful is the purified 2-hydroxy-2-sulfonatoacetic acid and its sodium salts, available under the trade name Blancolen® from the same company.

The reducing agents are typically used in the form of a solution in a suitable solvent, preferably water. The reducing agent may be used as a pure substance or any mixture of the above reducing agents may be used.

When the water-absorbent polymer particles are coated with a reducing agent, the amount of reducing agent used, based on the water-absorbent polymer particles, is preferably from 0.01 to 5% by weight, more preferably from 0.05 to 2% by weight, most preferably from 0.1 to 1% by weight.

Suitable polyols are polyethylene glycols having a molecular weight of from 400 to 20000 g/mol, polyglycerol, 3- to 100-tuply ethoxylated polyols, such as trimethylolpropane, glycerol, sorbitol and neopentyl glycol. Particularly suitable polyols are 7- to 20-tuply ethoxylated glycerol or trimethylolpropane, for example Polyol TP 70® (Perstorp AB, Perstorp, Sweden). The latter have the advantage in particular that they lower the surface tension of an aqueous extract of the water-absorbent polymer particles only insignificantly. The polyols are preferably used as a solution in aqueous or water-miscible solvents.

When the water-absorbent polymer particles are coated with a polyol, the use amount of polyol, based on the water-absorbent polymer particles, is preferably from 0.005 to 2% by weight, more preferably from 0.01 to 1% by weight, most preferably from 0.05 to 0.5% by weight.

The water-absorbent polymer particles can further be moistened with water and/or steam to improve the damage stability. The moisture content is preferably at least 1% by weight, more preferably from 2 to 20% by weight, most preferably 5 to 12% by weight, based on the water-absorbent polymer particles.

The coating is preferably performed in mixers with moving mixing tools, such as screw mixers, disk mixers, paddle mixers and drum coater. Suitable mixers are, for example, horizontal Pflugschar® plowshare mixers (Gebr. Lödige Maschinenbau GmbH; Paderborn; Germany), Vrieco-Nauta Continuous Mixers (Hosokawa Micron BV; Doetinchem; the Netherlands), Processall Mixmill Mixers (Processall Incorporated; Cincinnati; US) and Ruberg continuous flow mixers (Gebrüder Ruberg GmbH & Co KG, Nieheim, Germany). Moreover, it is also possible to use a fluidized bed for mixing.

Agglomeration

The water-absorbent polymer particles can further selectivily be agglomerated. The agglomeration can take place after the polymerization, the thermal postreatment, the thermal surface-postcrosslinking or the coating.

Useful agglomeration assistants include water and water-miscible organic solvents, such as alcohols, tetrahydrofuran and acetone; water-soluble polymers can be used in addition.

For agglomeration a solution comprising the agglomeration assistant is sprayed onto the water-absorbing polymeric particles. The spraying with the solution can, for example, be carried out in mixers having moving mixing implements, such as screw mixers, paddle mixers, disk mixers, plowshare mixers and shovel mixers. Useful mixers include for example Lödige® mixers, Bepex® mixers, Nauta® mixers, Processall® mixers and Schugi® mixers. Vertical mixers are preferred. Fluidized bed apparatuses are particularly preferred.

Combination of thermal posttreatment, surface-postcrosslinking and optionally coating

In a preferred embodiment of the present invention the steps of thermal posttreatment and thermal surface-postcrosslinking are combined in one process step. Such combination allows the use of low cost equipment and moreover the process can be run at low temperatures, that is cost-efficient and avoids discoloration and loss of performance properties of the finished product by thermal degradation.

The mixer may be selected from any of the equipment options cited in the thermal posttreatment section. Ruberg continuous flow mixers, Becker shovel mixers and Pflugschar® plowshare mixers are preferred.

In this particular preferred embodiment the surface-postcrosslinking solution is sprayed onto the water-absorbent polymer particles under agitation.

Following the thermal posttreatment/surface-postcrosslinking the water-absorbent polymer particles are dried to the desired moisture level and for this step any dryer cited in the surface-postcrosslinking section may be selected. However, as only drying needs to be accomplished in this particular preferred embodiment it is possible to use simple and low cost heated contact dryers like a heated screw dryer, for example a Holo-Flite® dryer (Metso Minerals Industries Inc.; Danville; U.S.A.). Alternatively a fluidized bed may be used. In cases where the product needs to be dried with a predetermined and narrow residence time it is possible to use torus disc dryers or paddle dryers, for example a Nara paddle dryer (NARA Machinery Europe; Frechen; Germany).

In a preferred embodiment of the present invention, polyvalent cations cited in the surface-postcrosslinking section are applied to the particle surface before, during or after addition of the surface-postcrosslinker by using different addition points along the axis of a horizontal mixer.

In a very particular preferred embodiment of the present invention the steps of thermal post-treatment, surface-postcrosslinking, and coating are combined in one process step. Suitable coatings are cationic polymers, surfactants, and inorganic inert substances that are cited in the coating section. The coating agent can be applied to the particle surface before, during or after addition of the surface-postcrosslinker also by using different addition points along the axis of a horizontal mixer.

The polyvalent cations and/or the cationic polymers can act as additional scavengers for residual surface-postcrosslinkers. In a preferred embodiment of the present invention the surface-postcrosslinkers are added prior to the polyvalent cations and/or the cationic polymers to allow the surface-postcrosslinker to react first.

The surfactants and/or the inorganic inert substances can be used to avoid sticking or caking during this process step under humid atmospheric conditions. It appears to be important that the polar group and the nonpolar group of the surfactant remain joined even under the conditions of the thermal aftertreatment. Surfactants having a hydrolysis-sensitive carboxylic ester group at this position are less suitable. So, preferred surfactants are surfactants having a polar group and a nonpolar group, the polar group and the nonpolar group of the surfactant not being joined via a carboxylic ester group, and the polar group having at least one hydroxyl group, a cationic group or an anionic group and the nonpolar group having a C_4- to C_{20}-alkyl chain, especially Plantacare® 818 UP (BASF SE, Ludwigshafen, Germany). Preferred inorganic inert substances are precipitated silicas and fumed silcas in form of powder or dispersion.

The amount of total liquid used for preparing the solutions/dispersions is typically from 0.01% to 25% by weight, preferably from 0.5% to 12% by weight, more preferably from 2% to 7% by weight, most preferably from 3% to 6% by weight, in respect to the weight amount of water-absorbent polymer particles to be processed.

Preferred embodiments are depicted in figures 1 to 15.

Fig. 1: Process scheme
Fig. 2: Process scheme using dry air
Fig. 3: Arrangement of the T_outlet measurement
Fig. 4: Arrangement of the dropletizer units with 3 droplet plates
Fig. 5: Arrangement of the dropletizer units with 9 droplet plates
Fig. 6: Arrangement of the dropletizer units with 9 droplet plates
Fig. 7: Dropletizer unit (longitudinal cut)
Fig. 8: Dropletizer unit (cross sectional view)
Fig. 9: Bottom of the internal fluidized bed (top view)
Fig. 10: openings in the bottom of the internal fluidized bed
Fig. 11: Rake stirrer for the intern fluidized bed (top view)
Fig. 12: Rake stirrer for the intern fluidized bed (cross sectional view)
Fig. 13: Process scheme (surface-postcrosslinking)
Fig. 14: Process scheme (surface-postcrosslinking and coating)
Fig. 15: Contact dryer for surface-postcrosslnking

The reference numerals have the following meanings:

1	Drying gas inlet pipe
2	Drying gas amount measurement
3	Gas distributor
4	Dropletizer unit(s)
4a	Dropletizer unit
4b	Dropletizer unit
4c	Dropletizer unit
5	Reaction zone (cylindrical part of the spray dryer)
6	Cone
7	T_outlet measurement
8	Tower offgas pipe
9	Dust separation unit
10	Ventilator
11	Quench nozzles
12	Condenser column, counter current cooling
13	Heat exchanger
14	Pump

15	Pump
16	Water outlet
17	Ventilator
18	Offgas outlet
19	Nitrogen inlet
20	Heat exchanger
21	Ventilator
22	Heat exchanger
24	Water loading measurement
25	Conditioned internal fluidized bed gas
26	Internal fluidized bed product temperature measurement
27	Internal fluidized bed
28	Rotary valve
29	Sieve
30	End product
31	Static mixer
32	Static mixer
33	Initiator feed
34	Initiator feed
35	Monomer feed
36	Fine particle fraction outlet to rework
37	Gas drying unit
38	Monomer separator unit
39	Gas inlet pipe
40	Gas outlet pipe
41	Water outlet from the gas drying unit to condenser column
42	Waste water outlet
43	T_outlet measurement (average temperature out of 3 measurements around tower circumference)
45	Monomer premixed with initiator feed
46	Spray dryer tower wall
47	Dropletizer unit outer pipe
48	Dropletizer unit inner pipe
49	Dropletizer cassette
50	Teflon block
51	Valve
52	Monomer premixed with initiator feed inlet pipe connector
53	Droplet plate

54	Counter plate
55	Flow channels for temperature control water
56	Dead volume free flow channel for monomer solution
57	Dropletizer cassette stainless steel block

58	Bottom of the internal fluidized bed with four segments
59	Split openings of the segments
60	Rake stirrer
61	Prongs of the rake stirrer

62	Mixer
63	Optional coating feed
64	Postcrosslinker feed
65	Thermal dryer (surface-postcrosslinking)
66	Cooler
67	Optional coating/water feed
68	Coater
69	Coating/water feed

70	Base polymer feed
71	Discharge zone
72	Weir opening
73	Weir plate
74	Weir height 100%
75	Weir height 50%
76	Shaft
77	Discharge cone
78	Inclination angle α
79	Temperature sensors (T_1 to T_6)
80	Paddle (shaft offset 90°)

The drying gas is fed via a gas distributor (3) at the top of the spray dryer as shown in Fig. 1. The drying gas is partly recycled (drying gas loop) via a baghouse filter or cyclone unit (9) and a condenser column (12). The pressure inside the spray dryer is below ambient pressure.

The spray dryer outlet temperature is preferably measured at three points around the circumference at the end of the cylindrical part as shown in Fig. 3. The single measurements (43) are used to calculate the average cylindrical spray dryer outlet temperature.

In one preferred embodiment a monomer separator unit (38) is used for recycling of the monomers from the condenser column (12) into the monomer feed (35). This monomer separator unit is for example especially a combination of micro-, ultra-, nanofiltration and osmose membrane units, to separate the monomer from water and polymer particles. Suitable membrane separator systems are described, for example, in the monograph “Membranen: Grundlagen, Verfahren und Industrielle Anwendungen”, K. Ohlrogge and K. Ebert, Wiley-VCH, 2012 (ISBN: 978-3-527-66033-9).

The product accumulated in the internal fluidized bed (27). Conditioned internal fluidized bed gas is fed to the internal fluidized bed (27) via line (25). The relative humidity of the internal fluidized bed gas is preferably controlled by the temperature in the condensor column (12) and using the Mollier diagram.

The spray dryer offgas is filtered in a dust separation unit (9) and sent to a condenser column (12) for quenching/cooling. After dust separation (9) a recuperation heat exchanger system for preheating the gas after the condenser column (12) can be used. The dust separation unit (9) may be heat-traced on a temperature of preferably from 80 to 180°C, more preferably from 90 to 150°C, most preferably from 100 to 140°C.

Example for the dust separation unit are baghouse filter, membranes, cyclones, dust compactors and for examples described, for example, in the monographs “Staubabscheiden”, F. Löffler, Georg Thieme Verlag, Stuttgart, 1988 (ISBN 978-3137122012) and “Staubabscheidung mit Schlauchfiltern und Taschenfiltern”, F. Löffler, H. Dietrich and W. Flatt, Vieweg, Braunschweig, 1991 (ISBN 978-3540670629).

Most preferable are cyclones, for example, cyclones/centrifugal separators of the types ZSA/ZSB/ZSC from LTG Aktiengesellschaft and cyclone separators from Ventilatorenfabrik Oelde GmbH, Camfil Farr International and MikroPul GmbH.

Excess water is pumped out of the condenser column (12) by controlling the (constant) filling level in the condenser column (12). The water in the condenser column (12) is pumped countercurrent to the gas via quench nozzles (11) and cooled by a heat exchanger (13) so that the temperature in the condenser column (12) is preferably from 40 to 71°C, more preferably from 46 to 69°C, most preferably from 49 to 65°C and more even preferably from 51 to 60°C. The water in the condenser column (12) is set to an alkaline pH by dosing a neutralizing agent to wash out vapors of monomer a). Aqueous solution from the condenser column (12) can be sent back for preparation of the monomer solution.

The condenser column offgas may be split to the gas drying unit (37) and the conditioned internal fluidized bed gas (27).

The principle of a gas drying unit is described in the monograph “Leitfaden für Lüftungs- und Klimaanlagen - Grundlagen der Thermodynamik Komponenten einer Vollklimaanlage Normen und Vorschriften“, L. Keller, Oldenbourg Industrieverlag, 2009 (ISBN 978-3835631656).

As gas drying unit can be used, for example, an air gas cooling system in combination with a gas mist eliminators or droplet separator (demister), for examples, droplet vane type separator for horizontal flow (e.g. type DH 5000 from Munters AB, Sweden) or vertical flow (e.g. type DV 270 from Munters AB, Sweden). Vane type demisters remove liquid droplets from continuous gas flows by inertial impaction. As the gas carrying entrained liquid droplets moves through the sinusoidal path of a vane, the higher density liquid droplets cannot follow and as a result, at every turn of the vane blades, these liquid droplets impinge on the vane surface. Most of the droplets adhere to the vane wall. When a droplet impinges on the vane blade at the same location, coalescence occurs. The coalesced droplets then drain down due to gravity.

As air gas cooling system, any gas/gas or gas/liquid heat exchanger can be used. Preferred are sealed plate heat exchangers.

In one embodiment dry air can be used as feed for the gas distributor (3). If air used as gas, then air can be transported via air inlet pipe (39) and can be dried in the gas drying unit (37), as described before. After the condenser column (12), the air, which not used for the internal fluidized bed is transported via the outlet pipe outside (40) of the plant as shown in Fig. 2.

The water, which is condensed in the gas drying unit (37) can be partially used as wash water for the condenser column (12) or disposed.

The gas temperatures are controlled via heat exchangers (20) and (22). The hot drying gas is fed to the cocurrent spray dryer via gas distributor (3). The gas distributor (3) consists preferably of a set of plates providing a pressure drop of preferably 1 to 100mbar, more preferably 2 to 30mbar, most preferably 4 to 20mbar, depending on the drying gas amount. Turbulences and/or a centrifugal velocity can also be introduced into the drying gas if desired by using gas nozzles or baffle plates.

Conditioned internal fluidized bed gas is fed to the internal fluidized bed (27) via line (25). The steam content of the fluidized bed gas can be controlled by the temperature in the condenser column (12). The product holdup in the internal fluidized bed (27) can be controlled via rotational speed of the rotary valve (28).

The amount of gas in the internal fluidized bed (27) is selected so that the particles move free and turbulent in the internal fluidized bed (27). The product height in the internal fluidized bed (27) is with gas preferably at least 10%, more preferably at least 20%, more preferably at least 30%, even more preferably at least 40% higher than without gas.

The product is discharged from the internal fluidized bed (27) via rotary valve (28). The product holdup in the internal fluidized bed (27) can be controlled via rotational speed of the rotary valve (28). The sieve (29) is used for sieving off overs/lumps.

The monomer solution is preferably prepared by mixing first monomer a) with a neutralization agent and secondly with crosslinker b). The temperature during neutralization is controlled to preferably from 5 to 60°C, more preferably from 8 to 40°C, most preferably from 10 to 30°C, by using a heat exchanger and pumping in a loop. A filter unit is preferably used in the loop after the pump. The initiators are metered into the monomer solution upstream of the dropletizer by means of static mixers (31) and (32) via lines (33) and (34) as shown in Fig. 1 and Fig. 2. Preferably a peroxide solution having a temperature of preferably from 5 to 60°C, more preferably from 10 to 50°C, most preferably from 15 to 40°C, is added via line (33) and preferably an azo initiator solution having a temperature of preferably from 2 to 30°C, more preferably from 3 to 15°C, most preferably from 4 to 8°C, is added via line (34). Each initiator is preferably pumped in a loop and dosed via control valves to each dropletizer unit. A second filter unit is preferably used after the static mixer (32). The mean residence time of the monomer solution admixed with the full initiator package in the piping before dropletization is preferably less than 60s, more preferably less than 30s, most preferably less than 10s.

For dosing the monomer solution into the top of the spray dryer preferably three dropletizer units are used as shown in Fig. 4. However, any number of dropletizers can be used that is required to optimize the throughput of the process and the quality of the product. Hence, in the present invention at least one dropletizer is employed, and as many dropletizers as geometrically allowed may be used.

A dropletizer unit consists of an outer pipe (47) having an opening for the dropletizer cassette (49) as shown in Fig. 7. The dropletizer cassette (49) is connected with an inner pipe (48). The inner pipe (48) having a PTFE block (50) at the end as sealing can be pushed in and out of the outer pipe (51) during operation of the process for maintenance purposes.

The temperature of the dropletizer cassette (57) is controlled to preferably 5 to 80°C, more preferably 10 to 70°C, most preferably 30 to 60°C, by water in flow channels (55) as shown in Fig. 8.

The dropletizer cassette has preferably from 10 to 2000 bores, more preferably from 50 to 1500 bores, most preferably from 100 to 1000 bores. The diameter of the bores size area is 1900 to 22300 µ^2, more preferably from 7800 to 20100 µm^2, most preferably from 11300 to 17700 µm^2. The bores can be of circular, rectangular, triangular or any other shape. Circular bores are preferred with a bore size from 50 to 170 µm, more preferably from 100 to 160 µm, most preferably from 120 to 150 µm. The ratio of bore length to bore diameter is preferably from 0.5 to 10, more preferably from 0.8 to 5, most preferably from 1 to 3. The droplet plate (53) can have a greater thickness than the bore length when using an inlet bore channel. The droplet plate (53) is preferably long and narrow as disclosed in WO 2008/086976 A1. Multiple rows of bores per droplet plate can be used, preferably from 1 to 20 rows, more preferably from 2 to 5 rows.

The dropletizer cassette (57) consists of a flow channel (56) having essential no stagnant volume for homogeneous distribution of the premixed monomer and initiator solutions and two droplet plates (53). The droplet plates (53) have an angled configuration with an angle of preferably from 1 to 90°, more preferably from 3 to 45°, most preferably from 5 to 20°. Each droplet plate (53) is preferably made of a heat and/or chemically resistant material, such as stainless steel, polyether ether ketone, polycarbonate, polyarylsulfone, such as polysulfone, or polyphenylsulfone, or fluorous polymers, such as perfluoroalkoxyethylene, polytetrafluoroethylene, polyvinylidenfluorid, ethylene-chlorotrifluoroethylene copolymers, ethylene-tetrafluoroethylene copolymers and fluorinated polyethylene. Coated droplet plates as disclosed in WO 2007/031441 A1 can also be used. The choice of material for the droplet plate is not limited except that droplet formation must work and it is preferable to use materials which do not catalyze the start of polymerization on its surface.

The arrangement of dropletizer cassettes is preferably rotationally symmetric or evenly distributed in the spray dryer (for example see Fig. 3 to 5).

In a preferred embodiment the angle configuration of the droplet plate (53) is in the middle lower then outside, for example: 4a = 3°, 4b = 5° and 4c = 8° (Fig 5).

The throughput of monomer including initiator solutions per dropletizer unit is preferably from 10 to 4000kg/h, more preferably from 100 to 1000kg/h, most preferably from 200 to 600kg/h. The throughput per bore is preferably from 0.1 to 10kg/h, more preferably from 0.5 to 5kg/h, most preferably from 0.7 to 2kg/h.

The start-up of the cocurrent spray dryer (5) can be done in the following sequence:

- starting the condenser column (12),
- starting the ventilators (10) and (17),
- starting the heat exchanger (20),
- heating up the drying gas loop up to 95°C,
- starting the nitrogen feed via the nitrogen inlet (19),
- waiting until the residual oxygen is below 4% by weight,
- heating up the drying gas loop,
- at a temperature of 105°C starting the water feed (not shown) and
- at target temperature stopping the water feed and starting the monomer feed via dropletizer unit (4)

The shut-down of the cocurrent spray dryer (5) can be done in the following sequence:

- stopping the monomer feed and starting the water feed (not shown),
- shut-down of the heat exchanger (20),
- cooling the drying gas loop via heat exchanger (13),

- at a temperature of 105°C stopping the water feed,
- at a temperature of 60°C stopping the nitrogen feed via the nitrogen inlet (19) and
- feeding air into the drying gas loop (not shown)

To prevent damages the cocurrent spray dryer (5) must be heated up and cooled down very carefully. Any quick temperature change must be avoided.

The openings in the bottom of the internal fluidized bed may be arranged in a way that the water-absorbent polymer particles flow in a cycle as shown in Fig. 9. The bottom shown in Fig. 9 comprises of four segments (58). The openings (59) in the segments (58) are in the shape of slits that guides the passing gas stream into the direction of the next segment (58). Fig. 10 shows an enlarged view of the openings (59).

The opening may have the shape of holes or slits. The diameter of the holes is preferred from 0.1 to 10mm, more preferred from 0.2 to 5mm, most preferred from 0.5 to 2mm. The slits have a length of preferred from 1 to 100mm, more preferred from 2 to 20mm, most preferred from 5 to 10mm, and a width of preferred from 0.5 to 20mm, more preferred from 1 to 10mm, most preferred from 2 to 5mm.

Fig. 11 and Fig. 12 show a rake stirrer (60) that may be used in the internal fluidized bed. The prongs (61) of the rake have a staggered arrangement. The speed of rake stirrer is preferably from 0.5 to 20 rpm, more preferably from 1 to 10 rpm most preferably from 2 to 5 rpm.

For start-up the internal fluidized bed may be filled with a layer of water-absorbent polymer particles, preferably 5 to 50 cm, more preferably from 10 to 40 cm, most preferably from 15 to 30 cm.

Water-absorbent polymer particles

The present invention further provides water-absorbent polymer particles obtainable by the process according to the invention.

The present invention further provides water-absorbent polymer particles having an average particle diameter (d_{50}) from 150 to 400 µm, preferably from 170 to 379 µm, more preferably from 190 to 370 µm, most preferably from 200 to 330 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 5% by weight, preferably less than 2% by weight, more preferably less than 1% by weight, most preferably less than 0.5% by weight, an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 15% by weight, preferably less than 10% by weight, more preferably less than 5% by weight, most preferably less than 2% by weight, a centrifuge retention capacity

(CRC) from 20 to 85 g/g, preferably from 25 to 80 g/g, more preferably from 30 to 75 g/g, most preferably from 40 to 70 g/g, and an absorption under load (AUL) of

$$AUL > -0.000415 \times CRC^3 + 0.0145 \times CRC^2 + 1.1166 \times CRC - 5.27 \text{ (Fig. 16: y0(x))}$$

preferred

$$AUL > -0.000415 \times CRC^3 + 0.0145 \times CRC^2 + 1.1166 \times CRC - 3.77 \text{ (Fig. 16: y1(x))}$$

more preferred

$$AUL > -0.000415 \times CRC^3 + 0.0145 \times CRC^2 + 1.1166 \times CRC - 3.27 \text{ (Fig. 16: y2(x))}$$

most preferred

$$AUL > -0.000415 \times CRC^3 + 0.0145 \times CRC^2 + 1.1166 \times CRC - 2.77 \text{ (Fig. 16: y3(x))}$$

wherein AUL [g/g] is the absorption under load and CRC [g/g] is the centrifuge retention capacity.

The present invention further provides water-absorbent polymer particles having an average particle diameter (d_{50}) from 150 to 400 µm, preferably from 170 to 379 µm, more preferably from 190 to 350 µm, most preferably from 200 to 330 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 5% by weight, preferably less than 2% by weight, more preferably less than 1% by weight, most preferably less than 0.5% by weight, an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 15% by weight, preferably less than 10% by weight, more preferably less than 5% by weight, most preferably less than 2% by weight, a centrifuge retention capacity (CRC) from 20 to 50 g/g, preferably from 25 to 48 g/g, more preferably from 30 to 46 g/g, most preferably from 30 to 45 g/g and an absorption under high load (AUHL) of

$$AUHL = -0{,}00207 \times CRC^3 + 0{,}1755 \times CRC^2 - 4{,}485\ CRC + 57{,}726 \text{ (Fig. 27: y0(x))}$$

wherein AUHL [g/g] is the absorption under high load and CRC [g/g] is the centrifuge retention capacity.

The present invention further provides water-absorbent polymer particles having an average particle diameter (d_{50}) from 150 to 400 µm, preferably from 170 to 379 µm, more preferably from 190 to 350 µm, most preferably from 200 to 330 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 5% by weight, preferably less than 2% by weight, more preferably less than 1% by weight, most preferably less than 0.5% by weight, an amount of water-absorbent polymer particles having a particle size of more than

500 µm of less than 5% by weight, preferably less than 2% by weight, more preferably less than 1% by weight, most preferably less than 0.5% by weight, a centrifuge retention capacity (CRC) from 20 to 85 g/g, preferably from 25 to 80 g/g, more preferably from 25 to 75 g/g, most preferably from 30 to 70 g/g, and a degree of polydispersity α of the particle size of

$$\alpha = (d_{84.13} - d_{15,87})/(2 \times d_{50})$$

wherein α is less than 0.3, preferred α less than 0.28, more preferred α less than 0.25, most preferred α less than 0.20, and

wherein $d_{15,87}$, d_{50} and $d_{84,13}$ are the values of the mesh size which gives rise to a cumulative 15,87%, 50,00%, and 84,13% by weight.

Preferred are water-absorbent polymer particles having an average particle diameter (d_{50}) from 170 to 379 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 2% by weight, an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 2% by weight, and a centrifuge retention capacity (CRC) from 25 to 80 g/g.

More preferred are water-absorbent polymer particles having an average particle diameter (d_{50}) from 190 to 350 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 1% by weight, an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 1% by weight, and a centrifuge retention capacity (CRC) from 35 to 75 g/g.

Most preferred are water-absorbent polymer particles having an average particle diameter (d_{50}) from 200 to 330 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 0.5% by weight, an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 0.5% by weight, and a centrifuge retention capacity (CRC) from 38 to 72 g/g.

The inventive water-absorbent polymer particles have roundness from preferably from 0.80 to 0.95, more preferably from 0.82 to 0.93, even more preferably from 0.84 to 0.91, most preferably from 0.85 to 0.90.

Water-absorbent polymer particles with relatively low roundness are obtained by reverse suspension polymerization when the polymer beads are agglomerated during or after the polymerization.

Water-absorbent polymer particles with relatively low roundness are also obtained by customary solution polymerization (gel polymerization). During preparation such water-absorbent polymers are ground and classified after drying to obtain irregular polymer particles.

The inventive water-absorbent polymer particles have a bulk density preferably from 0.6 to 1 g/cm³, more preferably from 0.65 to 0.95 g/cm³, most preferably from 0.7 to 0.9 g/cm³.

The inventive water-absorbent polymer particles have a HC 60 value of preferably at least 80, more preferably of at least 85, most preferably of at least 90.

The level of extractable constituents of the inventive water-absorbent polymer particles is preferably from 0.1 to 30% by weight, more preferably from 0.5 to 20% by weight, most preferably from 1 to 10% by weight.

The inventive water-absorbent polymer particles can be mixed with other water-absorbent polymer particles prepared by other processes, i.e. solution polymerization.

Fluid-absorbent articles

The present invention further provides fluid-absorbent articles. The fluid-absorbent articles comprise of

(A) an upper liquid-pervious layer
(B) a lower liquid-impervious layer
(C) a fluid-absorbent core between (A) and (B) comprising
from 5 to 90% by weight fibrous material and from 10 to 95% by weight water-absorbent polymer particles of the present invention;
preferably from 20 to 80% by weight fibrous material and from 20 to 80% by weight water-absorbent polymer particles of the present invention;
more preferably from 30 to 75% by weight fibrous material and from 25 to 70% by weight water-absorbent polymer particles of the present invention;
most preferably from 40 to 70% by weight fibrous material and from 30 to 60% by weight water-absorbent polymer particles of the present invention;
(D) an optional acquisition-distribution layer between (A) and (C), comprising
from 80 to 100% by weight fibrous material and from 0 to 20% by weight water-absorbent polymer particles of the present invention;
preferably from 85 to 99.9% by weight fibrous material and from 0.01 to 15% by weight water-absorbent polymer particles of the present invention;
more preferably from 90 to 99.5% by weight fibrous material and from 0.5 to 10% by weight water-absorbent polymer particles of the present invention;
most preferably from 95 to 99% by weight fibrous material and from 1 to 5% by weight water-absorbent polymer particles of the present invention;
(E) an optional tissue layer disposed immediately above and/or below (C); and
(F) other optional components.

Fluid-absorbent articles are understood to mean, for example, incontinence pads and incontinence briefs for adults or diapers for babies. Suitable fluid-absorbent articles including fluid-absorbent compositions comprising fibrous materials and optionally water-absorbent polymer particles to form fibrous webs or matrices for the substrates, layers, sheets and/or the fluid-absorbent core.

Suitable fluid-absorbent articles are composed of several layers whose individual elements must show preferably definite functional parameter such as dryness for the upper liquid-pervious layer, vapor permeability without wetting through for the lower liquid-impervious layer, a flexible, vapor permeable and thin fluid-absorbent core, showing fast absorption rates and being able to retain highest quantities of body fluids, and an acquisition-distribution layer between the upper layer and the core, acting as transport and distribution layer of the discharged body fluids. These individual elements are combined such that the resultant fluid-absorbent article meets overall criteria such as flexibility, water vapor breathability, dryness, wearing comfort and protection on the one side, and concerning liquid retention, rewet and prevention of wet through on the other side. The specific combination of these layers provides a fluid-absorbent article delivering both high protection levels as well as high comfort to the consumer.

The products as obtained by the present invention are also very suitable to be incorporated into low-fluff, low-fiber, fluff-less, or fiber-less hygiene article designs. Such designs and methods to make them are for example described in the following publications and literature cited therein and are expressly incorporated into the present invention: WO 2010/133529 A2, WO 2011/084981 A1, US 2011/0162989, US 2011/0270204, WO 2010/082373 A1, WO 2010/143635 A1, US 6,972,011, WO 2012/048879 A1, WO 2012/052173 A1 und WO 2012/052172 A1.

The present invention further provides fluid-absorbent articles, comprising water-absorbent polymer particles of the present invention and less than 15% by weight fibrous material and/or adhesives in the absorbent core.

The water-absorbent polymer particles and the fluid-absorbent articles are tested by means of the test methods described below.

Methods:

The measurements should, unless stated otherwise, be carried out at an ambient temperature of 23 ± 2°C and a relative atmospheric humidity of 50 ± 10%. The water-absorbent polymers are mixed thoroughly before the measurement.

Residual Monomers

The level of residual monomers in the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 210.3 (11) "Residual Monomers".

Particle Size Distribution

The particle size distribution of the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 220.3 (11) "Particle Size Distribution".

The average particle diameter (d_{50}) here is the value of the mesh size which gives rise to a cumulative 50% by weight.

The degree of polydispersity α of the particle size particle is calculated by

$$\alpha = (d_{84.13} - d_{15,87})/(2 \times d_{50})$$

wherein $d_{15,87}$ and $d_{84,13}$ is the value of the mesh size which gives rise to a cumulative 15,87% respective 84,13% by weight.

Moisture Content

The moisture content of the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 230.3 (11) "Mass Loss Upon Heating".

Free Swell Capacity (FSC)

The free swell capacity of the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 240.3 (11) "Free Swell Capacity in Saline, Gravimetric Determination", wherein for higher values of the free swell capacity larger tea bags have to be used.

Centrifuge Retention Capacity (CRC)

The centrifuge retention capacity of the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 241.3 (11) "Fluid Retention Capacity in Saline, After Centrifugation", wherein for higher values of the centrifuge retention capacity larger tea bags have to be used.

Absorption Under Load (AUL)

The absorption under load of the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 242.3 (11) "Gravimetric Determination of Absorption Under Pressure".

Absorption Under High Load (AUHL)

The absortion under high load of the water-absorbent polymer particles is determined analogously to the EDANA recommended test method No. WSP 242.3 (11) "Gravimetric Determination of Absorption Under Pressure", except using a weight of 49.2 g/cm² instead of a weight of 21.0 g/cm².

Bulk Density

The bulk density of the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 250.3 (11) "Gravimetric Determination of Density".

Extractables

The level of extractable constituents in the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 270.3 (11) "Extractables".

Free Swell Rate (FSR)

1.00 g (= W1) of the dry water-absorbent polymer particles is weighed into a 25 ml glass beaker and is uniformly distributed on the base of the glass beaker. 20 ml of a 0.9% by weight sodium chloride solution are then dispensed into a second glass beaker, the content of this beaker is rapidly added to the first beaker and a stopwatch is started. As soon as the last drop of salt solution is absorbed, confirmed by the disappearance of the reflection on the liquid surface, the stopwatch is stopped. The exact amount of liquid poured from the second beaker and absorbed by the polymer in the first beaker is accurately determined by weighing back the second beaker (=W2). The time needed for the absorption, which was measured with the stopwatch, is denoted t. The disappearance of the last drop of liquid on the surface is defined as time t.

The free swell rate (FSR) is calculated as follows:

$$\text{FSR [g/gs]} = \text{W2}/(\text{W1}\text{x}t)$$

When the moisture content of the hydrogel-forming polymer is more than 3% by weight, however, the weight W1 must be corrected for this moisture content.

Roundness

The roundness is determined with the PartAn® 3001 L Particle Analysator (Microtrac Europe GmbH; Meerbusch; Germany). The roundness is defined as

$$Roundness = \frac{4\pi A}{U^2}$$

where A is the cross-sectional area and U is the cross-sectional circumference of the polymer particles. The roundness is the volume-average roundness.

For the measurement, the product is introduced through a funnel and conveyed to the falling shaft with a metering channel. While the particles fall past a light wall, they are recorded selectively by a camera. The images recorded are evaluated by the software in accordance with the parameters selected.

Saline Flow Conductivity (SFC)

The saline flow conductivity of a swollen gel layer under a pressure of 0.3 psi (2070 Pa) is determined, as described in EP 2 535 698 A1, with a weight of 1.5 g of water-absorbing polymer particles as a urine permeability measurement (UPM) of a swollen gel layer. The flow is detected automatically.

The saline flow conductivity (SFC) is calculated as follows:

$$\text{SFC [cm}^3\text{s/g]} = (Fg(t=0) \times L_0)/(d \times A \times WP)$$

where Fg(t = 0) is the flow of NaCl solution in g/s, which is obtained using linear regression analysis of the Fg(t) data of the flow determinations by extrapolation to t = 0, L_0 is the thickness of the gel layer in cm, d is the density of the NaCl solution in g/cm^3, A is the area of the gel layer in cm^2, and WP is the hydrostatic pressure over the gel layer in dynes/cm^2.

Color Value (CIE Color Numbers [L, a, b])

Measurement of the color value is done by means of a colorimeter model „LabScan XE S/N LX17309" (HunterLab; Reston; U.S.A.) according to the CIELAB procedure (Hunterlab, Volume 8, 1996, Issue 7, pages 1 to 4). Colors are described by the coordinates L, a, and b of a three-dimensional system. L characterizes the brightness, whereby L = 0 is black and L = 100 is white. The values for a and b describe the position of the color on the color axis red/green resp. yellow/blue, whereby positive a values stand for red colors, negative a values for green colors, positive b values for yellow colors, and negative b values for blue colors.

The measurement of the color value is in agreement with the tristimulus method according to DIN 5033-6.

Fixed Height Absorption (FHA)

The fixed height absorption is a method to determine the ability of a swollen gel layer to transport fluid by wicking. It is executed and evaluated as described on page 9 and 10 in EP 1 493 453 A1. The following adjustments need to be made:

- Glass frit: 500 ml glass frit P40, as defined by ISO 4793, nominal pore size 16 to 40 µm, thickness 7 mm, e.g. Duran Schott pore size class 3.
- Wet strength tissue: maximum basis weight 24.6 g/cm², size 80 x 80 mm, minimum wet tensile strength 0.32 N/cm (CD direction), and 0.8 N/cm (MD direction), e.g. supplied by Fripa Papierfabrik Albert Friedrich KG, D-63883 Miltenberg.

The tissue is clamped with a metal ring on the bottom side of the sample holder.

$$\text{FHA [g/g]} = (m_3\text{-}m_2)/(m_2\text{-}m_1)$$

where m_1 is the weight of the empty sample holder in g, m_2 is the weight of the sample holder with dry water-absorbent polymer particles in g, and m_3 is the weight of the sample holder with swollen water-absorbent polymer particles in g.

The fixed height absorption is only determined in the context of the present invention with a hydrostatic column pressure corresponding to fixed height absorption at 20 cm.

Volumetric Absorption Under Load (VAUL)

The volumetric absorption under a load is used in order to measure the swelling kinetics, i.e. the characteristic swelling time, of water-absorbent polymer particles under different applied pressures. The height of swelling is recorded as a function of time.

The set-up is shown in Figure 17 and consists of

- An ultrasonic distance sensor (85) type BUS M18K0-XBFX-030-S04K (Balluff GmbH, Neuhausen a.d.F.; Germany) is placed above the cell. The sensor receives ultrasound reflected by the metal plate. The sensor is connected to an electronic recorder.
- A PTFE cell (86) having a diameter of 75 mm, a height of 73 mm and an internal diameter of 52 mm.
- A cylinder (87) made of metal or plastic having a diameter of 50 mm, a height of 71 mm and a mesh at the bottom.
- A metal reflector (88) having a diameter of 57 mm and a height of 45 mm.

- Metal ring weights (89) having a diameter of 100 mm and weights calibrated to 278.0 g or 554.0 g

It is possible to adjust the pressure applied to the sample by changing the combination of cylinder (86) and metal ring (88) weight as summarized in the following tables:

Available Equipment	Weight	psi
Metal reflector	13.0 g	0.009
Plastic cylinder	28.0 g	0.020
Metal cylinder	126.0 g	0.091
Small ring weight	278.0 g	0.201
Large ring weight	554.0 g	0.401

Possible Combinations	psi
Metal reflector + plastic cylinder	0.03
Metal reflector + metal cylinder	0.10
Metal reflector + metal cylinder + small ring weight	0.30
Metal reflector + metal cylinder + large ring weight	0.50
Metal reflector + metal cylinder + small ring weight + large ring weight	0.70

A sample of 2.0 g of water-absorbent polymer particles is placed in the PTFE cell (86). The cylinder (87) and the metal reflector (88) on top are placed into the PTFE cell (86). In order to apply higher pressure, metal rings weights (89) can be placed on the cylinder.

60.0 g of aqueous saline solution (0.9% by weight) are added into the PTFE cell (86) with a syringe and the recording is started. During the swelling, the water-absorbent polymer particles push the cylinder (87) up and the changes in the distance between the metal reflector (88) and the sensor (85) are recorded.

After 120 minutes, the experiment is stopped and the recorded data are transferred from the recorder to a PC using a USB stick. The characteristic swelling time is calculated according to the equation $Q(t) = Q_{\max} \cdot (1 - e^{-t/\tau})$ as described by “Modern Superabsorbent Polymer Technology” (page 155, equation 4.13), wherein Q(t) is the swelling of the water-absorbent polymer particles which is monitored during the experiment, Q_{max} corresponds to the maximum swelling reached after 120 minutes (end of the experiment) and τ is the characteristic swelling time (τ is the inverse rate constant k).

Using the add-in functionality “Solver” of Microsoft Excel software, a theoretical curve can be fitted to the measured data and the characteristic time for 0.03 psi is calculated.

The measurements are repeated for different pressures (0.1 psi, 0.3 psi, 0.5 psi and 0.7 psi) using combinations of cylinder and ring weights. The characteristic swelling times for the different pressures can be calculated using the equation $Q(t) = Q_{\max} \cdot (1 - e^{-t/\tau})$.

Wicking absorption

The wicking absorption is used in order to measure the total liquid uptake of water-absorbent polymer particles under applied pressure. The experimental set-up is shown in Figure 18.

A 500 mL glass bottle (90) (100 ml scale, height 26.5 cm) equipped with an exit tube of Duran® glass, is filled with 500 mL of aqueous saline solution (0.9% by weight). The glass bottle (90) has an opening at the bottom end that can be connected to the Plexiglas plate (93) through a flexible hose (91).

A balance (92) connected to a computer is placed on Plexiglas block (area 20 x 26 cm², height 6 cm). The glass bottle (90) is then placed on the balance.

A Plexiglas plate (93) (area 11 x 11 cm², height 3.5 cm) is placed on a lifting platform. A porosity P1 glass frit (94) of 7cm in diameter and 0.45 cm high has been liquid-tightly embedded in the Plexiglas plate (93), i.e. the fluid exits through the pores of the glass frit (94) and not via the edge between Plexiglas plate (93) and glass frit (94). A Plexiglas tube leads through the outer shell of Plexiglas plate (93) into the center of the Plexiglas plate up to the glass frit (94) to ensure fluid transportation. The fluid tube is then connected with the flexible hose (length 35 cm, 1.0 cm external diameter, 0.7 cm internal diameter) to the glass bottle (90).

The lifting platform is the used to adjust the upper side of the glass frit (94) to the level of the bottom end of the glass bottle (90), so that an always atmospheric flux of fluid from the glass bottle (90) to the measuring apparatus is ensured during measurement. The upper side of the glass frit (94) is adjusted such that its surface is moist but there is no standing film of water on the glass frit (94).

The aqueous saline solution in the glass bottle (90) is made up to 500 mL before every run.

In a Plexiglas cylinder (95) (external diameter 7 cm , internal diameter 6 cm , height 16 cm) and equipped with a 400 mesh (36µm) at the bottom are placed 26 g of water-absorbent polymer particles. The surface of the water-absorbent polymer particles is smoothed. The filling level is about 1.5 cm. Then, a weight (96) of 0.3 psi (21.0 g/cm²) is placed on top of the water-absorbent polymer particles.

The Plexiglas cylinder (95) is placed on the glass frit (94) and the electronic data recording started. A decrease in the weight of the balance (92) is registered as a function of time. This then indicates how much aqueous saline solution has been absorbed by the swelling gel of water-absorbent polymer particles at a certain time. The data are automatically captured every 10 seconds. The measurement is carried out at 0.3 psi (21.0 g/cm²) for a period of 120 minutes per sample. The total liquid uptake is the total amount of aqueous saline solution absorbed by each 26 g sample.

The EDANA test methods are obtainable, for example, from the EDANA, Avenue Eugène Plasky 157, B-1030 Brussels, Belgium.

Examples

Example 1

The process was performed in a concurrent spray drying plant with an integrated fluidized bed (27) as shown in Fig. 1. The reaction zone (5) had a height of 22m and a diameter of 3.4m. The internal fluidized bed (IFB) had a diameter of 3m and a weir height of 0.25m.

The drying gas was feed via a gas distributor (3) at the top of the spray dryer. The drying gas was partly recycled (drying gas loop) via a cyclone as dust separation unit (9) and a condenser column (12). The drying gas was nitrogen that comprises from 1% to 4% by volume of residual oxygen. Prior to the start of polymerization the drying gas loop was filled with nitrogen until the residual oxygen was below 4% by volume. The gas velocity of the drying gas in the reaction zone (5) was 0.79m/s. The pressure inside the spray dryer was 4mbar below ambient pressure.

The temperature of the gas leaving the reaction zone (5) was measured at three points around the circumference at the end of the cylindrical part of the spray dryer as shown in Fig. 3. Three single measurements (43) were used to calculate the average temperature (spray dryer outlet temperature). The drying gas loop was heated up and the dosage of monomer solution is started up. From this time the spray dryer outlet temperature was controlled to 115°C by adjusting the gas inlet temperature via the heat exchanger (20). The gas inlet temperature was 167°C and the steam content of the drying gas is shown in Tab. 1.

The product accumulated in the internal fluidized bed (27) until the weir height was reached. Conditioned internal fluidized bed gas having a temperature of 117° was fed to the internal fluidized bed (27) via line (25). The gas velocity of the internal fluidized bed gas in the internal fluidized bed (27) was 0.65m/s. The residence time of the product was 150min. The temperature of the water-absorbent polymer particles in the internal fluidized bed (27) was 78°C.

The spray dryer offgas was filtered in cyclone as dust separation unit (9) and sent to a condenser column (12) for quenching/cooling. Excess water was pumped out of the condenser column (12) by controlling the (constant) filling level inside the condenser column (12). The water inside the condenser column (12) was cooled by a heat exchanger (13) and pumped counter-current to the gas. The temperature and the steam content of the gas leaving the condenser column (12) are shown in Tab. 1. The water inside the condenser column (12) was set to an alkaline pH by dosing sodium hydroxide solution to wash out acrylic acid vapors.

The gas leaving the condenser column (12) was split to the drying gas inlet pipe (1) and the conditioned internal fluidized bed gas (25). The gas temperatures were controlled via heat exchangers (20) and (22). The hot drying gas was fed to the concurrent spray dryer via gas distributor (3). The gas distributor (3) consists of a set of plates providing a pressure drop of 2 to 4mbar depending on the drying gas amount.

The product was discharged from the internal fluidized bed (27) via rotary valve (28) into sieve (29). The sieve (29) was used for sieving off overs/lumps having a particle diameter of more than 800 µm. The weight amounts of overs/lumps are summarized in Tab. 1.

The monomer solution was prepared by mixing first acrylic acid with 3-tuply ethoxylated glycerol triacrylate (internal crosslinker) and secondly with 37.3%by weight sodium acrylate solution. The temperature of the resulting monomer solution was controlled to 10°C by using a heat exchanger and pumping in a loop. A filter unit having a mesh size of 250µm was used in the loop after the pump. The initiators were metered into the monomer solution upstream of the dropletizer by means of static mixers (31) and (32) via lines (33) and (34) as shown in Fig.1. Sodium peroxodisulfate solution having a temperature of 20°C was added via line (33) and [2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride solution together with Brüggolite® FF7 having a temperature of 5°C was added via line (34). Each initiator was pumped in a loop and dosed via control valves to each dropletizer unit. A second filter unit having a mesh size of 140µm was used after the static mixer (32). For dosing the monomer solution into the top of the spray dryer three dropletizer units were used as shown in Fig. 4.

A dropletizer unit consisted of an outer pipe (47) having an opening for the dropletizer cassette (49) as shown in Fig. 5. The dropletizer cassette (49) was connected with an inner pipe (48). The inner pipe (48) having a PTFE block (50) at the end as sealing can be pushed in and out of the outer pipe (47) during operation of the process for maintenance purposes.

The temperature of the dropletizer cassette (49) was controlled to 8°C by water in flow channels (55) as shown in Fig. 8. The dropletizer cassette (49) had 256 bores having a diameter of 170µm and a bore spacing of 15mm. The dropletizer cassette (49) consisted of a flow channel (56) having essential no stagnant volume for homogeneous distribution of the premixed monomer and initiator solutions and one droplet plate (53). The droplet plate (53) had an angled configuration with an angle of 3°. The droplet plate (53) was made of stainless steel and had a length of 630mm, a width of 128mm and a thickness of 1mm.

The feed to the spray dryer consisted of 9,56% by weight of acrylic acid, 33,73% by weight of sodium acrylate, 0.018% by weight of 3-tuply ethoxylated glycerol Triacrylate (purity approx. 85% by weight), 0.071% by weight of [2,2’-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, 0.0028% by weight of Brüggolite® FF7 (Brüggemann Chemicals; Heilbronn; Germany), 0.071% by weight of sodiumperoxodisulfate and water. The degree of neutralization was 73%. The feed per bore was 1.4 kg/h.

The resulting water-absorbent polymer particles were analyzed. The conditions and results are summarized in Tab. 1 to 3.

Example 2

The example was performed analogous to example 1, except that 0,014% by weight 3-tuply ethoxylated glycerol triacrylate was used instead of 0.018% by weight of 3-tuply ethoxylated glycerol triacrylate

Example 3

The example was performed analogous to example 1, except that 0,011% by weight 3-tuply ethoxylated glycerol triacrylate was used instead of 0.018% by weight of 3-tuply ethoxylated glycerol triacrylate

Example 4

The example was performed analogous to example 1, except that 0,007% by weight 3-tuply ethoxylated glycerol triacrylate was used instead of 0.018% by weight of 3-tuply ethoxylated glycerol triacrylate

Example 5

The example was performed analogous to example 1, except that no 3-tuply ethoxylated glycerol triacrylate was used.

Example 6

The example was performed analogous to example 1, except that 0,012% by weight 3-tuply ethoxylated glycerol triacrylate was used instead of 0.018% by weight of 3-tuply ethoxylated glycerol triacrylate.

Example 7

The example was performed analogous to example 6, except that the feed to the spray dryer comprised further 0,053% by weight of Blancolen® HP (Brüggemann Chemicals; Heilbronn; Germany).

Tab. 1: Process conditions of the polymerization for examples 1 to 7

Steam Content CC	Steam Content GD	T gas inlet	T gas outlet	T gas IFB	T IFB	T CC	T GDU
kg/kg	kg/kg	°C	°C	°C	°C	°C	°C
0.1100	0.0651	167	115	105	78	54	45

Steam Content CC: steam content of the gas leaving the condenser column (12)
Steam Content GD: steam content of the gas prior to the gas distributor (3)
T gas inlet: temperature of the gas prior to the gas distributor (3)
T gas outlet: temperature of the gas leaving the reaction zone (5)
T gas IFB temperature of the gas entering the internal fluidized bed (27) via line (25)
T IFB: temperature of the water-absorbent polymer particles in the fluidized bed (27)
T CC: temperature of the gas leaving the condenser column (12)
T GDU: temperature of the gas leaving the gas drying unit (37)

Tab. 2: Properties of the water-absorbent polymer particles (base polymer)

Example	Bulk Density	CRC	AUL	Residual Monomers	Extractables	Moisture	L	a	b
	g/cm³	g/g	g/g	ppm	wt.%	wt.%			
1	73.9	49.6	10.4	5220	4.6	7.9	93.18	2.48	1.56
2	74.4	51.9	9.7	4715	3.8	8.4	93.1	2.3	1.7
3	72.2	57.0	8.3	4940	6.7	8.6	93.3	2.3	1.6
4	73.5	64.8	7.5	4862	9.4	8.8	92.8	2.2	1.9
5	74.7	38.0	5.7	4123	3.8	8.3	93.5	2.2	2.2
6	69,8	48,1	8,6	5922	9,6	8.7	92,5	2,3	1,8
7	70.6	57.9	8.3	5541	9.8	8.1	92.8	1.9	3.5

Tab. 3: Particles Size Distribution (PSD) of the water-absorbent polymer particles (base polymer), measured by sieve fraction analysis

Example	0-100µm	100-200µm	200-250µm	250-300µm	300-400µm	400-500µm	500-600µm	600-850µm	850-1000µm	>1000µm
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
1	0.1	2.2	6.2	12.6	44.4	26.7	5.7	1.9	0.2	0.0
2	0.1	2.1	6.5	12.9	43.6	28.7	4.6	1.4	0.1	0.0
3	0.1	1.7	5.8	12.2	43.8	26.1	6.4	3.7	0.2	0.0
4	0.0	0.7	3.0	8.6	41.1	32.5	9.1	4.6	0.2	0.0
5	0.2	2.2	5.8	11.4	45.1	27.9	5.7	1.7	0.1	0.0
6	0.1	1.4	7.1	10.6	35.2	31.6	8.6	4.8	0.4	0.2
7	0.3	2.4	5.8	9.3	38.9	27.8	8.0	6.6	0.8	0.3

Example 8

1200 g of the water-absorbent polymer particles prepared in example 1 (base polymer) were put into a laboratory ploughshare mixer (model MR5, manufactured by Gebrüder Lödige Maschinenbau GmbH, Paderborn, Germany). A surface-postcrosslinker solution was prepared by mixing 24 g of ethylene carbonate, 2.4 g aluminum lactate and 60 g of deionized water, into a beaker, as described in Tab. 4. At a mixer speed of 200 rpm, the aqueous solution was sprayed onto the polymer particles within one minute by means of a spray nozzle. The mixing was continued for additional 5 minutes. The product was removed and transferred into another ploughshare mixer (model MR5, manufactured by Gebrüder Lödige Maschinenbau GmbH; Paderborn; Germany) which was heated to 160°C before. After mixing for further minutes at 150 or 160°C with sample taking every 10 minutes, the product was removed from the mixer. The trial conditions and the results are summarized in Tab. 5 and 6.

Examples 9 to 14

The example was performed analogous to example 8, except that polymer particles prepared in examples 2 to 7 were used and the temperature of the thermal surface-postcrosslinking was 150 or 160°C, as described in Tab. 4.

Examples 13 a and b

The example was performed analogous to example 13, except that the polymer particles prepared in example 6 were sieved using a 400 µm sieve prior to the thermal surface-postcrosslinking. Both fractions were separately thermal surface-postcrosslinked.

Examples 14 a and b

The example was performed analogous to example 14, except that the polymer particles prepared in example 7 were sieved using a 400 µm sieve prior to the thermal surface-postcrosslinking. Both fractions were separately thermal surface-postcrosslinked.

Examples 14 c to f

The example was performed analogous to example 14, except that the polymer particles prepared in example 7 were sieved using 200, 300, 400, 500, and 850 µm sieves prior to the thermal surface-postcrosslinking. The sieve fractions 200 to 300, 300 to 400, 400 to 500, and 500 to 850 µm were separately thermal surface-postcrosslinked.

Tab. 4: Process conditions of the surface-postcrosslinking (SXL)

Example	Base polymer	Sieve Cut	EC (SXL)	Water (SXL)	Al-Lactate (dry) (SXL)	Temperature (SXL)
	Example	µm	wt.% bop	wt.% bop	wt.% bop	°C
8*)	1	0 – 850	2.0	5.0	0.2	160
9*)	2	0 – 850	2.0	5.0	0.2	160
10*)	3	0 – 850	2.0	5.0	0.2	160
11*)	4	0 – 850	2.0	5.0	0.2	160
12*)	5	0 – 850	2.0	5.0	0.2	160
13*)	6	0 – 850	2.0	5.0	0.2	150
13a	6	0 – 400	2.0	5.0	0.2	150
13b*)	6	400 – 850	2.0	5.0	0.2	150
14*)	7	0 – 850	2.0	5.0	0.2	150
14a	7	0 – 400	2.0	5.0	0.2	150
14b*)	7	400 – 850	2.0	5.0	0.2	150
14c	7	200 – 300	2.0	5.0	0.2	150
14d	7	300 – 400	2.0	5.0	0.2	150
14e*)	7	400 – 500	2.0	5.0	0.2	150
14f*)	7	500 – 850	2.0	5.0	0.2	150

EC:	Ethylene carbonate
bop:	based on polymer
*)	comparative

Tab. 5: Properties of the water-absorbent polymer particles after surface-postcrosslinking (SXL)

Example	Base Polymer	Sieve Cut µm	Time min	CRC g/g	AUL g/g
8*)	Example 1	0 - 850	30	38.7	35.7
			40	35.2	33.2
			50	33.3	32.5
			60	31.9	31.2
			70	30.2	30.5
			80	29.9	29.6
9*)	Example 2	0 - 850	30	39.9	36.1
			40	36.1	34.4
			50	34.5	33.0
			60	32.3	31.7
			70	31.3	31.5
			80	30.7	30.5
10*)	Example 3	0 - 850	30	43.3	36.2
			40	40.5	35.8
			50	38.2	35.1
			60	36.8	34.4
			70	35.2	33.8
			80	34.6	33.5
11*)	Example 4	0 - 850	30	45.7	36.4
			40	42.8	36.5
			50	40.9	36.6
			60	38.8	35.8
			70	37.8	35.3
			80	36.8	34.7
12*)	Example 5	0 - 850	30	61.3	21.7
			40	53.3	33.1
			50	48.0	35.7
			60	45.1	36.3
			70	43.0	36.3
			80	40.9	36.0
			90	35.1	33.3
			100	34.4	32.9

Tab. 5: Properties of the water-absorbent polymer particles after surface-postcrosslinking (SXL) (continued)

Example	Base Polymer	Sieve Cut µm	Time min	CRC g/g	AUL g/g
13*)	Example 6	0 - 850	30	50.0	34.6
			40	48.9	35.5
			50	47.0	35.7
			60	46.1	36.4
			70	44.2	36.3
13a		0 - 400	30	57.2	34.5
			40	55.4	36.5
			50	53.7	37.7
			60	51.8	38.6
			70	50.8	38.7
13b*)		400 - 850	30	43.7	34.4
			40	42.3	34.5
			50	41.1	34.4
			60	40.5	34.3
			70	39.9	34.1
14*)	Example 7	0 - 850	20	48.0	33.6
			30	44.4	34.7
			40	42.5	35.0
			50	41.4	34.9
			60	40.6	34.7
14a		0 - 400	20	57.0	28.5
			30	53.6	32.3
			40	50.6	34.5
			50	49.0	35.3
			60	47.0	36.0
14b*)		400 - 850	20	65.5	21.3
			30	61.5	30.0
			40	57.8	33.7
			50	55.2	36.1
			60	54.0	36.9
14c		200 - 300	60	50.8	39.2
14d		300 - 400	60	48.2	38.4
14e*)		400 - 500	60	45.1	35.6
14f*)		500 - 850	60	44.6	33.1

*) comparative

Tab. 6: Particles Size Distribution (PSD) and average particle size (d_{50}) of the water-absorbent polymer particles, measured by sieve fraction analysis.

Example	0-50 µm	50-100 µm	100-150 µm	150-200 µm	200-300 µm	300-400 µm	400-500 µm	500-600 µm	600-850 µm	>850 µm	$D_{15.87}$	d_{50}	$d_{84.13}$	α
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	µm	µm	µm	
8*)	0.00	0.00	0.02	0.56	10.56	42.87	31.00	8.18	6.80	0.01	318	384	481	0,21
9*)	0.01	0.00	0.10	0.44	10.05	42.08	32.10	7.99	7.22	0.03	320	387	481	0,21
10*)	0.00	0.01	0.20	1.71	17.54	46.02	24.84	5.47	4.18	0.03	268	361	455	0,26
11*)	0.02	0.04	0.11	0.66	12.60	47.35	28.46	6.50	4.27	0.02	311	373	466	0,21
12*)	0.00	0.02	0.15	1.11	15.54	48.26	26.28	5.37	3.24	0.02	286	365	455	0,23
13*)	0.02	0.02	0.06	0.44	10.42	45.14	31.07	7.64	5.20	0.01	319	382	475	0,20
13a	0.03	0.04	0.11	0.79	18.57	78.22	2.21	0.03	0.00	0.00	276	340	380	0,15
13b*)	0.00	0.00	0.00	0.01	0.04	4.53	66.16	17.39	11.85	0.02	437	461	524	0,09
14*)	0.01	0.02	0.16	0.79	14.07	44.69	30.91	6.10	3.24	0.01	298	374	465	0,22
14a	0.02	0.03	0.27	1.32	23.55	71.25	3.45	0.11	0.00	0.00	253	336	380	0,19
14b*)	0.00	0.00	0.00	0.00	0.07	4.01	72.69	15.15	8.04	0.04	439	459	509	0,08
14c	0.00	0.00	0.02	6.10	85.45	8.41	0.02	0.00	0.00	0.00	216	245	284	0,14
14d	0.00	0.00	0.02	0.30	5.93	87.90	5.61	0.21	0.03	0.00	334	350	384	0,07
14e*)	0.00	0.00	0.00	0.03	0.67	8.02	84.89	5.54	0.83	0.02	428	448	484	0,06
14f*)	0.00	0.00	0.01	0.21	0.45	0.89	3.14	60.64	32.50	2.16	525	549	604	0,07

*) comparative

Example 15

1200 g of the water-absorbent polymer particles prepared in example 1 (base polymer) were put into a laboratory ploughshare mixer (model MR5, manufactured by Gebrüder Lödige Maschinenbau GmbH, Paderborn, Germany). A surface-postcrosslinker solution was prepared by mixing 30 g of ethylene carbonate, 3,0 g aluminum lactate and 60 g of deionized water, into a beaker. At a mixer speed of 200 rpm, the aqueous solution was sprayed onto the polymer particles within one minute by means of a spray nozzle. The mixing was continued for additional 5 minutes. The product was removed and transferred into another ploughshare mixer (model MR5, manufactured by Gebrüder Lödige Maschinenbau GmbH; Paderborn; Germany) which was heated to 160°C before. After mixing for 55 minutes at160°C the product was removed from the mixer. The trial conditions and the results are summarized in Tab. 7 and 8 and Fig. 19 to 25.

Examples 15 a to g

The example was performed analogous to example 15, except that the polymer particles prepared in example 7 were sieved using 100, 200, 300, 400, 500, 600, 710, 850 and 1000 μm sieves prior to the thermal surface-postcrosslinking. The sieve fractions 100 to 200, 200 to 300, 300 to 400, 400 to 500, 500 to 600, 600 to 710, and 710 to 850 μm were separately thermal surface-postcrosslinked. The trial conditions and the results are summarized in Tab. 7 and 8 and Fig. 19 to 25.

Example 16 (comparative example)

By continuously mixing water, 50% by weight sodium hydroxide solution and acrylic acid, a 42.7% by weight acrylic acid/sodium acrylate solution was prepared such that the degree of neutralization was 69.0 mol%. After the components had been mixed, the monomer solution was cooled continuously to a temperature of 30°C by means of a heat exchanger and degassed with nitrogen. The polyethylenically unsaturated crosslinker used was 3-tuply ethoxylated glyceryl triacrylate (purity approx. 85% by weight). The amount used, based on the acrylic acid (boaa) used, was 0.35% by weight. To initiate the free-radical polymerization, the following components were used: 0.0008% by weight boaa of hydrogen peroxide, metered in as a 2.5% by weight aqueous solution, 0.13% by weight boaa of sodium peroxodisulfate, metered in as a 15% by weight aqueous solution, and 0.0023% by weight boaa of ascorbic acid, metered in as a 0.5% by weight aqueous solution. The throughput of the monomer solution was 800 kg/h.

The individual components were metered continuously into a continuous kneader reactor (model ORP 250 Contikneter, List AG, Arisdorf, Switzerland). In the first third of the reactor, 26.3 kg/h of removed undersize with a particle size of less than 150 μm were additionally added.

The reaction solution had a feed temperature of 30°C. The residence time of the reaction mixture in the reactor was approx. 15 minutes.

Some of the polymer gel thus obtained was extruded with an SLRE 75 R extruder (Sela Maschinen GmbH; Harbke; Germany). The temperature of the polymer gel in the course of extrusion was 95°C. The perforated plate had 12 holes having a hole diameter of 8 mm. The thickness of the perforated plate was 16 mm. The ratio of internal length to internal diameter of the extruder (L/D) was 4. The specific mechanical energy (SME) of the extrusion was 26 kWh/t. The extruded polymer gel was distributed on metal sheets and dried at 175°C in an air circulation drying cabinet for 90 minutes. The loading of the metal sheets with polymer gel was 0.81 g/cm².

The dried polymer gel was ground by means of a one-stage roll mill (three milling runs, 1st milling run with gap width 1000 µm, 2nd milling run with gap width 600 µm and 3rd milling run with gap width 400 µm). The ground dried polymer gel was classified and a synthetic particle size distribution (PSD) with the following composition was mixed:

600 to 710 µm: 10.6% by weight
500 to 600 µm: 27.9% by weight
300 to 500 µm: 42.7% by weight
200 to 300 µm: 13.8% by weight
150 to 200 µm: 5.0% by weight

1.2 kg of this polymer (base polymer) were coated in a plowshare mixer with heating jacket (model Pflugschar M5, Gebr. Lödige Maschinenbau GmbH, Paderborn, Germany) at 23°C and a shaft speed of 200 revolutions per minute by means of a two-substance spray nozzle with 54.6 g of a mixture of 0.07% by weight of N-hydroxyethyl-2-oxazolidinone, 0.07% by weight of 1,3-propanediol, 0.7% by weight of propylene glycol, 2.27% by weight of a 22% by weight aqueous aluminum lactate solution, 0.448% by weight of a 0.9% by weight aqueous sorbitan monolaurate solution and 0.992% by weight of isopropanol, the percentages by weight each being based on base polymer.

After the spray application, the product temperature was increased to 185°C and the reaction mixture was held at this temperature and a shaft speed of 50 revolutions per minute for 35 minutes. The resulting product was cooled to ambient temperature and classified again with a 850 µm sieve. The trial conditions and the results are summarized in Tab. 7 and 8 and Fig. 19 to 25.

Example 16 a to g (comparative examples)

The example was performed analogous to example 16, except that the polymer particles prepared in example 7 were sieved using 100, 200, 300, 400, 500, 600, 710, 850 and 1000 µm sieves prior to the thermal surface-postcrosslinking. The sieve fractions 100 to 200, 200 to 300, 300 to 400, 400 to 500, 500 to 600, 600 to 710, and 710 to 850 were separately thermal surface-postcrosslinked. The trial conditions and the results are summarized in Tab. 7 and 8 and Fig. 19 to 25.

Tab. 7: Properties of the water-absorbent polymer particles after surface-postcrosslinking (SXL)

	Sieve Fraction	Average Sieve Width	FSC	CRC	AUHL	SFC	CRC + AUHL	FHA	τ 0.3psi	Wicking uptake
	µm	µm	g/g	g/g	g/g	10^{-7}cm^{3}s/g	g/g	g/g	s	g
Example 15a	100 - 200	150	40.8	24.8	23.1	51	47.9	23.5	144	-
Example 15b	200 - 300	250	48.1	29.7	26.0	48	55.7	26.0	232	266
Example 15c	300 - 400	350	50.8	31.9	26.2	55	58.1	26.5	321	298
Example 15d*)	400 - 500	450	48.8	31.0	25.6	64	56.6	25.5	404	267
Example 15e*)	500 - 600	550	47.3	29.7	24.3	69	54.0	24.1	478	227
Example 15f*)	600 - 710	655	48.2	29.2	23.8	64	53.0	23.3	563	-
Example 15g*)	710 - 850	780	48.3	29.2	23.6	50	52.8	23.1	633	-
Example 15*)	0 - 850		47.1	30.3	24.6	62	54.9	25.4	-	290
Example 16a	100 - 200	150	35.9	20.3	21.0	116	41.3	20.9	46	
Example 16b	200 - 300	250	42.6	22.9	22.5	102	45.4	21.9	81	284
Example 16c	300 - 400	350	46.8	25.2	23.3	88	48.5	21.6	136	242
Example 16d*)	400 - 500	450	50.0	27.4	23.9	74	51.2	19.8	206	223
Example 16e*)	500 - 610	550	51.5	28.3	24.0	77	52.3	19.4	279	203
Example 16f*)	610 - 710	655	51.6	29.4	23.9	68	53.3	17.8	360	186
Example 16g*)	710 - 850	780	50.9	29.7	23.6	65	53.3	14.0	478	-
Example 16	0 - 850		46.1	26.6	23.8	92	50.4	20.8	-	227

*) comparative

Tab. 8: Particles Size Distribution (PSD) and average particle size (d_{50}) of the water-absorbent polymer particles, measured by sieve fraction analysis.

	0- 100 µm	100- 200 µm	200- 300 µm	300- 400 µm	400- 500 µm	500- 600 µm	600- 710 µm	710- 850 µm	850- 1000 µm	$D_{15.87}$	d_{50}	$d_{84.13}$	α
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%		µm	µm	
Example 15*)	0.31	5.31	21.35	54.32	13.34	3.42	1.54	0.40	0.01	284	344	410	0,18
Example 16*)	0.02	2.92	15.51	19.24	30.10	26.60	5.40	0.21	0.00	249	442	553	0,34

*) comparative

Example 17

1200 g of the water-absorbent polymer particles prepared in example 1 (base polymer) were put into a laboratory ploughshare mixer (model MR5, manufactured by Gebrüder Lödige Maschinenbau GmbH, Paderborn, Germany). A surface-postcrosslinker solution was prepared by mixing 30 g of ethylene carbonate, 3,0 g aluminum lactate and 60 g of deionized water, into a beaker, as described in Table 4. At a mixer speed of 200 rpm, the aqueous solution was sprayed onto the polymer particles within one minute by means of a spray nozzle. The mixing was continued for additional 5 minutes. The product was removed and transferred into another ploughshare mixer (model MR5, manufactured by Gebrüder Lödige Maschinenbau GmbH; Paderborn; Germany) which was heated to 160°C before. After mixing for further minutes at 160°C with sample taking every 10 minutes, the product was removed from the mixer. The trial conditions and the results are summarized in Tab. 9 and 11 and Fig. 26.

Example 17 a

The example was performed analogous to example 17, except that the polymer particles prepared in example 1 were sieved using a 400 µm sieve prior to the thermal surface-postcrosslinking. The sieve fraction 0 to 400 µm was separately thermal surface-postcrosslinked. The trial conditions and the results are summarized in Tab. 9 and 11 and Fig. 26.

Example 18

The example was performed analogous to example 17, except that water-absorbent polymer particles prepared in example 6 (base polymer) were used as base polymer. The trial conditions and the results are summarized in Tab. 10 and 11 and Fig. 26.

Example 18a

The example was performed analogous to example 18, except that the polymer particles prepared in example 6 were sieved using a 400 µm sieve prior to the thermal surface-postcrosslinking. The sieve fraction 0 to 400 µm was separately thermal surface-postcrosslinked. The trial conditions and the results are summarized in Tab. 10 and 11 and Fig. 26.

Tab. 9: Properties of the water-absorbent polymer particles after surface-postcrosslinking (SXL)

	Time	FSC	CRC	AUL	AUHL	(CRC+AUHL)	SFC	FHA	FSR
	min	g/g	g/g	g/g	g/g	g/g	$10^{-7}cm^3 \times s/g$	g/g	g/g
Example 17a	20	70,0	52,1	34,0	14,1	66,2			
	30	62,5	43,7	37,1	25,7	69,4			
	40	59,3	40,5	36,5	27,3	67,8			
	50	56,4	37,2	35,2	27,6	64,8	7		
	60	54,5	35,5	34,2	27,7	63,2	11		
	70	52,0	33,9	33,3	27,1	61,0	18		
	80	51,5	33,0	32,8	26,8	59,8	23		
	90	50,9	32,3	32,2	26,8	59,1	33		
	100	49,3	31,3	31,6	26,3	57,6	34	27,0	0,27
Example 17*)	20	62,9	44,1	35,1	23,1	67,2			
	30	56,2	37,3	33,4	27,1	64,4			
	40	52,8	34,0	32,1	26,9	60,9			
	50	49,9	32,4	31,1	26,3	58,6	31		
	60	48,7	31,0	30,2	25,7	56,7	40		
	70	47,5	30,2	29,7	25,2	55,4	52	25,4	0,2
	80	46,9	29,3	29,1	24,9	54,3	62		
	90	45,1	28,8	28,4	24,5	53,2	73		
	100	45,0	27,8	28,2	24,1	51,9	88		

*) comparative

Tab. 10: Properties of the water-absorbent polymer particles after surface-postcrosslinking (SXL)

	Time	FSC	CRC	AUL	AUHL	(CRC+AUHL)	SFC	FHA	FSR
	min	g/g	g/g	g/g	g/g	g/g	$10^{-7}cm^3$ × s/g	g/g	g/g
Example 18a	20	72,9	54,8	33,7	9,2	64,0			
	30	63,6	43,6	37,3	25,0	68,6			
	40	58,9	38,9	36,0	27,7	66,6	5		
	50	55,7	36,5	34,6	27,7	64,2	10		
	60	53,0	34,2	33,5	27,5	61,7	18		
	70	51,9	33,1	32,8	26,9	60,0	23		
	80	50,6	32,0	31,8	26,8	58,8	34		
	90	48,7	30,5	31,2	26,5	57,0	43		
	100	48,3	30,3	30,6	25,9	56,2	47	26,5	0,26
Example 18*)	20	63,3	44,1	35,2	23,9	68,0			
	30	55,9	37,0	33,5	26,9	63,9			
	40	52,9	34,2	32,2	26,4	60,7			
	50	50,8	32,3	31,1	26,1	58,4			
	60	49,1	30,7	30,4	25,4	56,2	39		
	70	47,1	29,9	29,2	24,8	54,7	48	24,7	0,2
	80	45,8	28,7	29,0	24,5	53,2	67		
	90	45,6	28,2	28,5	24,4	52,7			
	100	44,8	27,4	28,1	24,0	51,4			

*) comparative

Tab. 11: Particles Size Distribution (PSD) and average particle size (d_{50}) of the water-absorbent polymer particles, measured by sieve fraction analysis.

Exp.	0-50 µm	50-100 µm	100-150 µm	150-200 µm	200-300 µm	300-400 µm	400-500 µm	500-600 µm	600-850 µm	>850 µm	$d_{15.87}$	d_{50}	$d_{84.13}$	α
Unit	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	µm	µm	µm	
17*)	0,01	0,02	0,08	0,47	11,42	46,17	30,07	6,68	5,07	0,01	315	377	472	0,25
17a	0,03	0,04	0,12	0,76	18,46	78,22	2,35	0,02	0,00	0,00	276	339	358	0,06
18*)	0,01	0,02	0,13	0,72	13,07	46,45	31,87	5,08	2,64	0,01	305	374	465	0,24
18a	0,02	0,03	0,24	1,24	23,34	71,01	4,04	0,08	0,00	0,00	254	335	361	0,08

*) comparative

Claims

1. A process for producing surface-postcrosslinked water-absorbent polymer particles comprising polymerizing droplets of a monomer solution, comprising

   a) at least one ethylenically unsaturated monomer which bears acid groups and may be at least partly neutralized,
   b) optionally one or more crosslinker,
   c) at least one initiator,
   d) optionally one or more ethylenically unsaturated monomers copolymerizable with the monomers mentioned under a),
   e) optionally one or more water-soluble polymers, and
   f) water,

   in a surrounding heated gas phase or in a surrounding hydrophobic solvent, coating the water-absorbent polymer particles with at least one surface-postcrosslinker and thermal surface-postcrosslinking of the coated water-absorbent polymer particles, wherein the water-absorbent polymer particles are optionally classified prior to the coating, the water-absorbent polymer particles have an average particle diameter from 150 to 400 µm prior to the coating and after the optional classification, the amount of water-absorbent polymer particles having a particle size of less than 100 µm prior to the coating and after the optional classification is less than 5% by weight and the amount of water-absorbent polymer particles having a particle size of more than 500 µm prior to the coating and after the optional classification is less than 5% by weight.

2. A process according to claim 1, wherein the water-absorbent polymer particles have an average particle diameter from 190 to 350 µm prior to the coating and after the optional classification.

3. A process according to any of claims 1 or 2, wherein the amount of water-absorbent polymer particles having a particle size of less than 100 µm prior to the coating and after the optional classification is less than 0.5% by weight.

4. A process according to any of claims 1 to 3, wherein the amount of water-absorbent polymer particles having a particle size of more than 500 µm prior to the coating and after the optional classification is less than 0.5% by weight.

5. A process according to any of claims 1 to 4, wherein droplets of a monomer solution are polymerized in a surrounding heated gas phase, the droplets are generated by means of a plate having bores and the diameter of the bores is in the range from 50 to 170 µm.

6. A process according claim 5, wherein the diameter of the bores is in the range from 120 to 150 µm.

7. A process according any of claims 1 to 6, wherein the moisture content of the water-absorbent polymer prior to the coating and after the optional classification is in the range from 3 to 10% by weight.

8. A process according to any of claims 1 to 7, wherein temperature during the thermal surface-postcrosslinking is in the range from 140 to 160°C.

9. A process according to any of claims 1 to 8, wherein the at least one surface-postcrosslinker is selected from alkylene carbonates, 1,3-oxazolidin-2-ones, bis- and poly-1,3-oxazolidin-2-ones, bis- and poly-1,3-oxazolidines, 2-oxotetrahydro-1,3-oxazines, N-acyl-1,3-oxazolidin-2-ones, N-hydroxyethyl-1,3-oxazolidin-2-ones, cyclic ureas, bicyclic amide acetals, oxetanes, and morpholine-2,3-diones.

10. Water-absorbent polymer particles obtainable according to any of the claims 1 to 9.

11. Water-absorbent polymer particles having an average particle diameter from 150 to 400 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 5% by weight, an amount of water-absorbent polymer particles having a particle size of more than 500 µm of less than 5% by weight, a centrifuge retention capacity from 25 to 85 g/g, and an absorption under load of

$$AUL > -0.000415 \times CRC^3 + 0.0145 \times CRC^2 + 1.1166 \times CRC - 5.27$$

wherein AUL [g/g] is the absorption under load and CRC [g/g] is the centrifuge retention capacity.

12. Polymer particles according to claim 11, wherein the absorption under load is

$$AUL > -0.000415 \times CRC^3 + 0.0145 \times CRC^2 + 1.1166 \times CRC - 3.77$$

wherein AUL [g/g] is the absorption under load and CRC [g/g] is the centrifuge retention capacity.

13. Polymer particles according to any of claims 11 or 12, wherein the centrifuge retention capacity is from 45 to 65 g/g.

14. Water-absorbent polymer particles having an average particle diameter from 150 to 400 µm, an amount of water-absorbent polymer particles having a particle size of less than 100 µm of less than 5% by weight, an amount of water-absorbent polymer particles having a particle

size of more than 500 µm of less than 5% by weight, a centrifuge retention capacity from 20 to 60 g/g, and an absorption under load of

$$AUHL = -0{,}00207 \times CRC^3 + 0{,}1755 \times CRC^2 - 4{,}485\ CRC + 57{,}726$$

wherein AUHL [g/g] is the absorption under high load and CRC [g/g] is the centrifuge retention capacity.

15. Polymer particles according to claim 14, wherein the centrifuge retention capacity is from 30 to 50 g/g.

16. Polymer particles according to any of claims 10 or 15, wherein the average particle diameter is from 200 to 330 µm.

17. Polymer particles according to any of claims 10 or 16, wherein the amount of water-absorbent polymer particles having a particle size of less than 100 µm is less than 0.5% by weight.

18. Polymer particles according to any of claims 10 to 17, wherein the amount of water-absorbent polymer particles having a particle size of more than 500 µm is less than 0.5% by weight.

19. Polymer particles according to any of claims 10 to 18, wherein the degree of polydispersity α of the particle size is less than 0.3.

20. Polymer particles according to any of claims 10 to 19, wherein the roundness of the water-absorbent polymer particles is from 0.80 to 0.95.

21. Polymer particles according to any of claims 10 to 20, wherein water-absorbent polymer particles were thermal surface-postcrosslinked with at least one surface-postcrosslinker selected from alkylene carbonates, 1,3-oxazolidin-2-ones, bis- and poly-1,3-oxazolidin-2-ones, bis- and poly-1,3-oxazolidines, 2-oxotetrahydro-1,3-oxazines, N-acyl-1,3-oxazolidin-2-ones, N-hydroxyethyl-1,3-oxazolidin-2-ones, cyclic ureas, bicyclic amide acetals, oxetanes, and morpholine-2,3-diones.

22. A fluid-absorbent article, comprising water-absorbent polymer particles according to any of claims 10 to 21.

23. A fluid-absorbent article, comprising

(A) an upper liquid-pervious layer,
(B) a lower liquid-impervious layer.

(C) a fluid-absorbent core between the layer (A) and the layer (B), comprising from 5 to 90% by weight fibrous material and from 10 to 95% by weight water-absorbent polymer particles according to any of claims 10 to 21,

(D) an optional acquisition-distribution layer between (A) and (C), comprising from 80 to 100% by weight fibrous material and from 0 to 20% by weight water-absorbent polymer particles according to any of claims 10 to 21,

(E) an optional tissue layer disposed immediately above and/or below (C) and

(F) other optional components.

24. A fluid-absorbent article according to claim 23, wherein the fluid-absorbent article comprises in the fluid-absorbent core (C) less than 15% by weight fibrous material and/or adhesives.

Fig. 1

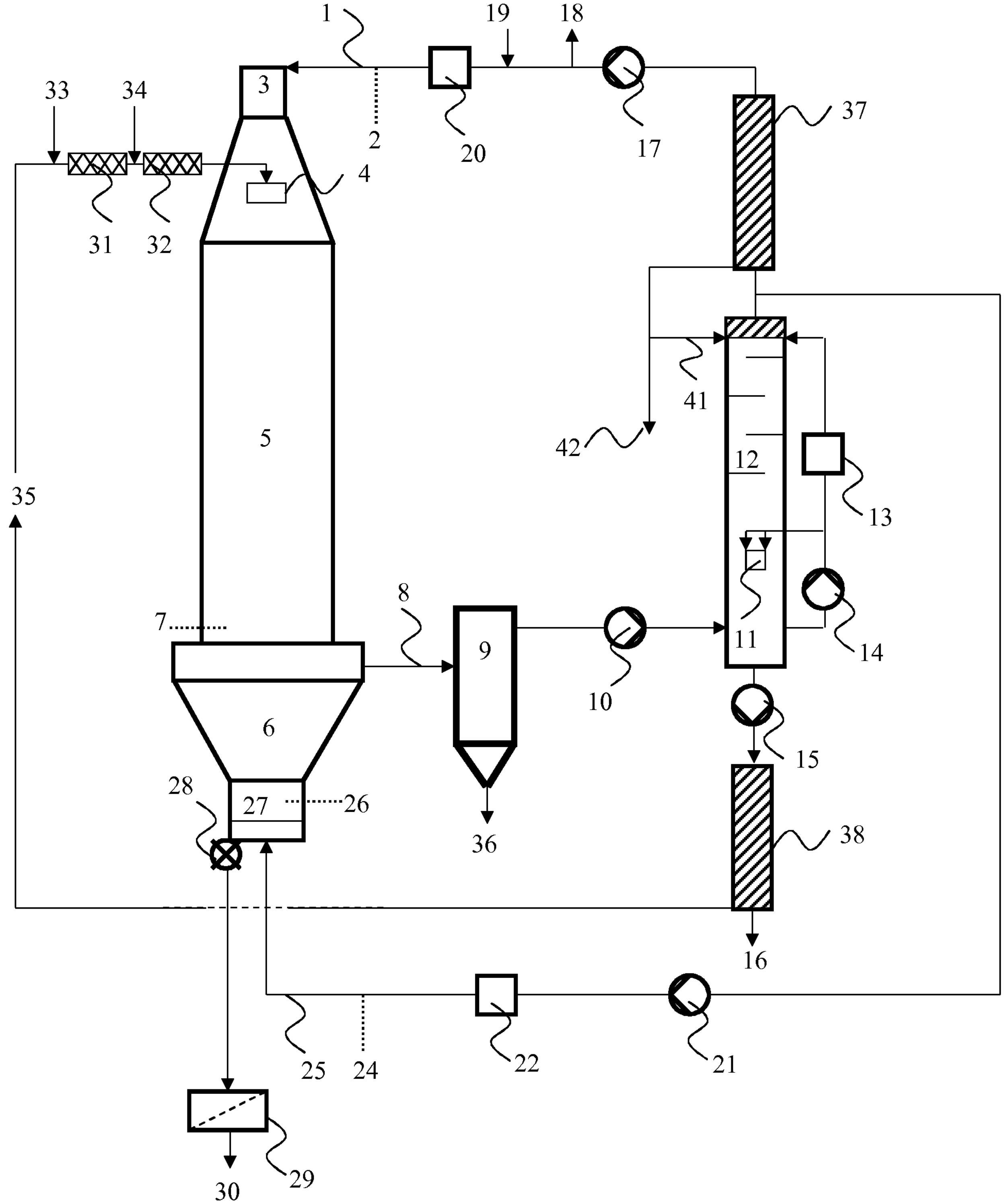

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Fig. 2

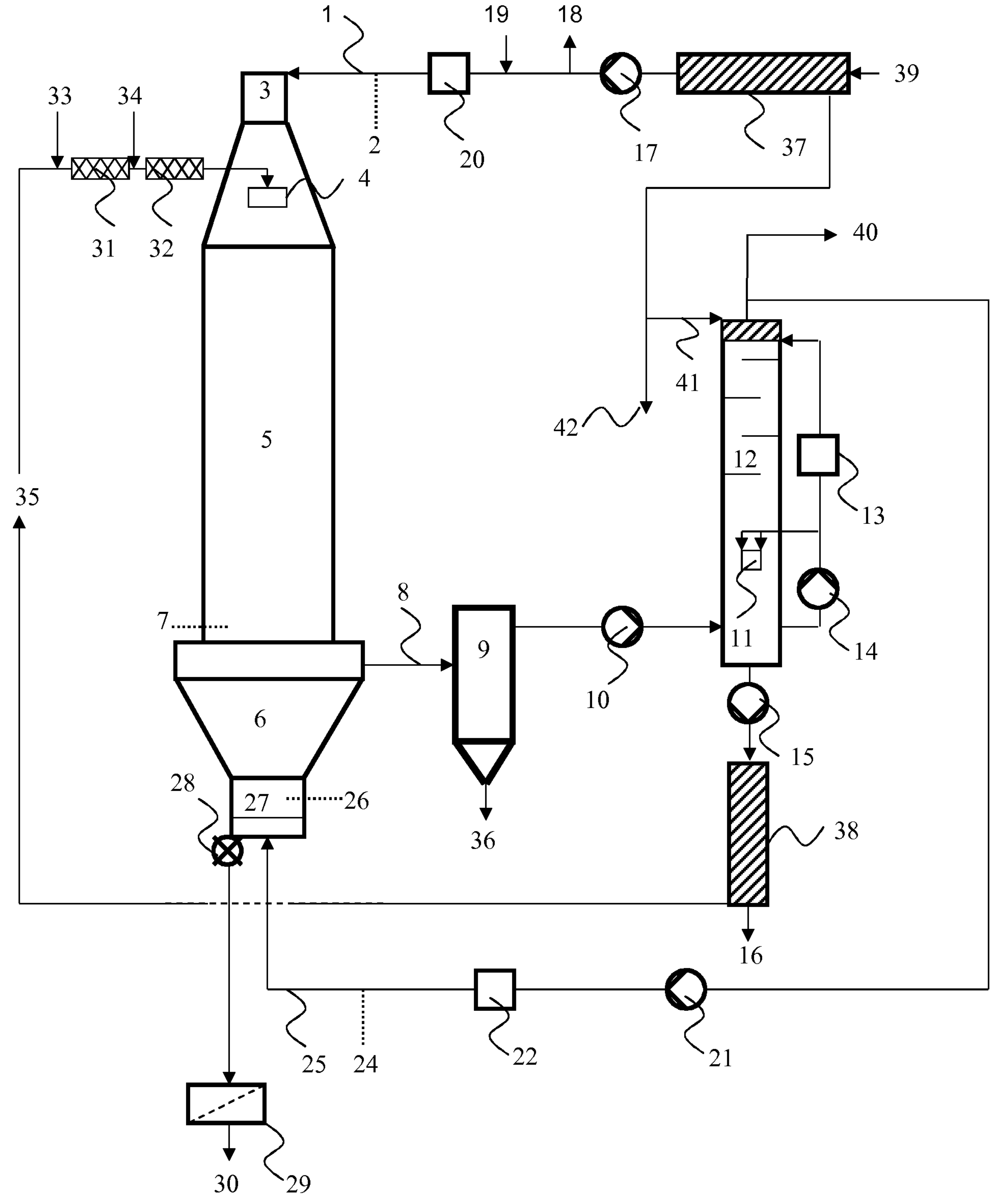
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Fig. 3

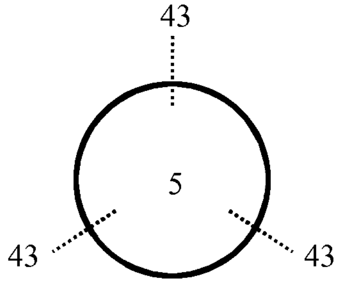

Fig. 4

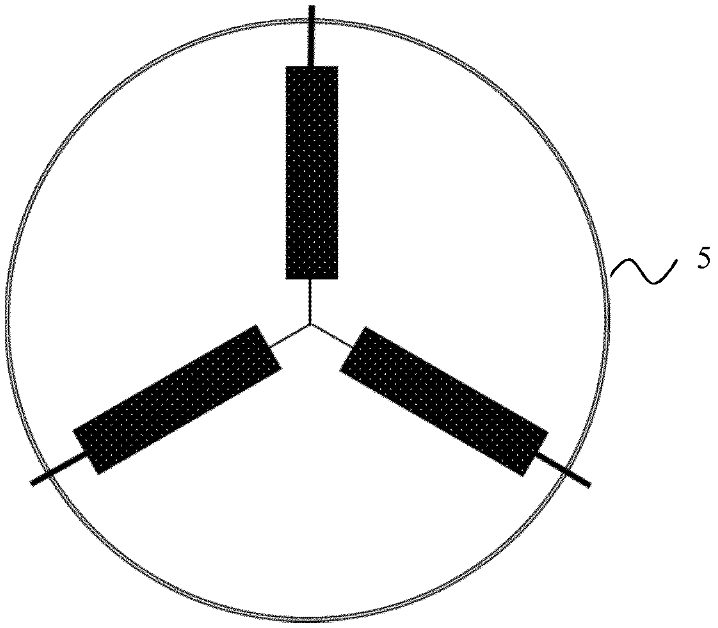

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Fig. 5

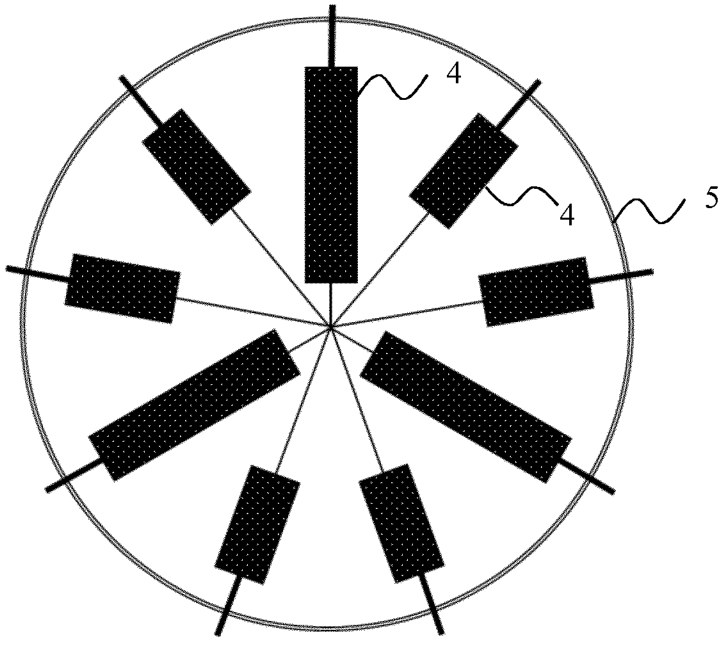
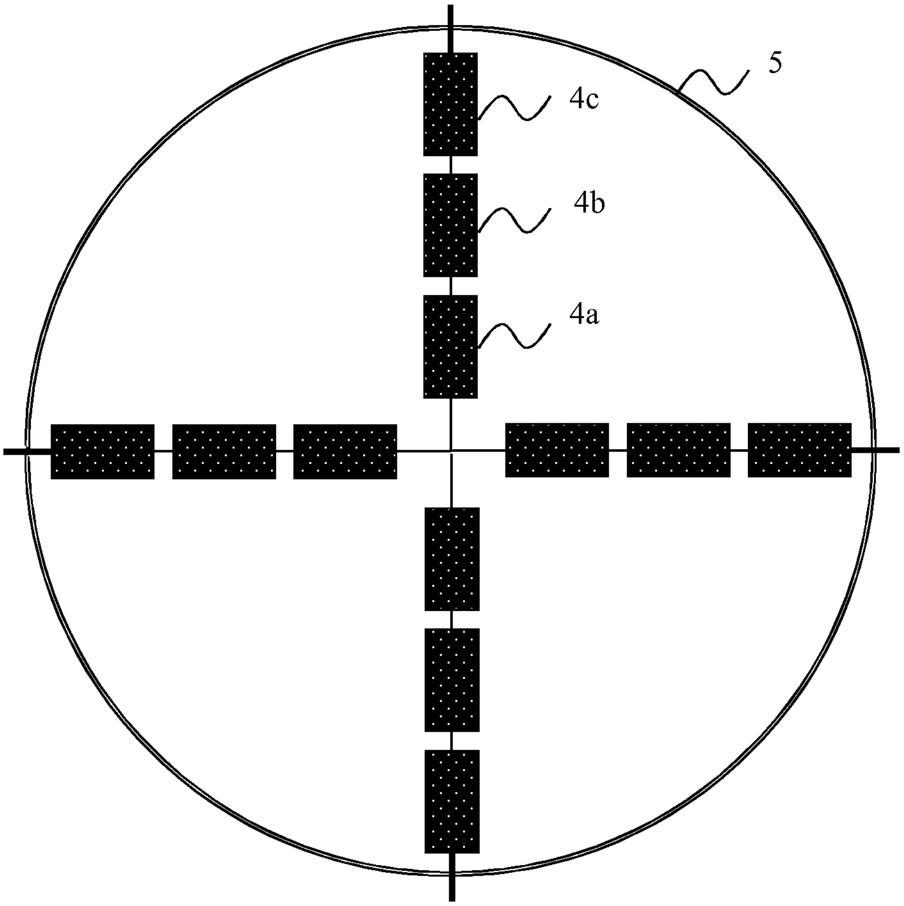


Fig. 6



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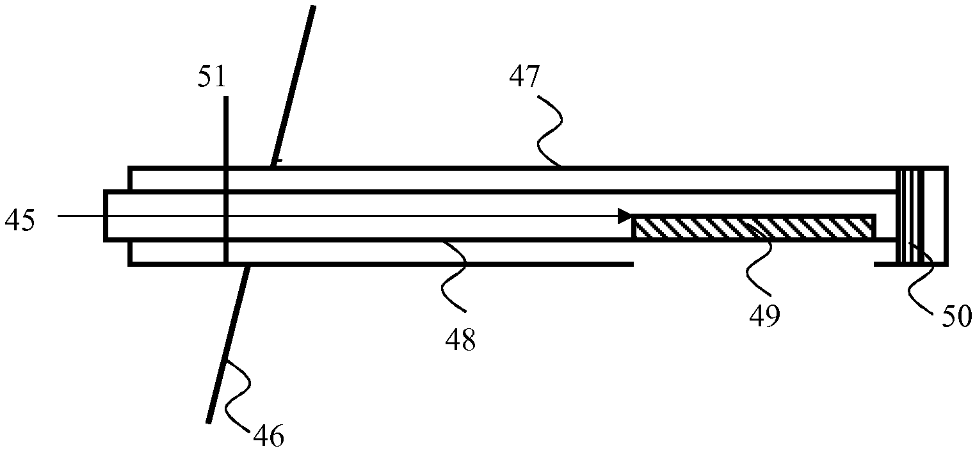

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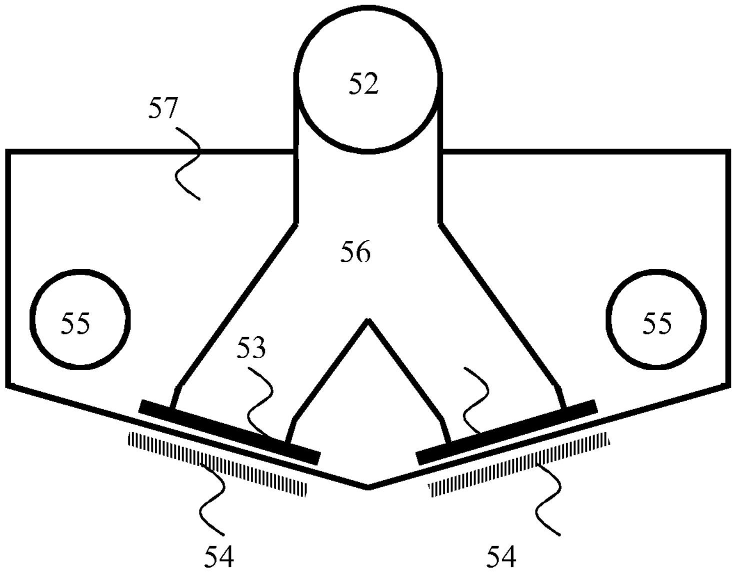

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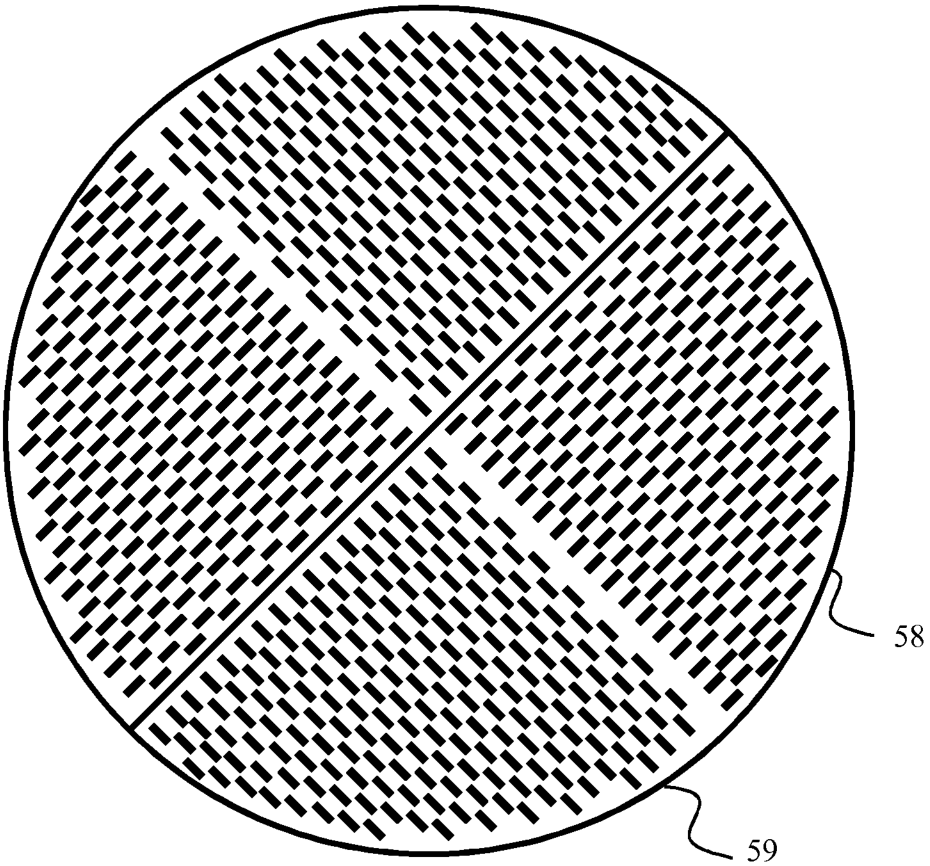

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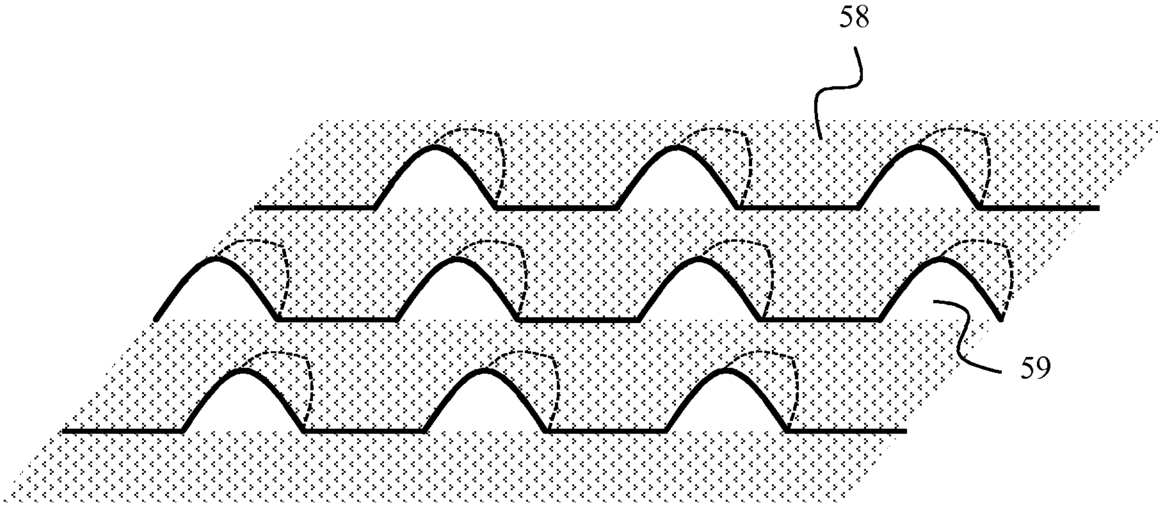


Fig. 11

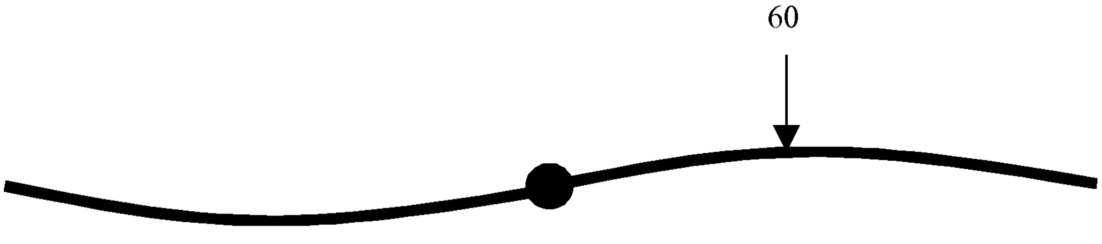


Fig. 12

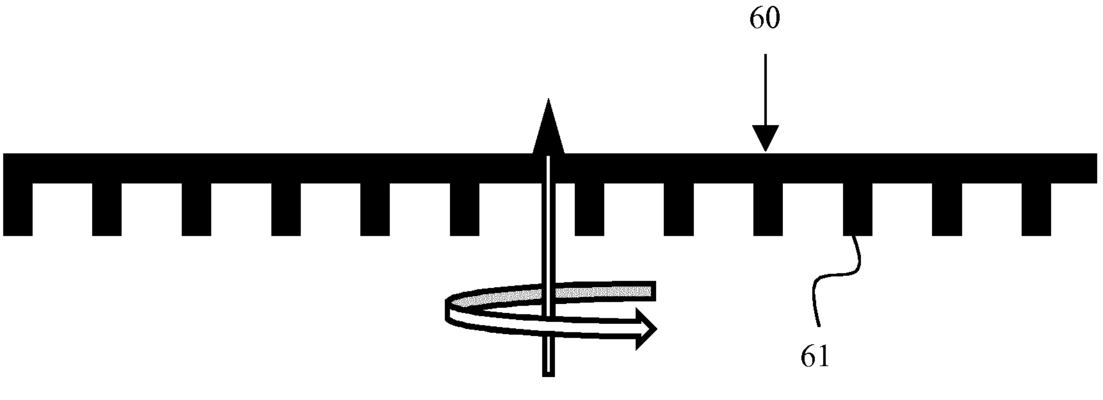


Fig. 13

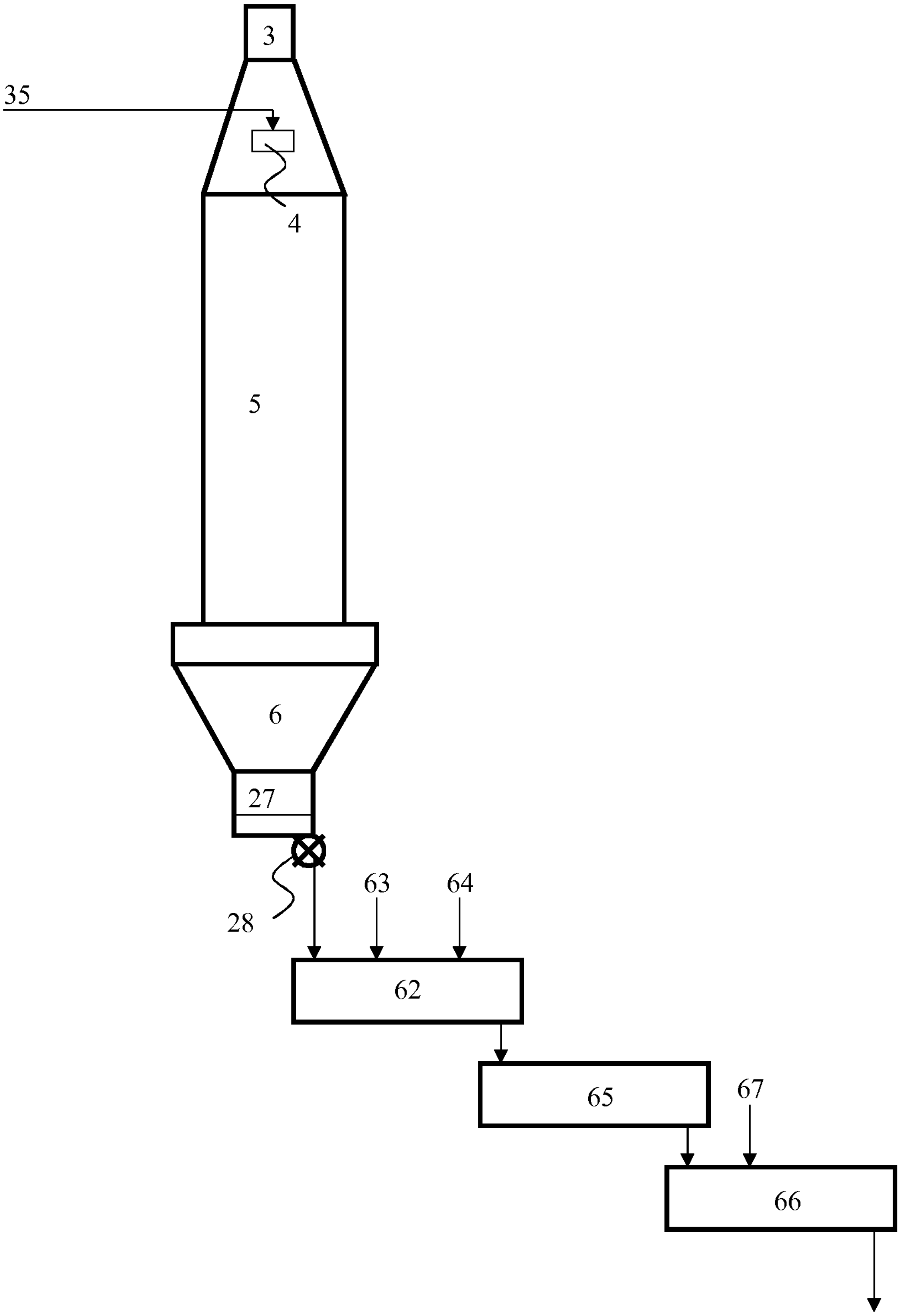


Fig. 14

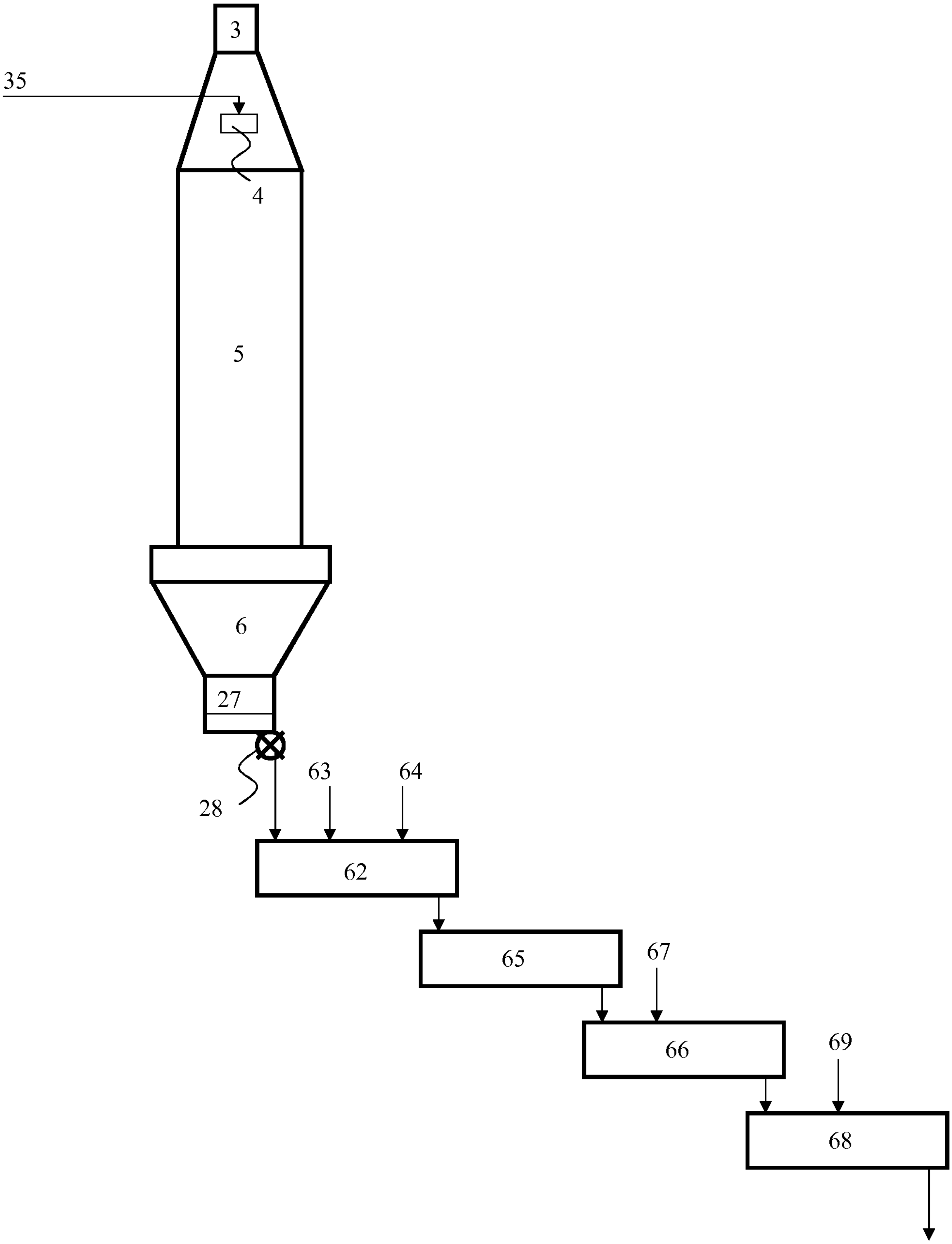


Fig. 15

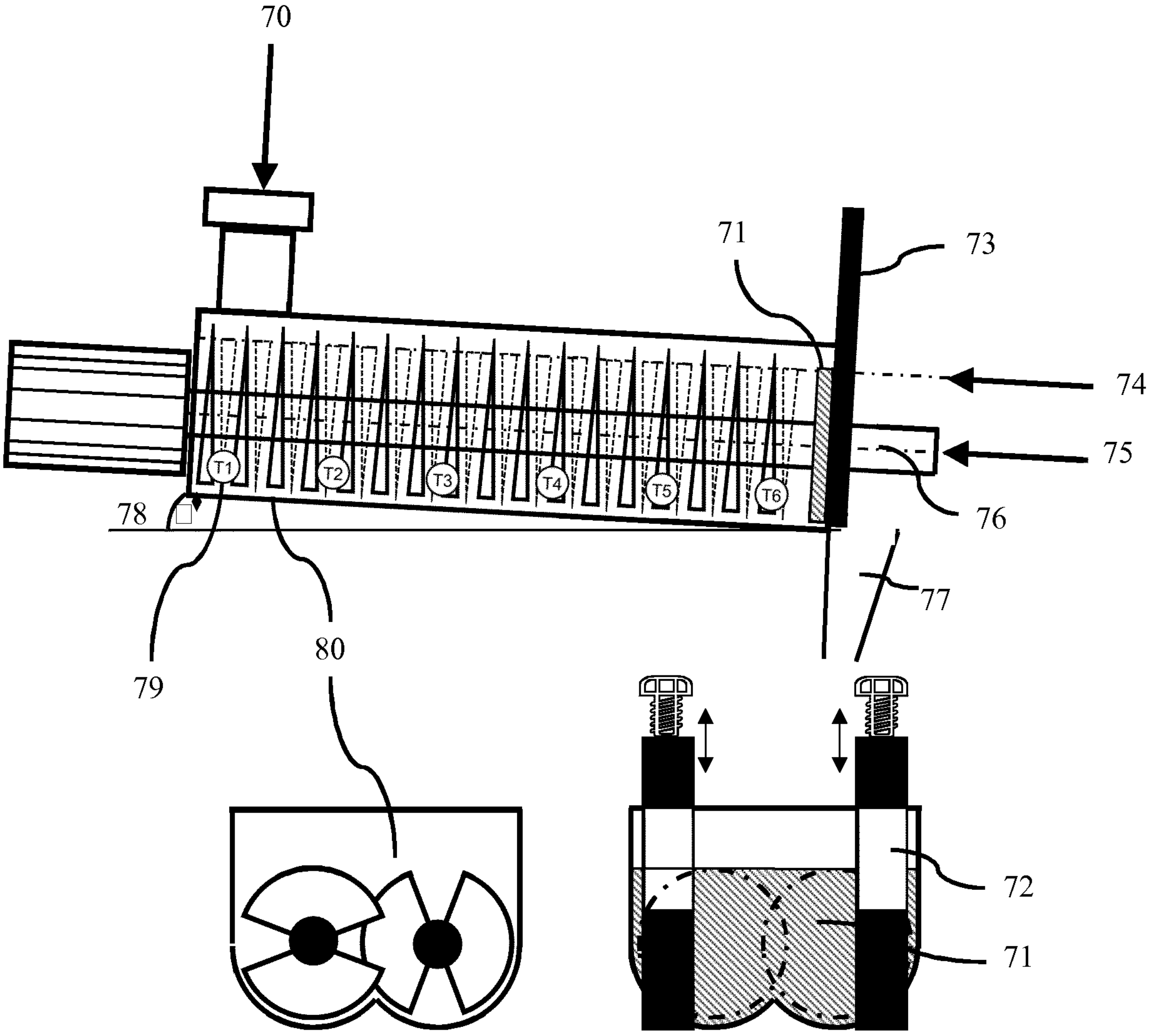
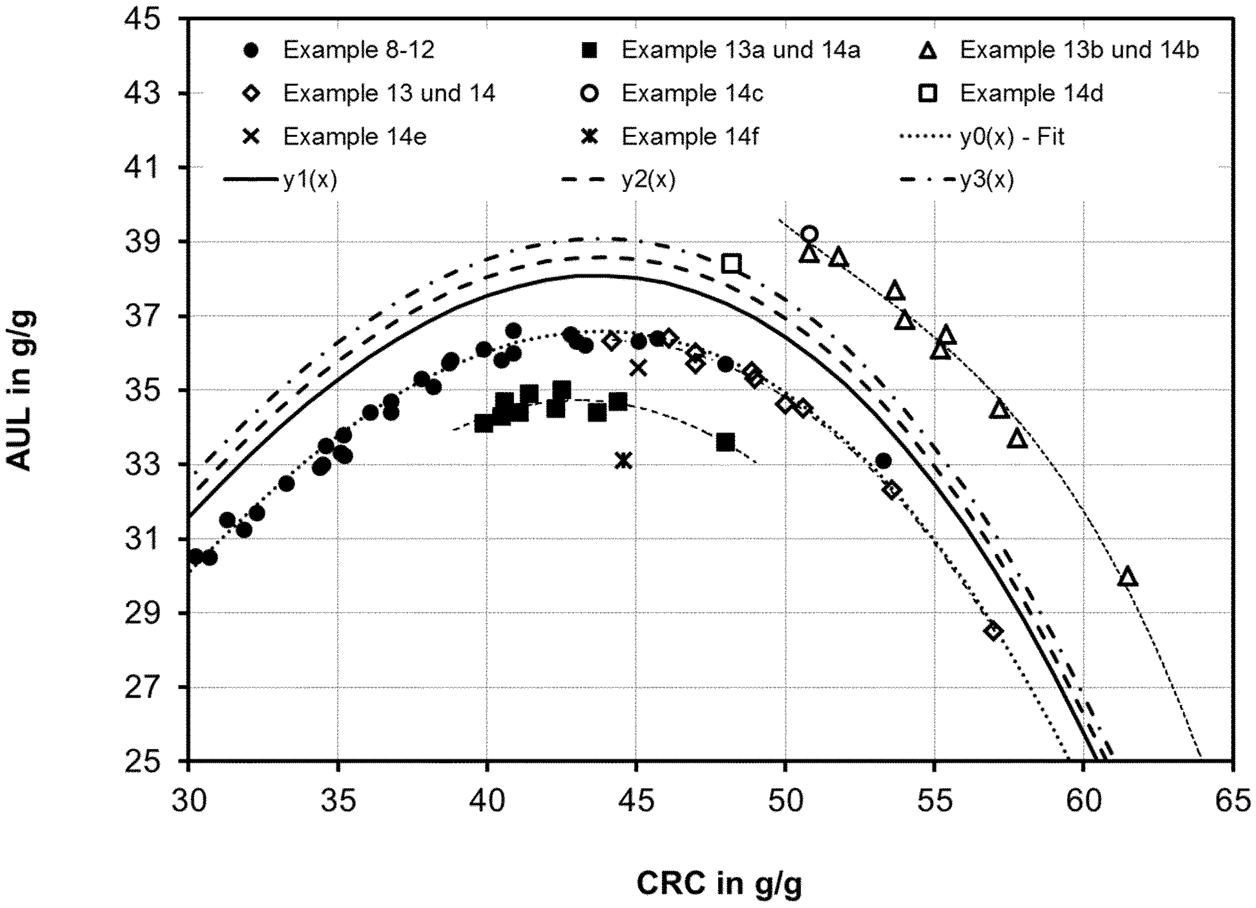


Fig. 16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AUL in g/g
CRC in g/g
● Example 8-12
■ Example 13a und 14a
△ Example 13b und 14b
◇ Example 13 und 14
○ Example 14c
□ Example 14d
× Example 14e
✱ Example 14f
······ y0(x) - Fit
—— y1(x)
– – y2(x)
– · – y3(x)

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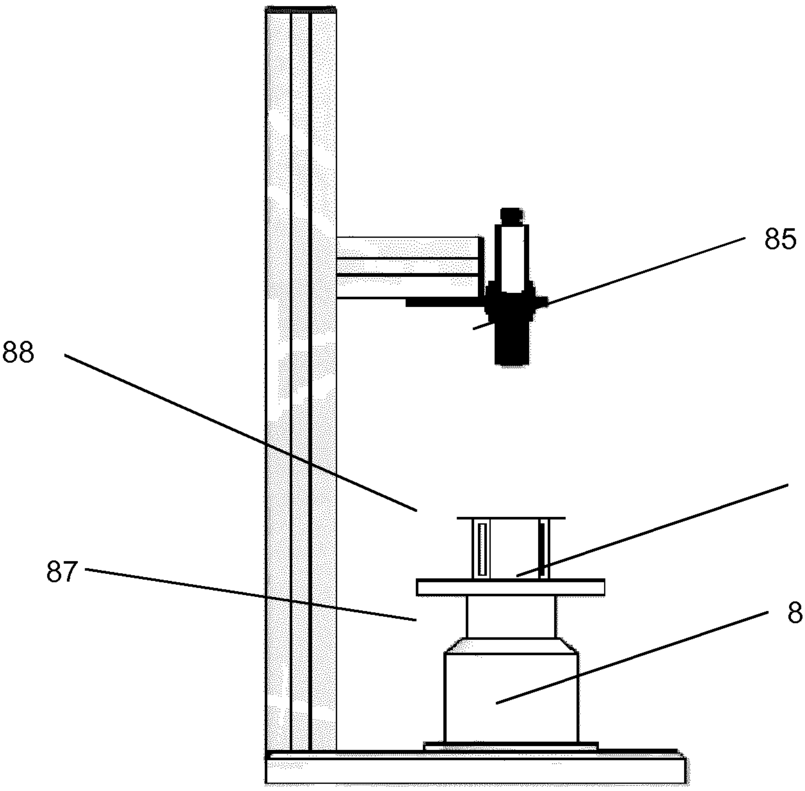
Fig. 17:



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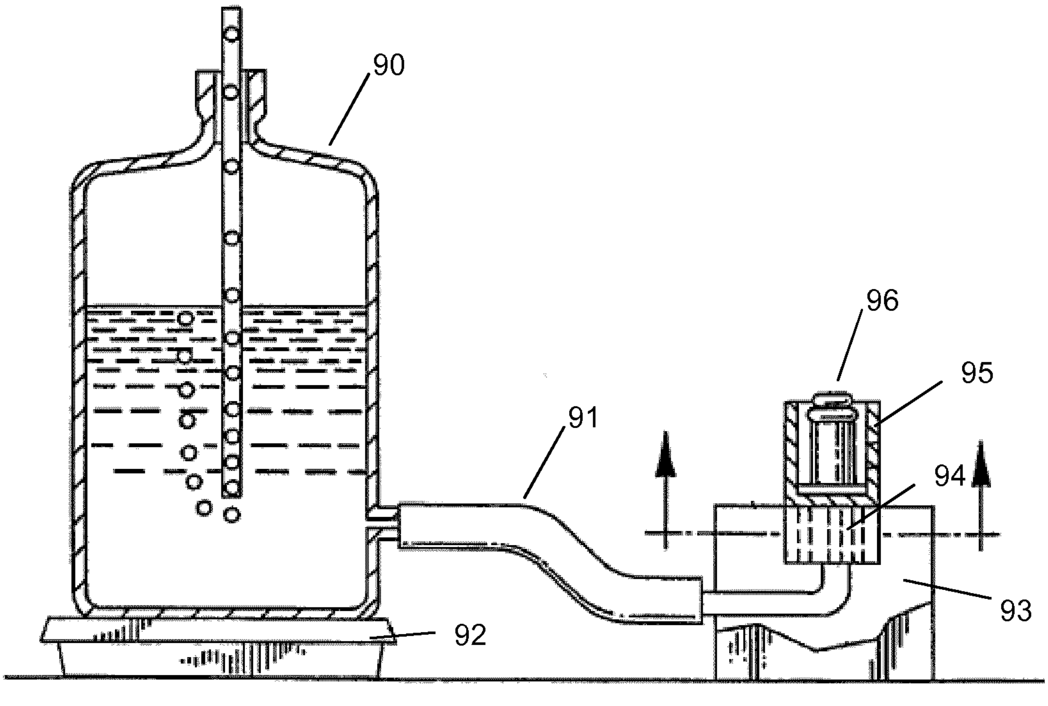

Fig. 19: CRC of the water-absorbent polymer particles after surface-postcrosslinking (SXL) as function of the particle size

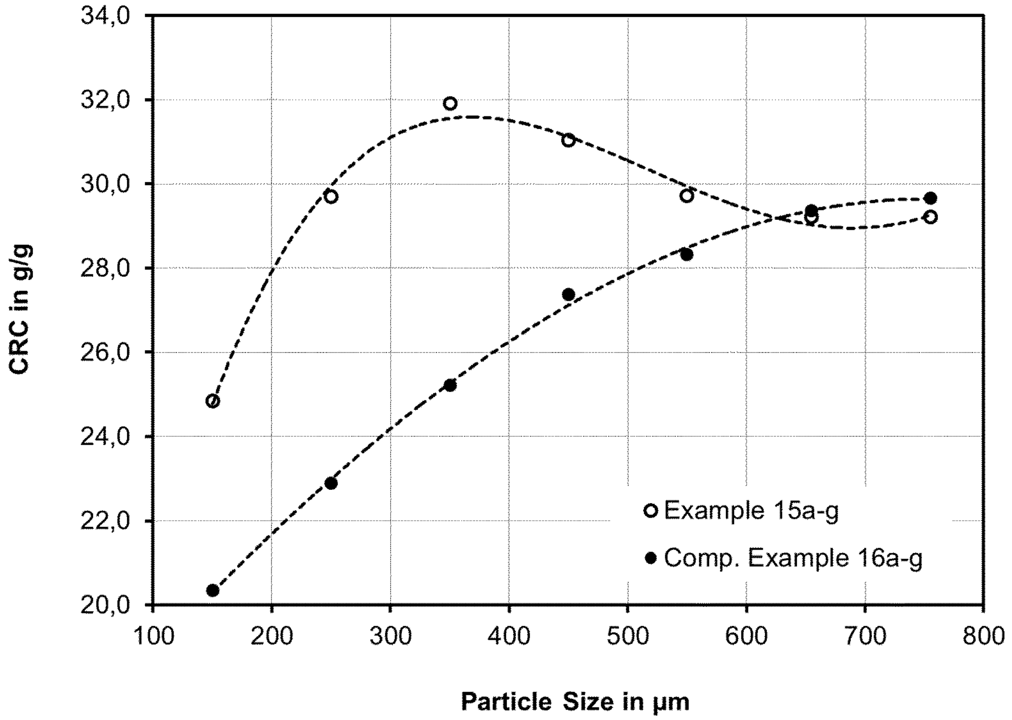

Fig. 20: AAP 0.7 psi of the water-absorbent polymer particles after surface-postcrosslinking (SXL) as function of the particle size

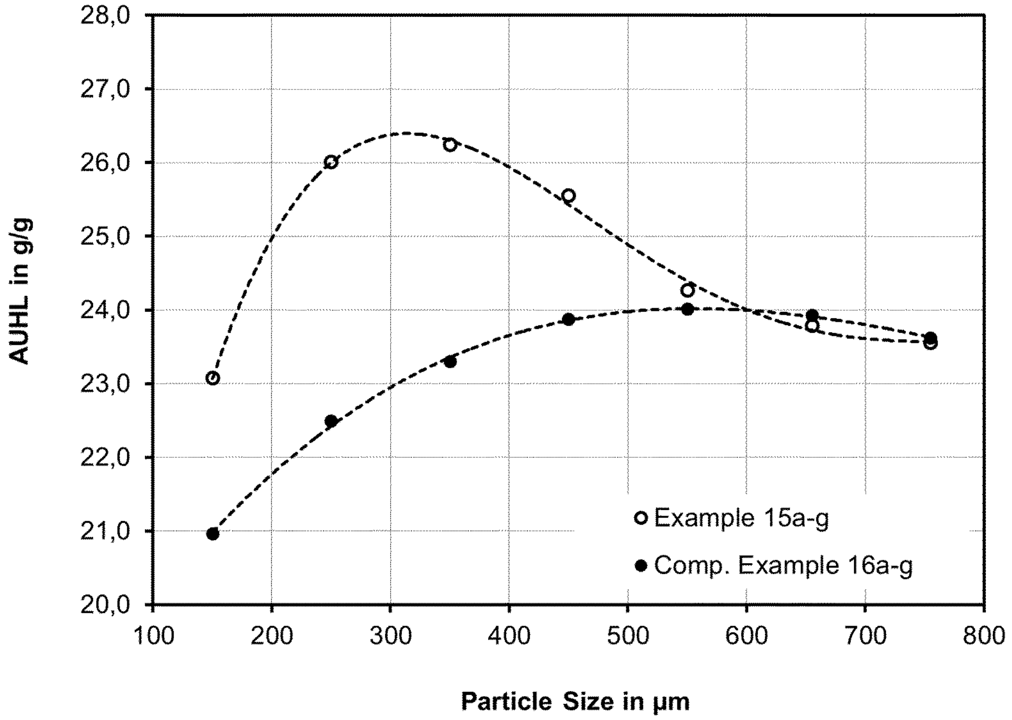

Fig. 21: [CRC+AUHL] of the water-absorbent polymer particles after surface-postcrosslinking (SXL) as function of the particle size

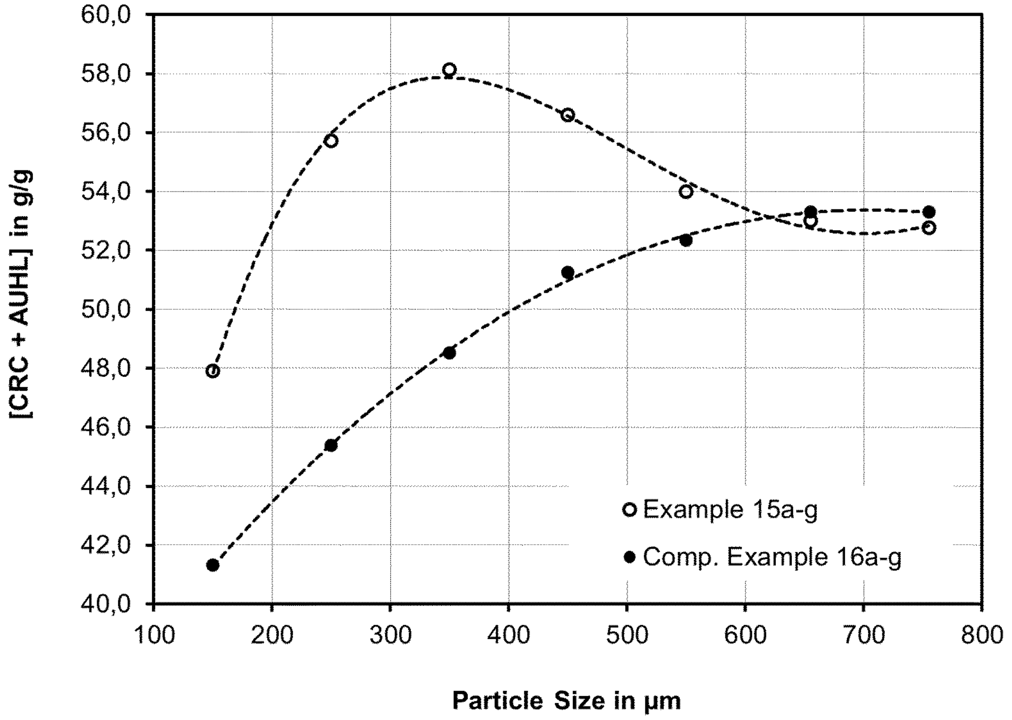

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Fig. 22: FSC of the water-absorbent polymer particles after surface-postcrosslinking (SXL) as function of the particle size

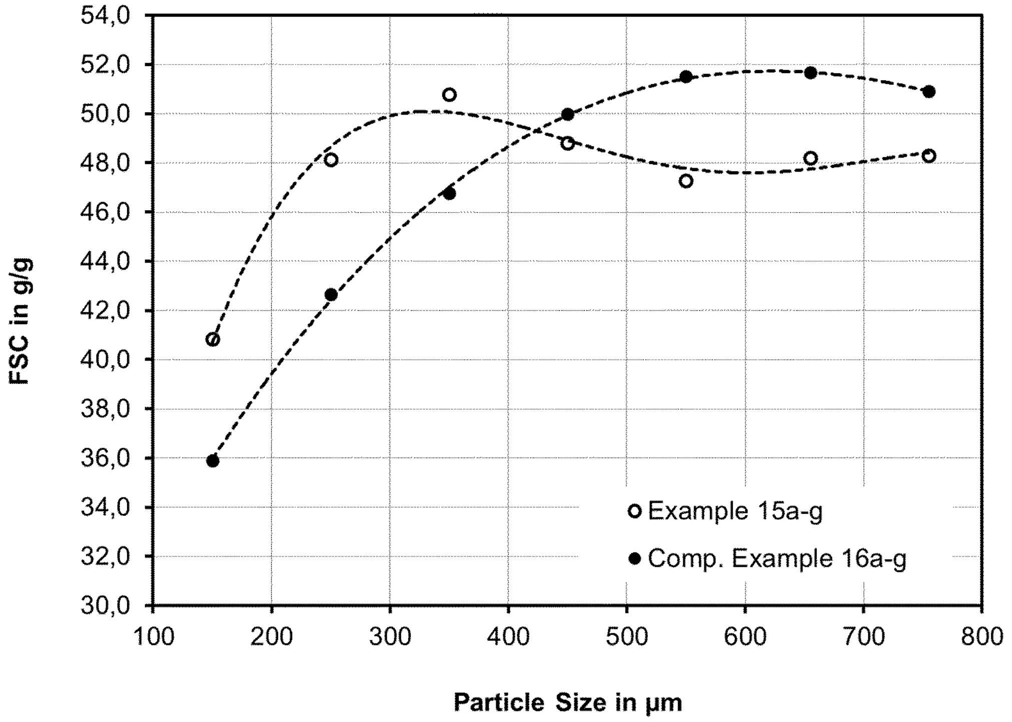


Fig. 23: FHA of the water-absorbent polymer particles after surface-postcrosslinking (SXL) as function of the particle size

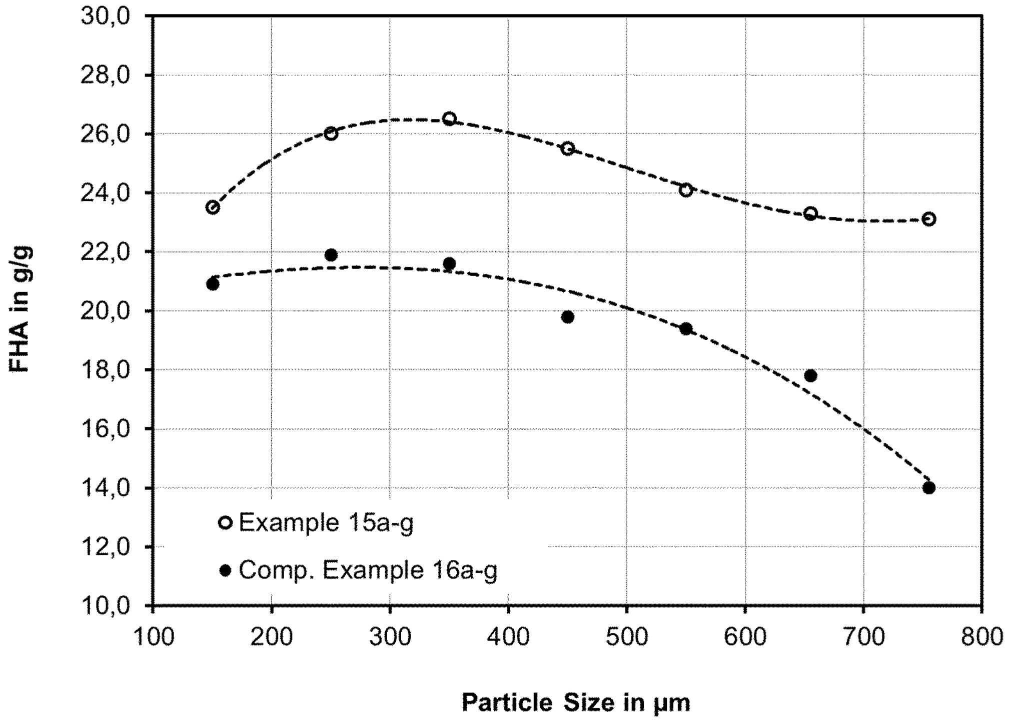


Fig. 24: Wicking uptake of the water-absorbent polymer particles after surface-postcrosslinking (SXL) as function of the particle size

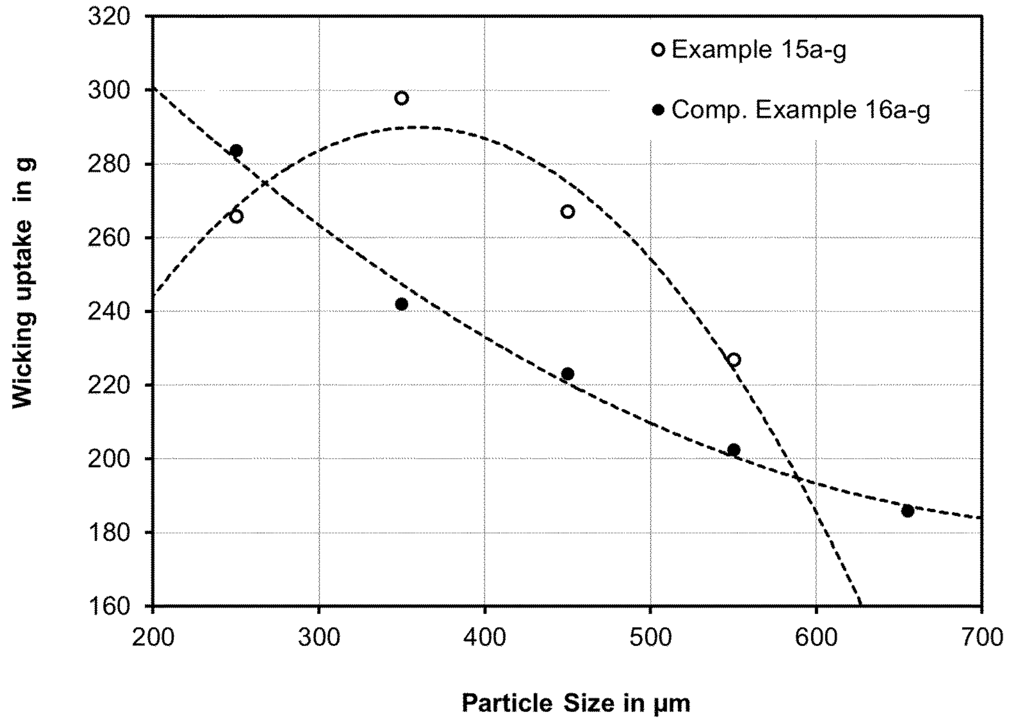


Fig. 25: FV-AUL of the water-absorbent polymer particles after surface-postcrosslinking (SXL) as function of the particle size

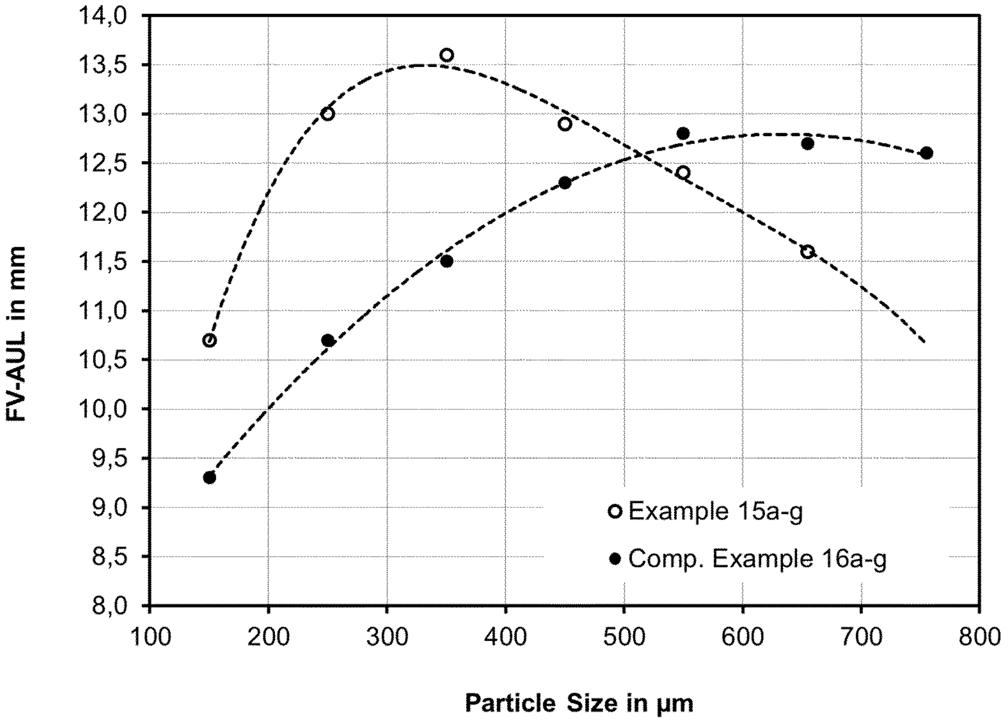


Fig. 26: SFC1.5 of the water-absorbent polymer particles after surface-postcrosslinking (SXL) as function of the particle size

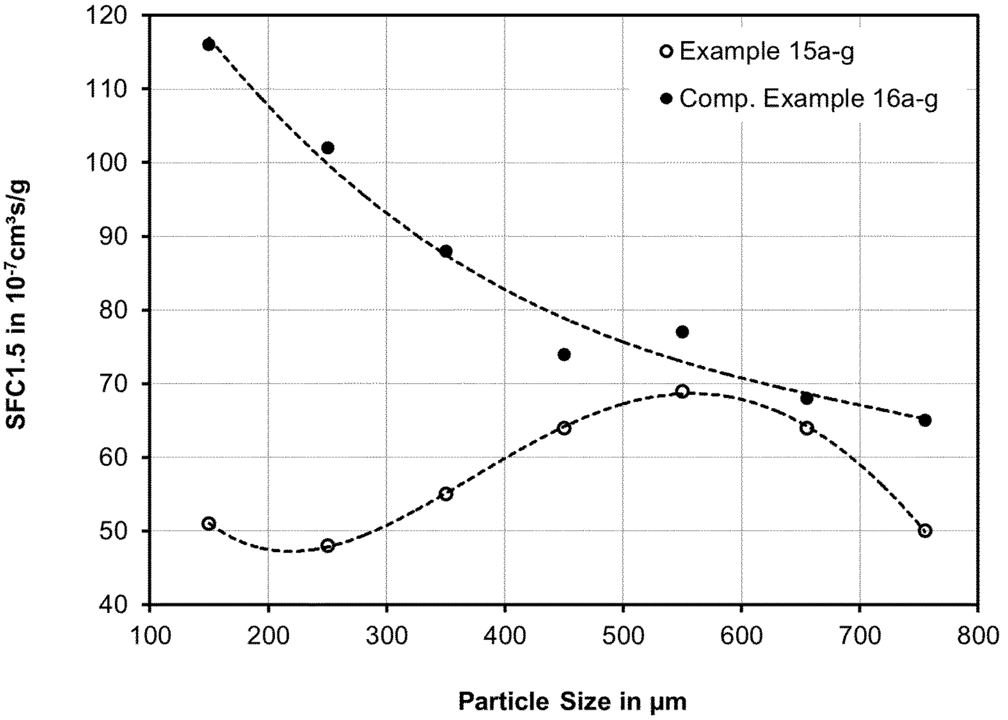
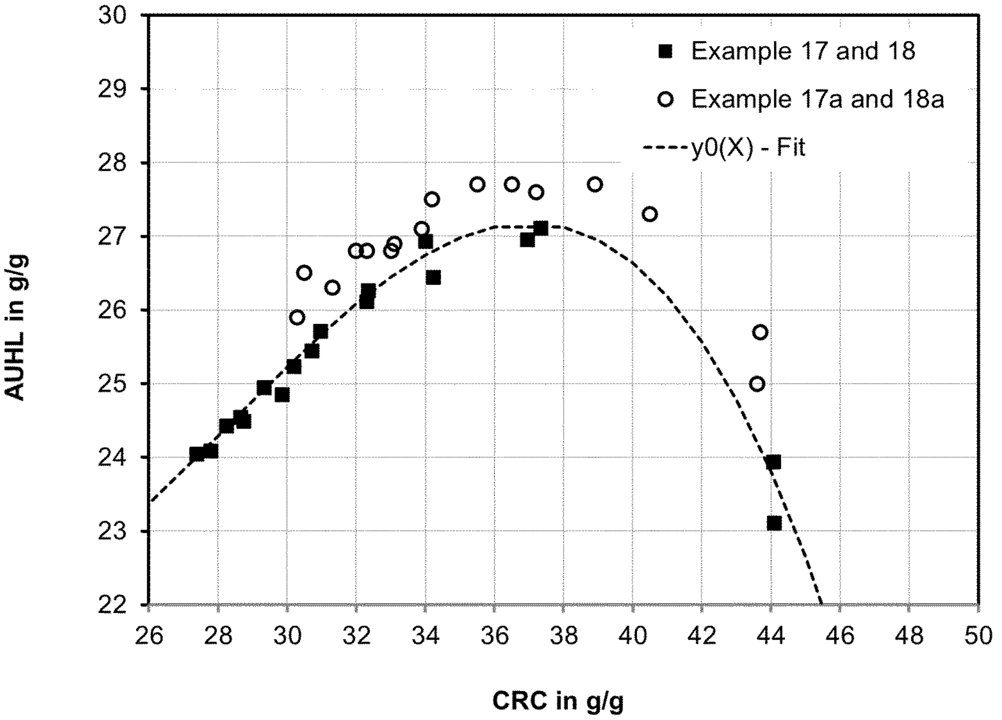


Fig. 27: AUHL of the water-absorbent polymer particles after surface-postcrosslinking (SXL) as function of the particle size



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/051587

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F220/06 C09D133/02 C08J3/24 C08F2/10
ADD.

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)
C08F C09D C08J

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2012/141792 A1 (STUEVEN UWE [DE] ET AL) 7 June 2012 (2012-06-07)	1-9
A	the whole document	11-21

Y	US 2011/059329 A1 (DOBRAWA RAINER [DE] ET AL) 10 March 2011 (2011-03-10)	1-9,23, 24
A	paragraph [0033] - paragraph [0121]; examples 1-2; tables 3,6	11-21

X	US 2011/223413 A1 (HERFERT NORBERT [DE] ET AL) 15 September 2011 (2011-09-15)	1,10,22
Y	examples 1, 2	23,24
A		11-21

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
25 April 2016	03/05/2016

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/051587

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