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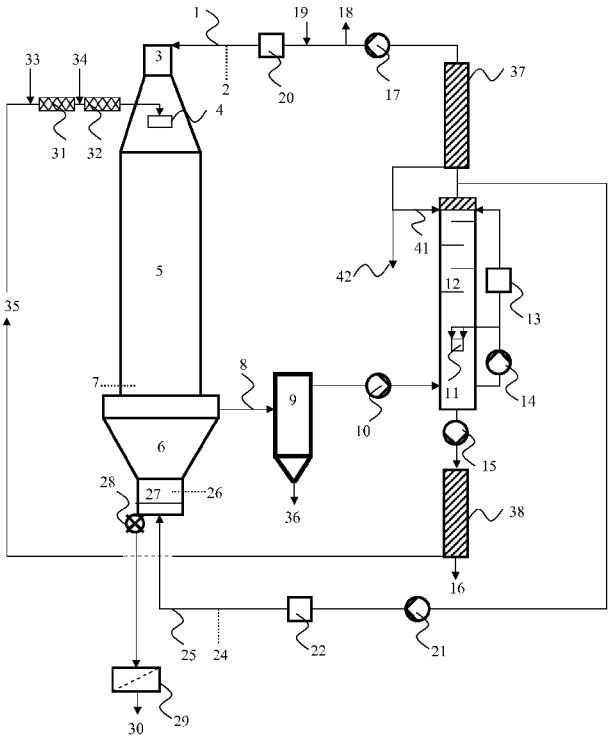
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[Continued on next page]

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

Fig. 1



(57) Abstract: The present invention relates to a process for producing water-absorbent polymer particles by polymerizing droplets of a monomer solution in a surrounding heated gas phase in a reactor comprising a gas distributor (3), a reaction zone (5) and a fluidized bed (27), the gas leaving the reactor is treated in a condenser column (12) with an aqueous solution, the treated gas leaving the condenser column (12) is recycled at least partly to the fluidized bed (27), wherein the gas leaving the condenser column (12) comprises from 0.05 to 0.3 kg steam per kg dry gas and the steam content of the gas entering the gas distributor(3) is less than 80% of the steam content of the gas leaving the condenser column (12).

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

Description

The present invention relates to a process for producing water-absorbent polymer particles by polymerizing droplets of a monomer solution in a surrounding heated gas phase in a reactor comprising a gas distributor (3), a reaction zone (5) and a fluidized bed (27), the gas leaving the reactor is treated in a condenser column (12) with an aqueous solution, the treated gas leaving the condenser column (12) is recycled at least partly to the fluidized bed (27), wherein the gas leaving the condenser column (12) comprises from 0.05 to 0.3 kg steam per kg dry gas and the steam content of the gas entering the gas distributor (3) is less than 80% of the steam content of the gas leaving the condenser column (12).

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).

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 is described, for example, in EP 0 348 180 A1, WO 96/40427 A1, US 5,269,980, WO 2008/009580 A1, WO 2008/052971 A1, WO2011/026876 A1, and WO 2011/117263 A1.

Polymerization of monomer solution droplets in a gas phase surrounding the 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 an improved process for the preparation of water-absorbent polymer particles by dropletization polymerization, i.e. less formation of undesired overs/lumps, less steam consumption, and reduced level of residual monomers in the water-absorbent polymer particles.

The object is achieved by a process for producing water-absorbent polymer particles by polymerizing droplets of a monomer solution in a surrounding heated gas phase in a reactor comprising a gas distributor (3), a reaction zone (5) and a fluidized bed (27), the gas leaving the reactor is treated in a condenser column (12) with an aqueous solution, the treated gas leaving

the condenser column (12) is recycled at least partly to the fluidized bed (27), wherein the gas leaving the condenser column (12) comprises from 0.05 to 0.3 kg steam per kg dry gas and the steam content of the gas entering the gas distributor (3) is less than 80% of the steam content of the gas leaving the condenser column (12).

The present invention is based on the finding that a high steam content of the gas in the reaction zone (5) causes problems for the operation of the process and that a high steam content of the gas in the internal fluidized bed (27) is necessary for a sufficient reduction of residual monomers in the water-absorbent polymer particles.

So, it is essential that the steam content of the gas in the reaction zone (5) must be lower than the steam content of the gas in the internal fluidized bed (27).

The present invention is further based on the finding that running the condenser column (12) at higher temperatures the steam content of the recycled gas that is used for the internal fluidized bed (27) can be adjusted on the desired values without adding steam from external sources.

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

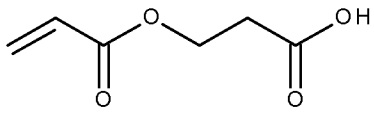
a) at least one ethylenically unsaturated monomer which bears acid groups and may be at least partly neutralized,
b) optionally one or more crosslinker,
c) at least one initiator,
d) optionally one or more ethylenically unsaturated monomers copolymerizable with the monomers mentioned under a),
e) optionally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

in a surrounding heated gas phase in a reactor comprising a gas distributor (3), a reaction zone (5) and a fluidized bed (27), the gas leaving the reactor is treated in a condenser column (12) with an aqueous solution, the treated gas leaving the condenser column (12) is recycled at least partly to the fluidized bed (27), wherein the gas leaving the condenser column (12) comprises from 0.05 to 0.3 kg steam per kg dry gas and the steam content of the gas entering the gas distributor (3) is less than 80% of the steam content of the gas leaving the condenser column (12).

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, hydrogencarbonates 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® (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.

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 and diethylaminopropyl methacrylate.

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, 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 0.01%, preferably from 0.02% to 1% by weight, more preferably from 0.05 to 0.8% by weight, most preferably from 0.06 to 0.6% 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.

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.

Most preferred is 2-hydroxy-2-sulfonatoacetic acid that is used in an amount of preferred from 0.02 to 1.0% by weight, more preferred 0.05 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, for example, sodium or potassium bisulfite, can be also added in the surface crosslinking step and/or in the coating step. Most preferred is the use of sodium bisulfite in the surface crosslinking step. Sodium bisulfite is used in an amount of preferably 0.0001 to 0.1% by weight, more preferred 0.005 to 0.05% by weight, most preferred 0.025 to 0.01% 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/cm³, more preferably from 1.05 to 1.25 g/cm³, most preferably from 1.1 to 1.2 g/cm³.

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.

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 accord-

ance 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 750, more preferably up to 500 bores, most preferably up to 250. The diameter of the bores is adjusted to the desired droplet size.

The spacing of the bores is usually from 5 to 50 mm, preferably from 6 to 40 mm, more preferably from 7 to 30 mm, most preferably from 8 to 25 mm. Smaller spacings of the bores may cause agglomeration of the polymerizing droplets.

The diameter of the bores is preferably from 50 to 500 µm, more preferably from 100 to 300 µm, most preferably from 150 to 250 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. Too high a 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.

The steam content of the gas leaving the condenser column (12) can be controlled by the temperature of the condenser column. The steam content can be calculated by using the Mollier-diagram, described, for example, in the monograph “Engineering Thermodynamics”, Infinity Science Series / Engineering series (3 ed.), Learning, R.K. Rajput, Jones & Bartlett, 2009, page 77 (ISBN 978-1-934015-14-8). The calculated steam content of the gas leaving the condenser column (12) in dependency on the temperature is given in the following table:

Temperature in °C	Steam Content in kg/kg	Temperature in °C	Steam Content in kg/kg
10	0,0076	42	0,0549
11	0,0082	43	0,0581
12	0,0087	44	0,0615
13	0,0093	45	0,0651
14	0,0100	46	0,0689
15	0,0107	47	0,0729
16	0,0114	48	0,0771
17	0,0122	49	0,0816
18	0,0130	50	0,0863
19	0,0138	51	0,0913
20	0,0147	52	0,0966
21	0,0157	53	0,1022
22	0,0167	54	0,1082
23	0,0178	55	0,1145
24	0,0189	56	0,1211
25	0,0201	57	0,1282
26	0,0214	58	0,1357
27	0,0227	59	0,1437
28	0,0242	60	0,1522
29	0,0257	61	0,1612
30	0,0273	62	0,1709
31	0,0289	63	0,1811
32	0,0307	64	0,1920
33	0,0326	65	0,2037
34	0,0345	66	0,2162
35	0,0366	67	0,2296
36	0,0388	68	0,2440
37	0,0412	69	0,2594
38	0,0436	70	0,2760
39	0,0462	71	0,2939
40	0,0489	72	0,3132

41	0,0518	73	0,3341

The steam content X is calculated with the formula $X = \frac{6.2069 \cdot \varphi \cdot p_S}{p_N - 10 \cdot \varphi \cdot p_S}$. The relative humidity φ in % in the condenser column is 100% at a standard atmospheric pressure of p_N = 1013 mbar.

The saturated steam pressure p_s is calculated with the formula $p_S = 10^{5.169 - \frac{1717.47}{232.63 + T}}$.

The temperature T is the temperature in the condenser column (12).

The steam content of the gas leaving the condenser column (12) is preferably from 0.07 to 0.26 kg per kg of dry gas, more preferably from 0.08 to 0.20 kg per kg of dry gas, most preferably from 0.09 to 0.15 kg/kg. The high steam content of the gas leaving the condenser column (12) can be used to reduce the level of residual monomers of the water-absorbent polymers in the internal fluidized bed (27). The amount of residual monomers in the water-absorbent polymers leaving the internal fluidized bed (27) is preferably from 0.0001 to 1% by weight, more preferably from 0.0005 to 0.8% by weight, most preferably from 0.001 to 0.5% by weight.

The steam content of the gas entering the gas distributer (3) is preferably less than 70 weight%, more preferably less than 60 weight%, most preferably less than 50 weight%, of the steam content of the gas leaving the condenser column (12). The gas entering in the gas distributer (3) may be dried with a gas drying unit to the desired steam content preferred from 0.008 to 0.010 kg per kg of dry gas, more preferably from 0.02 to 0.95 kg per kg of dry gas, more even preferably from 0.05 to 0.90 kg per kg of dry gas. The low steam content in the spray dryer can be used to minimize the product agglomeration on the internal surface of the spray dryer.

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 may be 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 cyclic carbonates, DE 198 07 502 A1 describes 2-oxazolidone and its derivatives such as 2-hydroxyethyl-2-oxazolidone, DE 198 07 992 C1 describes bis- and poly-2-oxazolidinones, DE 198 54 573 A1 describes 2-oxotetrahydro-1,3-oxazine and its derivatives, DE 198 54 574 A1 describes N-acyl-2-oxazolidones, 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.

Particularly preferred postcrosslinkers are ethylene carbonate, glycerine carbonate, mixtures of propylene glycol, 1,3-propandiole, 1,4-butanediol, mixtures of 1,3-propandiole and 1,4-butanediole, ethylene glycol diglycidyl ether and reaction products of polyamides and epichlorohydrin.

Very particularly preferred postcrosslinkers are 2-hydroxyethyl-2-oxazolidone, 2-oxazolidone, ethylene carbonate and 1,3-propanediol.

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.

The amount of postcrosslinker is preferably from 0.001 to 2% by weight, more preferably from 0.02 to 1% by weight, most preferably from 0.05 to 0.2% by weight, based in each case on the polymer.

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.

The amount of alkylene carbonate is preferably from 0.1 to 10% by weight, more preferably from 0.5 to 7.5% by weight, most preferably from 1.0 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 alkylene carbonate is in the range from 0.1 to 15% by weight, preferably from 0.15 to 12%by weight, more preferably from 0.2 to 10% by weight, most preferably from 0.25 to 2.5% 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 posttreatment 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 (Ho-

sokawa 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 bi-sulfite), 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 unsuitable. 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 Planatcare® 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. Pref-

erably 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 1500, more preferably from 50 to 1000, most preferably from 100 to 500, bores having a diameter of preferably from 50 to 500µm, more preferably from 100 to 300µm, most preferably from 150 to 250µm. The bores can be of circular, rectangular, triangular or any other shape. Circular bores are preferred. 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 co-

polymers 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 150 to 2500kg/h, more preferably from 200 to 1000kg/h, most preferably from 300 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 inventive water-absorbent polymer particles have a 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. 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.

The roundness can be determined, for example, with the PartAN® image analysis system (Microtrac Europe GmbH; Meerbusch; Germany):

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 selec-

tively by a camera. The images recorded are evaluated by the software in accordance with the parameters selected.

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 content of hydrophobic solvent of preferably less than 0.005% by weight, more preferably less than 0.002% by weight and most preferably less than 0.001% by weight. The content of hydrophobic solvent can be determined by gas chromatography, for example by means of the headspace technique. A hydrophobic solvent within the scope of the present invention is either immiscible in water or only sparingly miscible. Typical examples of hydrophobic solvents are pentane, hexane, cyclo-hexane, toluene.

Water-absorbent polymer particles which have been obtained by reverse suspension polymerization still comprise typically approx. 0.01% by weight of the hydrophobic solvent used as the reaction medium.

The inventive water-absorbent polymer have a dispersant content of preferably less than 0.5% by weight, more preferably less than 0.1% by weight and most preferably less than 0.05% by weight.

Water-absorbent polymer particles which have been obtained by reverse suspension polymerization still comprise typically at least 1% by weight of the dispersant, i.e. ethylcellulose, used to stabilize the suspension.

The inventive water-absorbent polymer particles have a bulk density preferably from 0.6 to 1 g/cm³, more preferably from 0.65 to 0.9 g/cm³, most preferably from 0.68 to 0.8 g/cm³.

The average particle diameter (APD) of the inventive water-absorbent polymer particles is preferably from 200 to 550 µm, more preferably from 250 to 500 µm, most preferably from 350 to 450 µm.

The particle diameter distribution (PDD) of the inventive water-absorbent polymer particles is preferably less than 0.7, more preferably less than 0.65, more preferably less than 0.6.

The inventive water-absorbent polymer particles have a centrifuge retention capacity (CRC) of preferably from 35 to 100 g/g, more preferably from 40 to 80 g/g, most preferably from 45 to 60 g/g.

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 inventive water-absorbent polymer particles have an absorbency under a load of 21.0 g/cm² (AUL) of preferably from 15 to 60 g/g, more preferably from 20 to 50 g/g, most preferably from 25 to 40 g/g.

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 25% by weight, most preferably from 1 to 20% 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.

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:

$$FSR\ [g/gs] = W2/(W1xt)$$

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.

Vortex

50.0 ± 1.0ml of 0.9% NaCl solution are added into a 100ml beaker. A cylindrical stirrer bar (30 x 6mm) is added and the saline solution is stirred on a stir plate at 60 rpm. 2.000 ± 0.010g of water-absorbent polymer particles are added to the beaker as quickly as possible, starting a stop watch as addition begins. The stopwatch is stopped when the surface of the mixture becomes “still” that means the surface has no turbulence, and while the mixture may still turn, the entire surface of particles turns as a unit. The displayed time of the stopwatch is recorded as Vortex time.

Residual Monomers

The level of residual monomers in the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 410.2-05 "Residual Monomers".

Roundness

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

Moisture Content

The moisture content of the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 430.2-05 "Moisture Content".

Centrifuge Retention Capacity (CRC)

The centrifuge retention capacity of the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 441.2-05 "Centrifuge Retention Capacity", wherein for higher values of the centrifuge retention capacity larger tea bags have to be used.

Absorbency Under No Load (AUNL)

The absorbency under no load of the water-absorbent polymer particles is determined analogously to the EDANA recommended test method No. WSP 442.2-05 "Absorption Under Pressure", except using a weight of 0.0 g/cm² instead of a weight of 21.0 g/cm².

Absorbency Under Load (AUL)

The absorbency under load of the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 442.2-05 "Absorption Under Pressure".

Absorbency Under High Load (AUHL)

The absorbency under high load of the water-absorbent polymer particles is determined analogously to the EDANA recommended test method No. WSP 442.2-05 "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 460.2-05 "Density".

Extractables

The level of extractable constituents in the water-absorbent polymer particles is determined by the EDANA recommended test method No. WSP 470.2-05 "Extractables".

Saline flow conductivity

The saline flow conductivity (SFC) of a swollen gel layer under a pressure of 0.3 psi (2070 Pa) is, as described in EP 0 640 330 A1, determined as the gel layer permeability of a swollen gel layer of water-absorbing polymer particles, the apparatus described on page 19 and in figure 8 in the cited patent application having been modified such that the glass frit (40) is not used, and the plunger (39) consists of the same polymer material as the cylinder (37) and now comprises 21 bores of equal size distributed homogeneously over the entire contact area. The procedure and evaluation of the measurement remain unchanged from EP 0 640 330 A1. The flow is detected automatically.

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

$$SFC\ [cm^3s/g] = (Fg(t=0)xL0)/(dxAxWP)$$

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, L0 is the thickness of the gel layer in cm, d is the density of the NaCl solution in g/cm³, A is the area of the gel layer in cm², and WP is the hydrostatic pressure over the gel layer in dyn/cm².

Gel bed permeability

The gel bed permeability (GBP) of a swollen gel layer under a pressure of 0.3 psi (2070 Pa) is, as described in US 2005/0256757 (paragraphs [0061] and [0075]), determined as the gel bed permeability of a swollen gel layer of water-absorbing polymer particles.

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.

Accelerated Aging Test

Measurement 1 (Initial color): A plastic dish with an inner diameter of 9 cm is overfilled with superabsorbent polymer particles. The surface is flattened at the height of the petri dish lip by means of a knife and the CIE color values and the HC 60 value are determined.

Measurement 2 (after aging): A plastic dish with an inner diameter of 9 cm is overfilled with superabsorbent polymer particles. The surface is flattened at the height of the petri dish lip by means of a knife. The plastic dish (without a cover) is then placed in a humidity chamber at 60 °C and a relative humidity of 86%. The plastic dish is removed from the humidity chamber after 7, 14, and 21 days, cooled down to room temperature and the CIE color values are determined.

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

Examples

Example 1 to 3 (comparative examples)

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 10.45% by weight of acrylic acid, 33.40% by weight of sodium acrylate, 0.018% by weight of 3-tuply ethoxylated glycerol triacrylate, 0.036% by weight of [2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, 0.0029% by weight of Brüggolite FF7, 0.054% by weight of sodiumperoxodisulfate and water. The degree of neutralization was 71%. The feed per bore was 1.4 kg/h.

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

Example 4 to 6 (inventive examples)

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 gas drying unit (37) and the conditioned internal fluidized bed gas (25). The gas drying unit (37) comprises a gas cooler and a demister. In the gas drying unit (37) the gas was cooled down to 40°C and heated up prior to the drying gas inlet pipe (1). 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 4 mbar 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 10.45% by weight of acrylic acid, 33.40% by weight of sodium acrylate, 0.018% by weight of 3-tuply ethoxylated glycerol triacrylate, 0.036% by weight of [2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, 0.0029% by weight of Brüggolite FF7, 0.054% by weight of sodiumperoxodisulfate and water. The degree of neutralization was 71%. The feed per bore was 1.4 kg/h.

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

Example 7

The example was performed analogous to example 6, except that 0.00075% by weight of Brüggolite® FF7 and 0.036% by weight Blancolen® HP were used instead of 0.0029% by weight of Brüggolite® FF7.

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

Example 8

The example was performed analogous to example 6, except that 0.011% by weight of 3-tuply ethoxylated glycerol triacrylate was used instead of 0.018% by weight of 3-tuply ethoxylated glycerol triacrylate.

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

Example 9

The example was performed analogous to example 8, except that 0.00075% by weight of Brüggolite® FF7 and 0.036% by weight Blancolen® HP were used instead of 0.0029% by weight of Brüggolite® FF7.

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

Example 10

The example was performed analogous to example 6, except that acrylic acid having a dimer concentration of approx. 5000 ppm was used instead of fresh acrylic acid having a dimer concentration less than 500 ppm.

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

Examples 11 to 15

In a Schugi Flexomix® (model Flexomix 160, manufactured by Hosokawa Micron B.V., Doetinchem, the Netherlands) with a speed of 2000 rpm, the base polymer was coated with a surface-postcrosslinker solution by using 2 or 3 round spray nozzle systems (model Gravity-Fed Spray Set-ups, External Mix Typ SU4, Fluid Cap 60100 and Air Cap SS-120, manufactured by Spraying Systems Co, Wheaton, Illinois, USA) and then filled via base polymer feed (70) and dried in a thermal dryer (65) (model NPD 5W-18, manufactured by GMF Gouda, Waddinxveen, the Netherlands) with a speed of the shaft (76) of 6 rpm. The thermal dryer (65) has two paddles with a shaft offset of 90° (80) and a fixed discharge zone (71) with two flexible weir plates (73). Each weir has a weir opening with a minimal weir height at 50% (75) and a maximal weir opening at 100% (74) as shown in Fig. 15.

The inclination angle α (78) between the floor plate and the thermal dryer was approx. 3°. The weir height of the thermal dryer was between 50 to 100%, corresponding to a residence time of approx. 40 to 150 min, by a product density of approx. 700 to 750 kg/m³. The product temperature in the thermal dryer was in a range of 120 to 165°C. After drying, the surface-postcrosslinked polymer was transported over discharge cone (77) in a cooler (model NPD 5W-18, manufactured by GMF Gouda, Waddinxveen, the Netherlands), to cool down the surface postcrosslinked polymer to approx. 60°C with a speed of 11 rpm and a weir height of 145mm. After cooling, the material was sieved with a minimum cut size of 150 µm and a maximum cut size of 710 µm.

Ethylene carbonate, water, Plantacare® UP 818 (BASF SE, Ludwigshafen, Germany) and aqueous aluminum lactate (26% by weight) were premixed and used as surface-postcrosslinker solution as summarized in Tab. 5. As aluminum lactate, Lothragon® Al 220 (manufactured by Dr. Paul Lohmann GmbH, Emmerthal, Germany) was used.

The resulting water-absorbent polymer particles were analyzed. The trial conditions and results are summarized in Tab. 4 to 6.

Examples 16 to 20

In a Schugi Flexomix® (model Flexomix 160, manufactured by Hosokawa Micron B.V., Doetinchem, the Netherlands) with a speed of 2000 rpm, the base polymer was coated with a surface-postcrosslinker solution by using 2 or 3 round spray nozzle systems (model Gravity-Fed Spray Set-ups, External Mix Typ SU4, Fluid Cap 60100 and Air Cap SS-120, manufactured by Spraying Systems Co, Wheaton, Illinois, USA) and then filled via base polymer feed (70) and dried in a thermal dryer (65) (model NPD 5W-18, manufactured by GMF Gouda, Waddinxveen, the Netherlands) with a speed of the shaft (76) of 6 rpm. The thermal dryer (65) has two paddles with a shaft offset of 90° (80) and a fixed discharge zone (71) with two flexible weir plates (73). Each weir has a weir opening with a minimal weir height at 50% (75) and a maximal weir opening at 100% (74) as shown in Fig. 15.

The inclination angle α (78) between the floor plate and the thermal dryer was approx. 3°. The weir height of the thermal dryer was between 50 to 100%, corresponding to a residence time of approx. 40 to 150 min, by a product density of approx. 700 to 750 kg/m³. The product temperature in the thermal dryer was in a range of 120 to 165°C. After drying, the surface-postcrosslinked polymer was transported over discharge cone (77) in a cooler (model NPD 5W-18, manufactured by GMF Gouda, Waddinxveen, the Netherlands), to cool down the surface postcrosslinked polymer to approx. 60°C with a speed of 11 rpm and a weir height of 145mm. After cooling, the material was sieved with a minimum cut size of 150 µm and a maximum cut size of 710 µm.

Ethylene carbonate, water, Plantacare® UP 818 (BASF SE, Ludwigshafen, Germany), aqueous aluminum lactate (26% by weight) and sodium bisulfie were premixed and used as surface-postcrosslinker solution as summarized in Tab. 5. As aluminum lactate, Lothragon® Al 220 (manufactured by Dr. Paul Lohmann GmbH, Emmerthal, Germany) was used.

5.0wt% of a 0.1% aqueous solution of Plantacare® 818 UP (BASF SE, Ludwigshafen, Germany) having a temperature of approx. 60°C was additionally added into the cooler using two nozzles in the first third of the cooler. The nozzles were placed below the product bed.

The resulting water-absorbent polymer particles were analyzed. The trial conditions and results are summarized in Tab. 4 to 6.

Tab. 1: Process conditions of the polymerization

Example	Steam Content CC	Steam Content GD	T gas inlet	T gas outlet	T gas IFB	T IFB	T CC	Overs/Lumbs
Unit	kg/kg	kg/kg	°C	°C	°C	°C	°C	wt.%
1	0.0489	0.0489	167	115	103	78	40	2.4
2	0.0651	0.0651	167	115	103	78	45	4.5
3	0.0863	0.0863	167	115	103	78	50	7.9
4	0.0651	0.0489	167	115	103	78	45	1.9
5	0.0863	0.0489	167	115	103	78	50	2.2
6	0.1145	0.0489	167	115	103	78	55	2.4
7	0.1022	0.0489	167	115	103	78	53	2.2
8	0.1022	0.0489	167	115	103	78	53	2.2
9	0.1022	0.0489	167	115	103	78	53	2.1
10	0.1022	0.0489	167	115	103	78	53	2.3

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 IFB: temperature of the gas entering the internal fluidized bed (27) via line (25)

T CC: temperature of the gas leaving the condenser column (12)

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

Example	Bulk Density	CRC	AUNL	AUL	Residual Monomers	Extractables	Moisture	L	a	b
Unit	g/cm^3	g/g	g/g	g/g	ppm	wt.%	wt.%			
1	71.9	44.3	51,0	24.3	17900	3.8	2.9	92.8	2.4	1.4
2*)	70.3	47.8	54,4	18.7	11200	4.3	3.6	92.6	2.6	1.7
3**)	-	-	-	-	-	-	-	-	-	-
4	71.3	49.5	55,4	18.9	9800	3.9	3.7	93.1	1.7	1.9
5	71.9	51.5	57,7	18.3	6400	3.8	7.6	92.9	1.9	2.1
6	72.1	52.5	58,1	15.9	2900	3.8	8.9	92.7	2.1	2.3
7	71.8	53.1	56.9	13.9	4700	4.2	8.1	93.4	2.0	1.7
8	67.8	61.8	48.1	7.4	4900	8.6	8.2	93.3	1.8	2.0
9	68.1	66.8	48.9	7,6	5100	19.8	8.1	94.3	1.4	2.1
10	71.5	51.9	54.9	15.8	4800	6.5	8.0	92.8	2.5	2.0

*) significant polymer built-up in the cone (6) of the spray dryer and the top of the reaction zone (5)

**) process stopped due to polymer built-up in the cone (6) of the spray dryer and the top of the reaction zone (5)

Tab. 3: Particle size distribution of the water-absorbent polymer particles (base polymer)

Example	<150	150	200	250	300	350	400	500	600	700	850	1000	1400	Roundness
Unit	µm	µm	µm	µm	µm	µm	µm	µm	µm	µm	µm	µm	µm	
1	0,01	0,11	1,22	3,47	9,25	14,55	33,62	19,79	10,18	5,70	1,82	0,28	0,00	0.81
2*)	0,00	0,02	0,23	0,82	2,03	4,44	16,41	18,72	20,30	25,35	10,95	0,73	0,00	0.74
3**)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	0,00	0,05	0,92	3,93	8,18	13,88	33,99	20,68	9,39	6,12	1,92	0,83	0,11	0.83
5	0,00	0,12	1,69	4,95	9,26	13,86	31,22	19,20	9,93	7,13	2,40	0,24	0,00	0.82
6	0,01	0,10	1,18	3,98	8,98	15,07	32,10	21,96	9,17	5,59	1,58	0,28	0,00	0.81
7	0,01	0,08	1,12	3,96	8,66	16,69	29,50	20,75	11,29	5,80	1,60	0,50	0,04	0.82
8	0,01	0,11	1,45	4,23	9,23	14,20	32,41	19,50	10,07	6,42	2,10	0,27	0,00	0.79
9	0,00	0,08	1,22	4,17	8,75	14,16	33,14	21,03	9,63	5,27	1,99	0,51	0,05	0.78
10	0,00	0,09	1,23	3,29	8,83	14,30	33,07	21,98	9,50	5,28	1,97	0,42	0,04	0.81

*) significant polymer built-up in the cone (6) of the spray dryer and the top of the reaction zone (5)

**) process stopped due to polymer built-up in the cone (6) of the spray dryer and the top of the reaction zone (5)

Tab. 4: Process conditions of the thermal dryer for the surface postcrosslinking (SXL)

Example	Product Temp. Set Value	Steam Pressure Wave	Steam Pressure Jacket	Heater T1	Heater T2	Heater T3	Heater T4	Heater T5	Heater T6	Through-put	Heater Weir	No. of Nozzles	Pos. of Nozzles
Unit	°C	bar	bar	°C	° C	°C	°C	°C	°C	kg/h	%		
11	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°
12	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°
13	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°
14	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°
15	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°
16	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°
17	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°
18	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°
19	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°
20	140	6.4	6.4	84	81	111	123	130	140	470	80	3	90/180/270°

Tab. 5: Process conditions of the surface postcrosslinking (SXL)

Example	Base polymer	EC (SXL)	Water (SXL)	Plantacare® 818 UP (dry) (SXL)	Al-Lactate (dry) (SXL)	Sodium bisulfite (dry) (SXL)	0.1% aqueous solution Plantacare® 818 UP (Cooler)
		wt.% bop	wt.% bop	ppm bop	wt.% bop	wt.% bop	wt.% bop
11	1	2.5	5.0	25	0.2		
12	2	2.5	5.0	25	0.2		
13	4	2.5	5.0	25	0.2		
14	5	2.5	5.0	25	0.2		
15	6	2.5	5.0	25	0.2		
16	6	2.5	5.0	25	0.2	0.05	5.0
17	7	2.5	5.0	25	0.2	0.05	5.0
18	8	2.5	5.0	25	0.2	0.05	5.0
19	9	2.5	5.0	25	0.2	0.05	5.0
20	10	2.5	5.0	25	0.2	0.05	5.0

EC: Ethylene carbonate
bop: based on polymer

Tab. 6: Properties of the water-absorbent polymer particles (after surface postcrosslinking)

Exp.	CRC	AUNL	AUL	AUHL	SFC	GBP	Vortex	FSR	Moisture	Residual Monomers	Extractables	Bulk Density	Fines <150µm	Overs >850 µm
Unit	g/g	g/g	g/g	g/g	$10^{-7}cm^3 \cdot s/g$	Da	s	g/g·s	wt.%	ppm	wt.%	g/100 ml	wt.%	wt.%
11	38.9	48.6	35.6	23.5	3	6	75	0.22	1.8	640	2.8	75.1	0.5	0.3
12	39.9	49.9	37.2	24.9	2	3	69	0.27	1.8	600	3.5	74.0	0.4	3.9
13	39.5	49.3	36.1	24.5	2	4	73	0.24	1.9	580	3.5	74.8	0.3	0.4
14	40.5	50.9	38.1	25.2	2	6	71	0.28	2.2	510	3.3	73.8	0.3	0.4
15	41.9	52.0	38.3	25.6	1	4	68	0.30	2.3	460	4.0	75.1	0.2	0.2
16	41.9	52.6	37.3	25.0	2	5	59	0.33	5.1	310	3.9	75.6	0.1	2.4
17	41.5	52.1	37.1	24.9	2	6	57	0.31	5.2	320	4.1	75.4	0.2	2.5
18	49.9	59.3	31.3	15.2	0	1	49	0.34	5.6	290	5.8	69.9	0.1	3.1
19	50.5	60.3	30.9	15.3	0	2	50	0.34	5.5	300	6.2	70.1	0.1	3.2
20	41.3	50.9	37.3	25.0	2	6	58	0.30	5.2	280	4.6	76.2	0.2	2.4

Tab. 7: Effect of Blancolen® HP in the monomer solution (Accelerated Aging Test)

Example	After 0 days			After 7 days			After 14 days			After 21 days		
Unit	L	a	b	L	a	b	L	a	b	L	a	b
Examples without Blancolen® HP in the monomer solution												
6	92.7	2.1	2.3	82.1	0.4	11.2	79.2	0.7	13.9	76.0	1.5	16.6
16	92.6	-1.1	8.2	77.4	2.3	10.5	71.8	3.9	12.9	67.0	5.2	14.9
8	93.3	1.8	2.0	82.3	0.6	11.4	79.9	1.0	13.8	76.2	1.7	16.7
18	93.8	-1.4	7.7	77.2	2.5	10.6	71.6	3.6	12.4	67.3	5.4	15.3
Examples with 2000 ppm Blancolen® HP in the monomer solution												
7	93.4	2.0	1.7	85.0	-1.3	9.5	83.1	-1.5	10.7	82.3	-1.6	11.9
17	93.1	-1.5	8.2	85.6	-0.9	8.8	84.7	-0.8	9.4	84.2	-0.8	10.5
9	94.3	1.4	2.1	85.0	-1.3	9.5	83.4	-1.8	10.3	82.7	-1.7	11.6
19	92.4	-1.0	8.5	85.7	-1.1	8.6	85.1	-1.0	9.3	84.1	-0.9	10.4

Claims

1. A process for producing water-absorbent polymer particles by 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 in a reactor comprising a gas distributor (3), a reaction zone (5) and a fluidized bed (27), the gas leaving the reactor is treated in a condenser column (12) with an aqueous solution, the treated gas leaving the condenser column (12) is recycled at least partly to the fluidized bed (27), wherein the gas leaving the condenser column (12) comprises from 0.05 to 0.3 kg steam per kg dry gas and the steam content of the gas entering the gas distributor (3) is less than 80% of the steam content of the gas leaving the condenser column (12).

2. A process according to claim 1, wherein the gas leaving the condenser column (12) comprises from 0.09 to 0.15 kg steam per kg dry gas.

3. A process according to any of claims 1 or 2, wherein the steam content of the gas entering the gas distributor (3) is less than 50% of the steam content of the gas leaving the condenser column (12).

4. A process according to any of claims 1 to 3, wherein the treated gas leaving the condenser column (12) is recycled at least partly to the gas distributor (3) and the treated gas leaving the condenser column (12) that is recycled at least partly to the gas distributor (3) is further treated in a gas drying unit (37).

5. A process according to claim 4, wherein the gas drying unit (37) comprises a gas cooler and a demister.

6. A process according claim 5, wherein the temperature of the gas leaving the gas drying unit (37) is less than 45°C.

7. A process according claim 6, wherein the temperature of the gas leaving the condenser column (12) is at least 45°C.

8. A process according to any of claims 1 to 7, wherein the gas velocity inside the reaction zone (5) is from 0.5 to 1.2 m/s.

9. A process according to any of claims 1 to 8, wherein temperature of the gas leaving the reaction zone (5) is from 110 to 120°C.

10. A process according to any of claims 1 to 9, wherein the residence time of the water-absorbent polymer particles in the fluidized (27) bed is from 120 to 240 minutes.

11. A process according to any of claims 1 to 10, wherein the gas velocity inside the fluidized bed (27) is from 0.5 to 1.5 m/s.

12. A process according to any of claims 1 to 11, wherein temperature of the water-absorbent polymer particles in the fluidized bed (27) is from 60 to 100°C.

13. A process according to any of claims 1 to 12, wherein the ethylenically unsaturated monomer which bears acid groups is an ethylenically unsaturated carboxylic acid.

14. A process according to any of claims 1 to 13, wherein the formed water-absorbent polymer particles have a centrifuge retention capacity of at least 15 g/g.

15. A process according to any of claims 1 to 14, wherein the gas is treated in the condenser column (12) with caustic.

16. A process according to any of claims 1 to 15, wherein the liquid effluent of the condenser column (12) is recycled for preparing the monomer solution.

Fig. 1

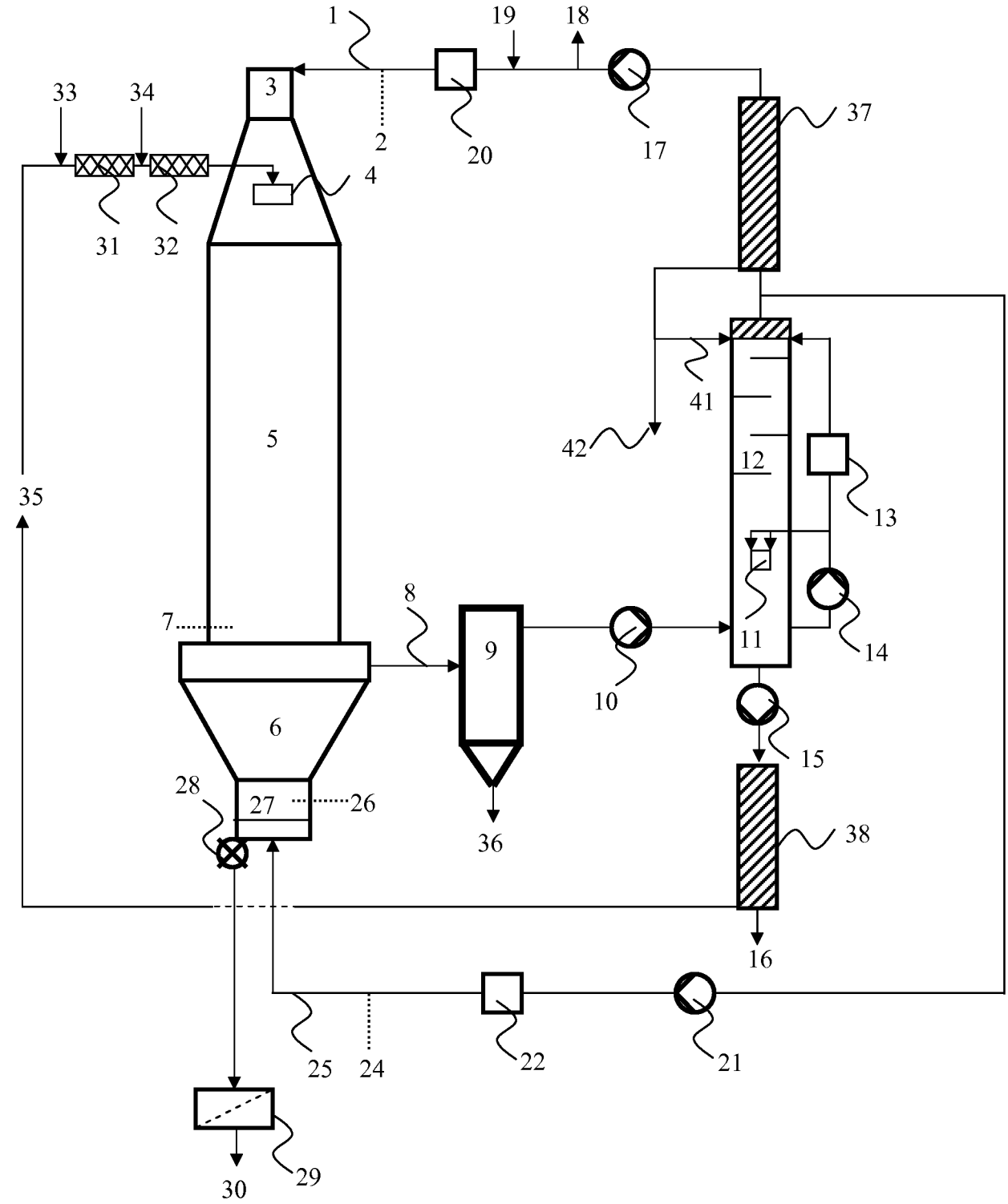

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Fig. 2

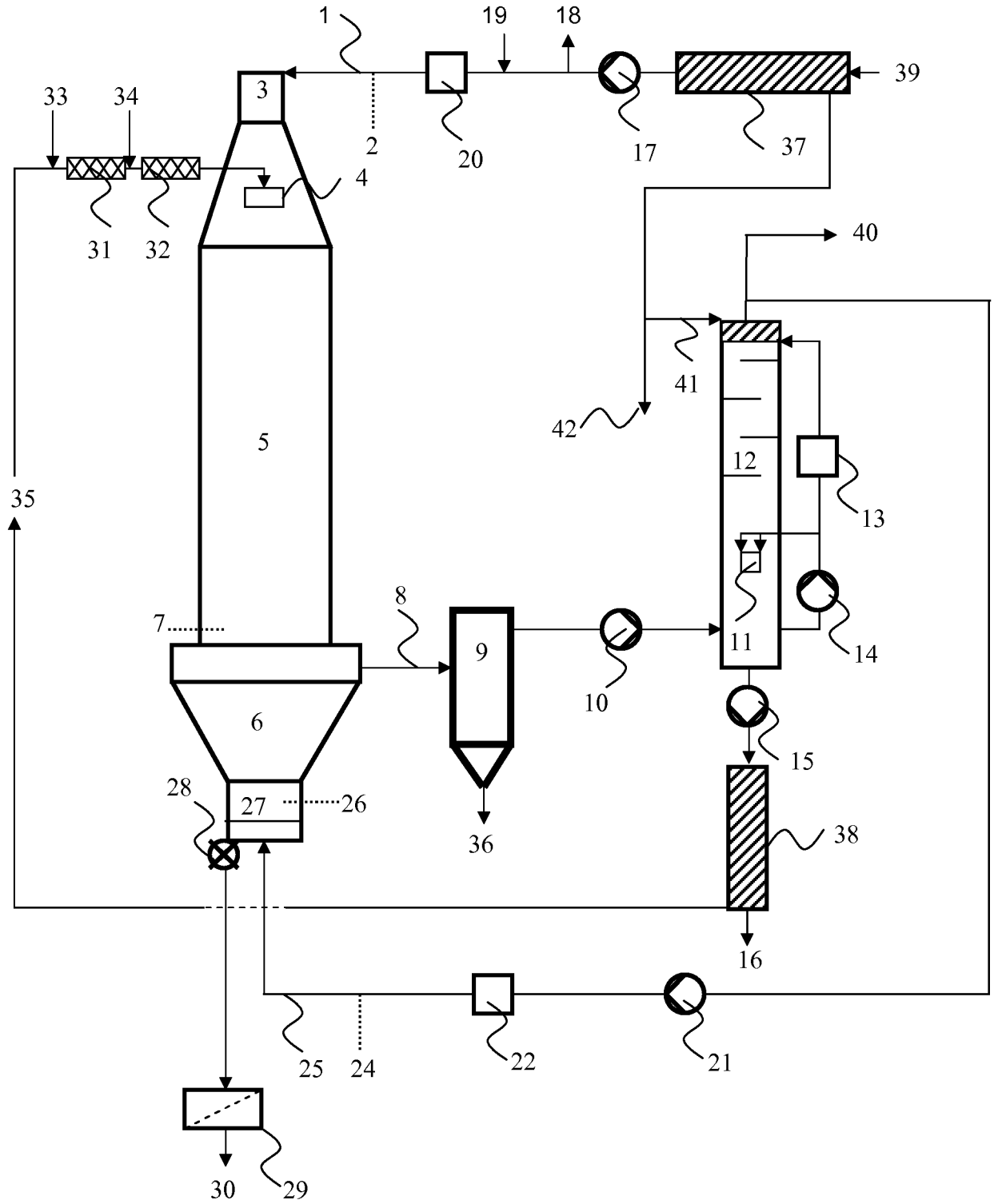

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Fig. 3

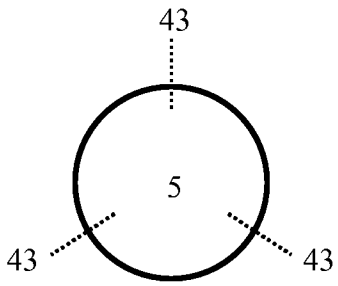


Fig. 4

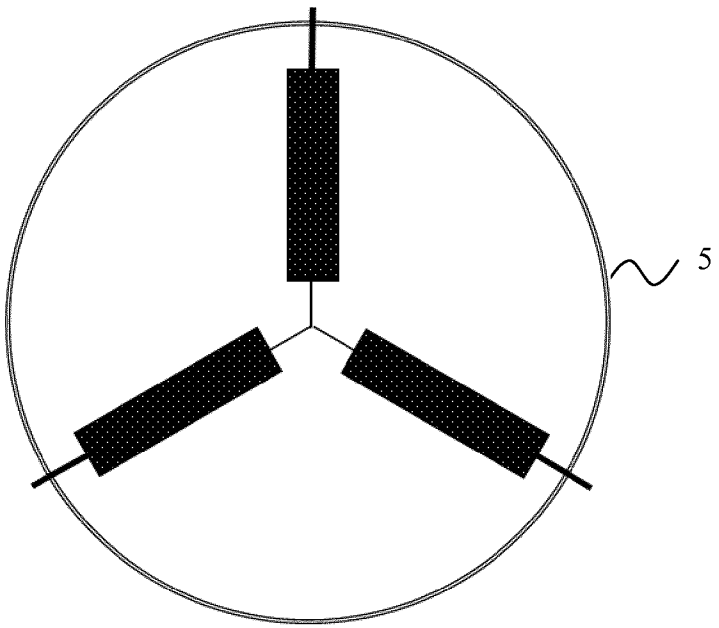


Fig. 5

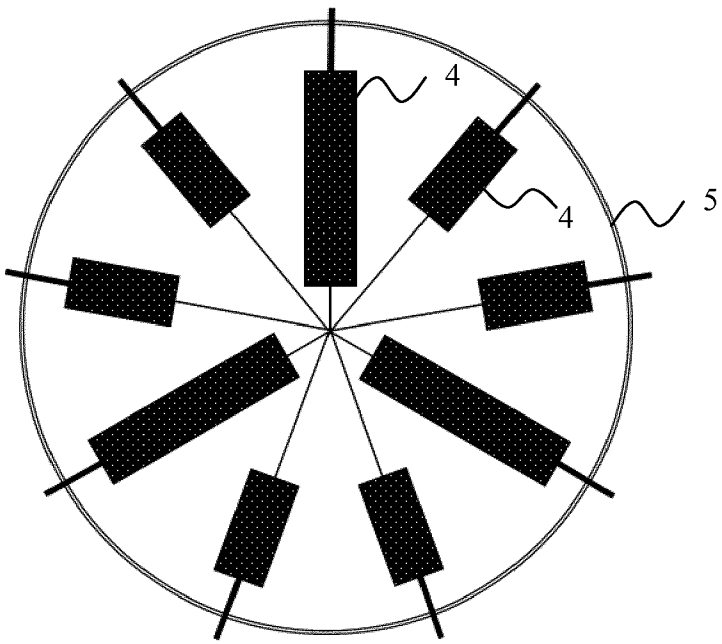


Fig. 6

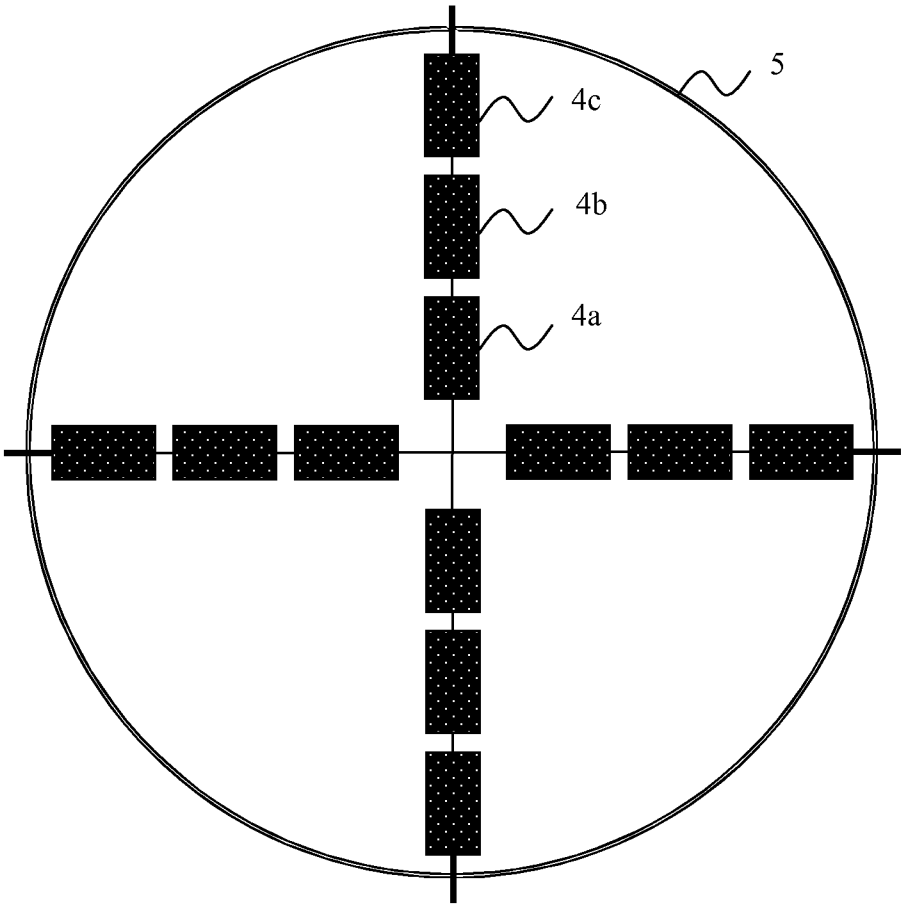


Fig. 7

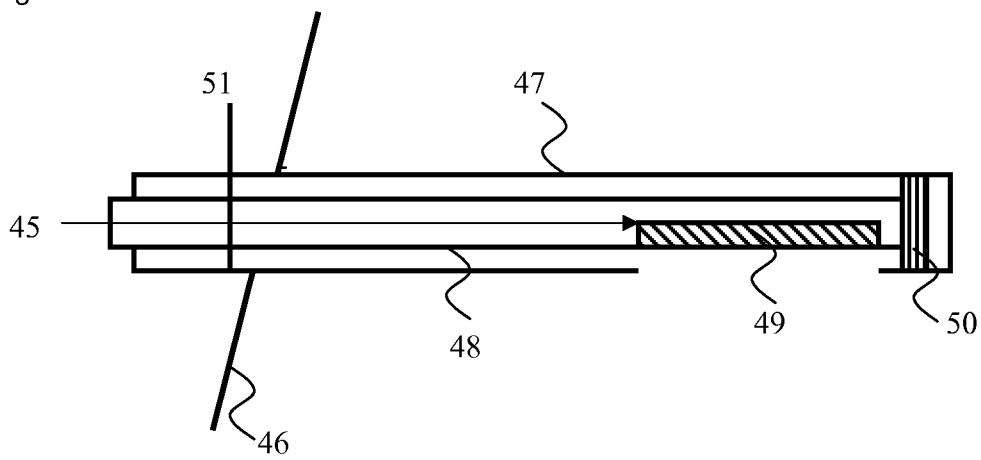


Fig. 8

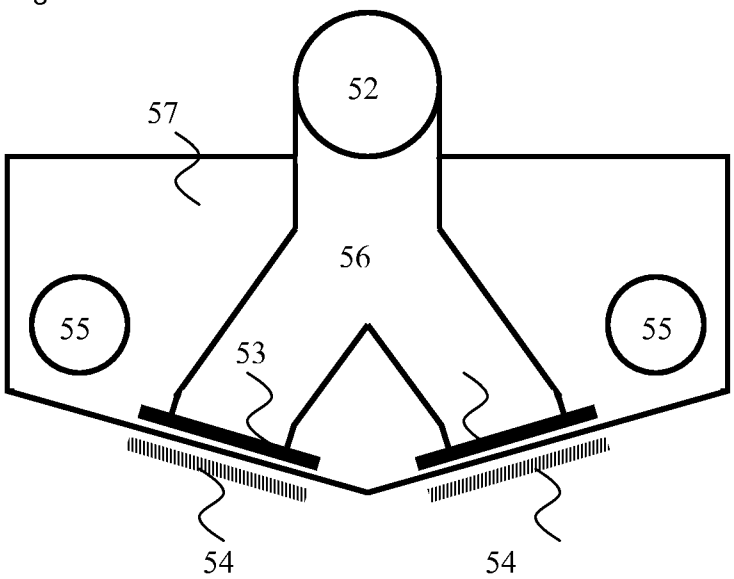


Fig. 9

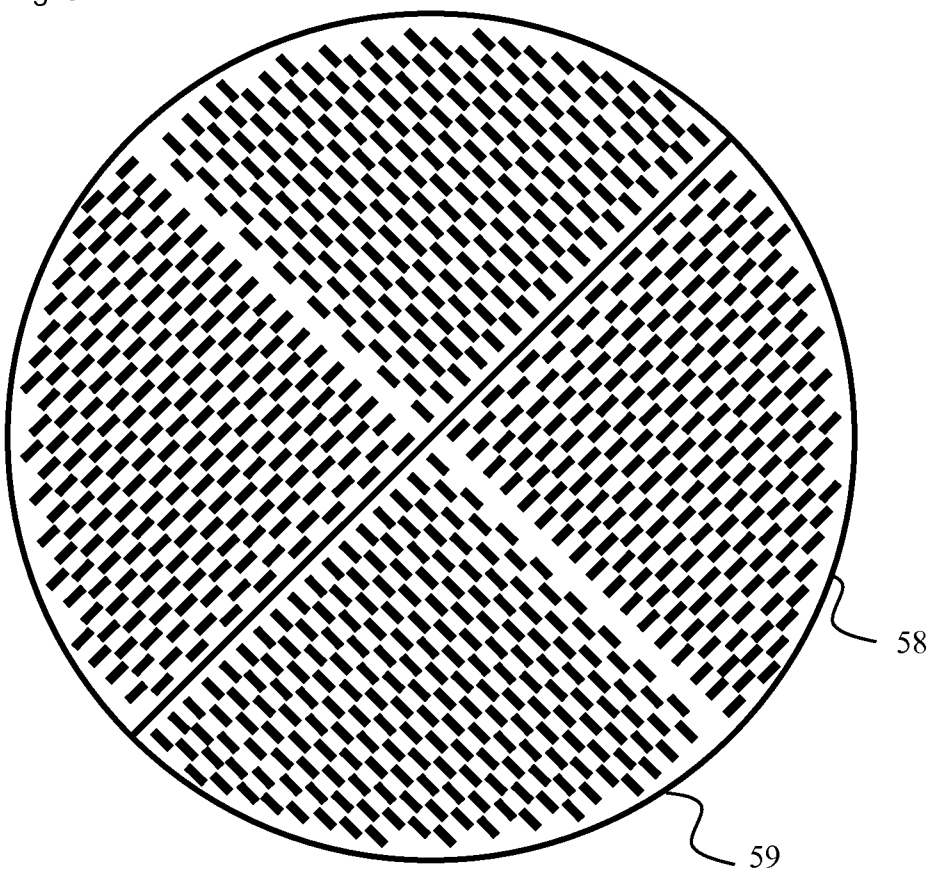


Fig. 10

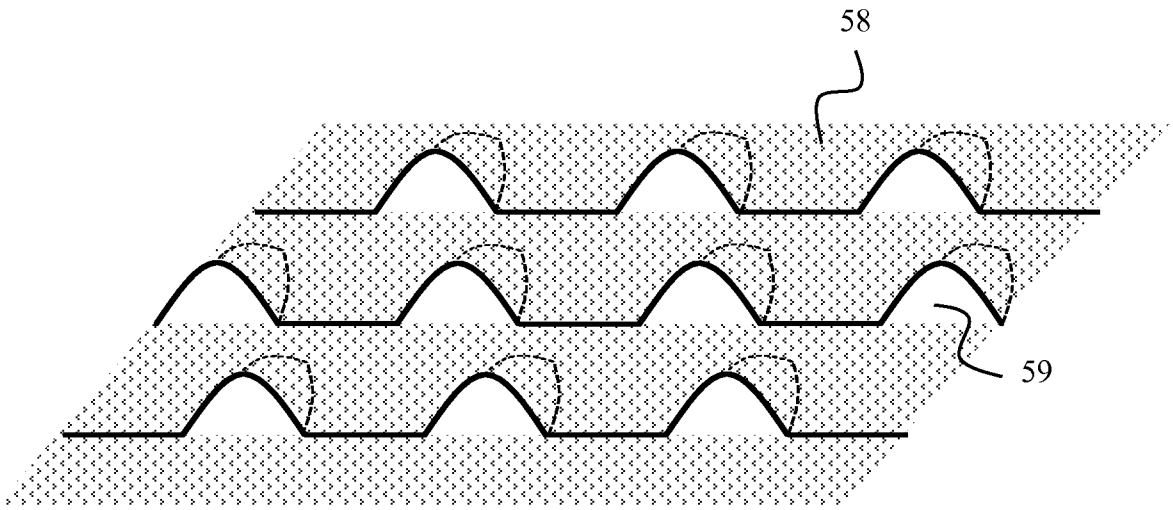


Fig. 11

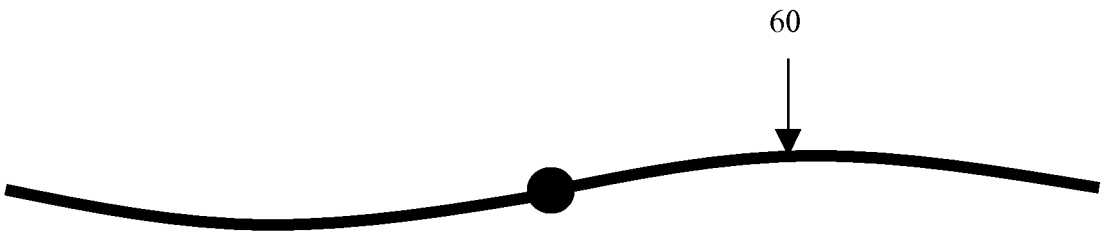


Fig. 12

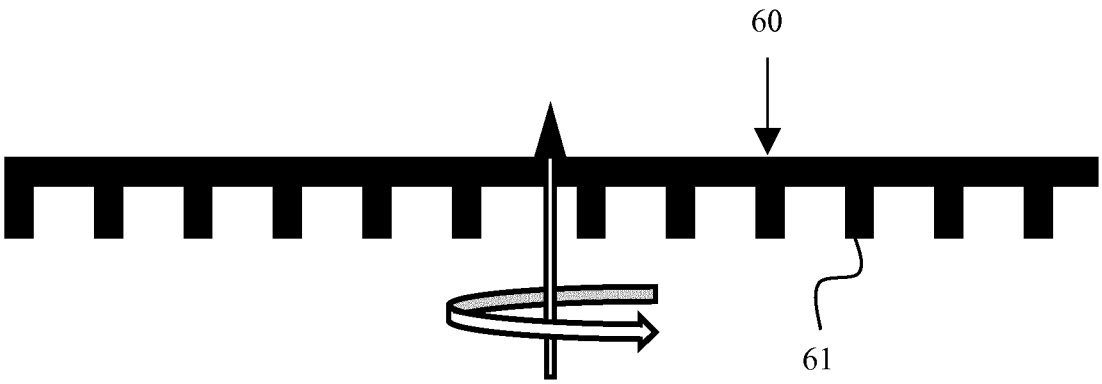


Fig. 13

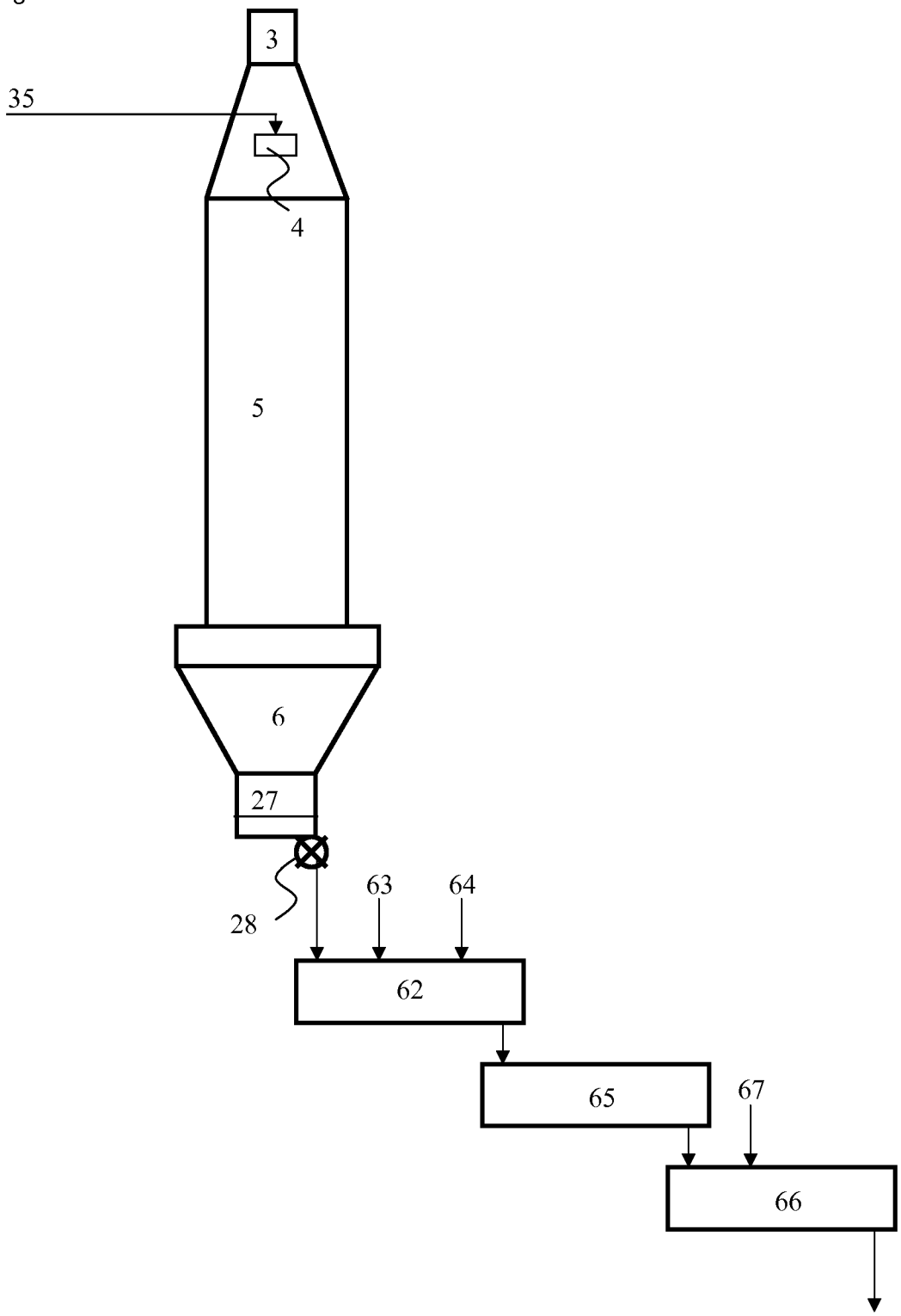


Fig. 14

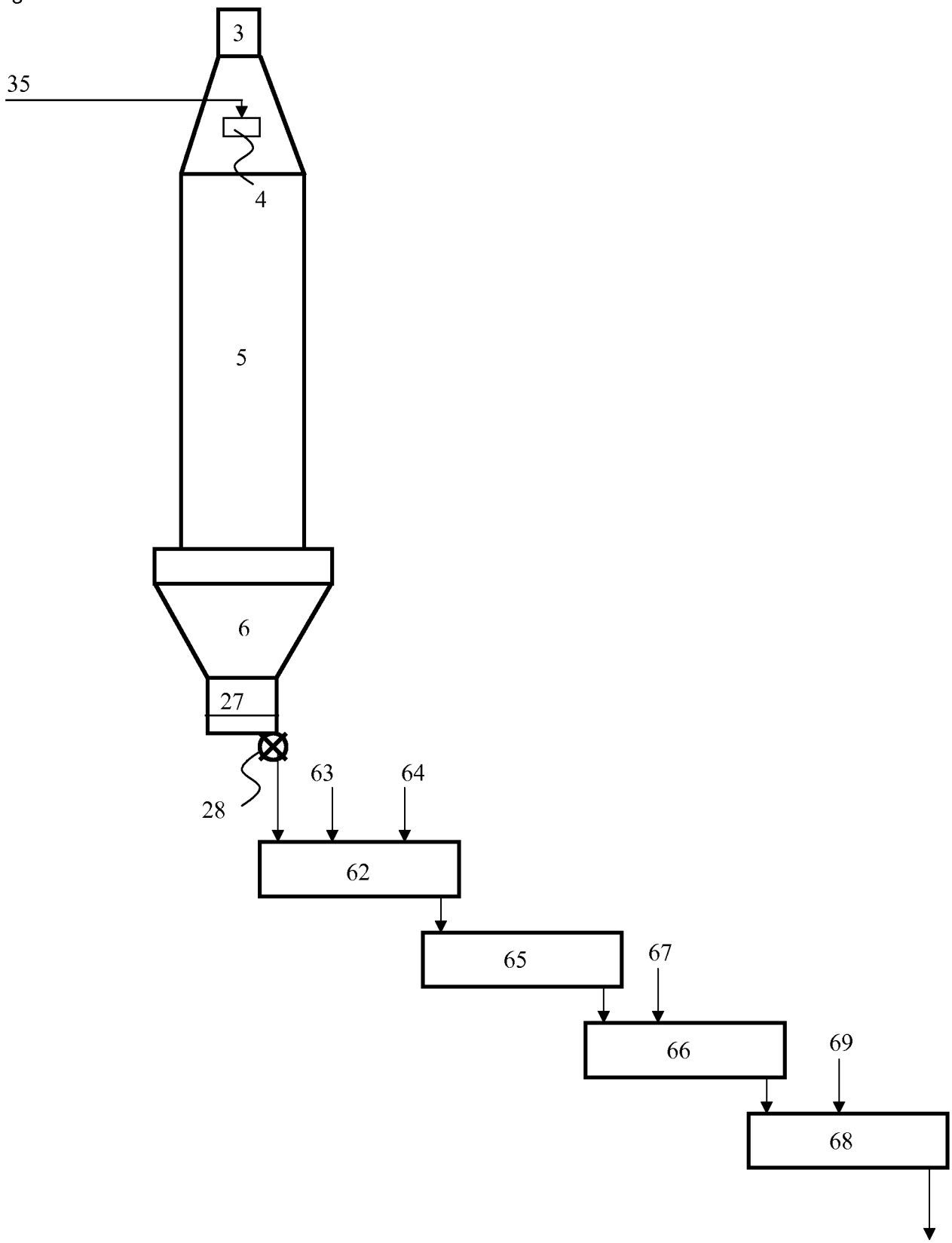
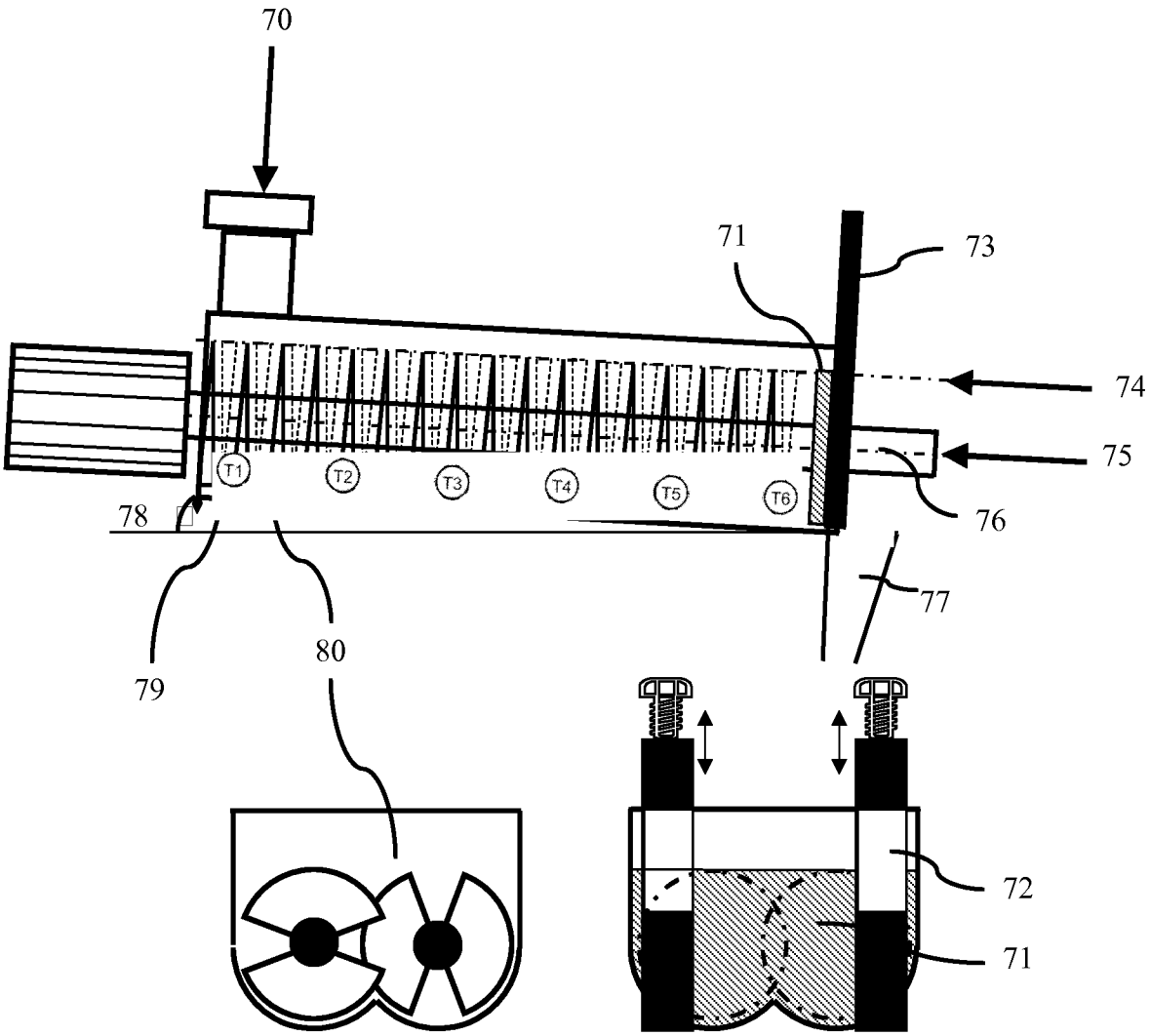


Fig. 15



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/050532

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61L15/60 C08F2/01 C08F6/00 C08L33/02 C08L101/14
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 A61L C08L

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.
A	WO 2008/095901 A1 (BASF SE [DE]; LOESCH DENNIS [DE]; KRUEGER MARCO [DE]; BLEI STEFAN [DE]) 14 August 2008 (2008-08-14) page 3, line 17 - line 25	1-16
A,P	WO 2014/079710 A1 (BASF SE [DE]) 30 May 2014 (2014-05-30) page 10, line 1 - line 12	1-16

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 April 2015	14/04/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Gold, Josef

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2015/050532

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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