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The present invention relates to the production of polymer resins with high absorptivity for water and aqueous fluids, in particular of absorbent resins in the form of agglomerated spherical particles.

5           Such absorbent resins are particularly useful in the manufacture of sanitary products, including disposable nappies for babies, sanitary towels and similar products. They are also useful in other applications, for example in agriculture, as soil conditioners or as water-retaining  
10 agents, and in civil engineering, as anti-condensation or dehydrating components in construction materials.

          The choice of absorbent resin depends upon the desired properties such as high absorbance, good compatibility with the other components of the sanitary  
15 product, low rewetting tendency, good mechanical strength of the water-swollen gel, which properties tend to depend on the chemical nature of the polymer, as well as upon having particle sizes of between 100 and 1,000 micrometres, with a narrow particle size distribution and in particular upon  
20 having as few small-sized particles as possible, which affect the handling and construction of the articles incorporating them. Also high rates of absorption, and good diffusion of liquids into, between and within the absorbent particles are characteristics that are related to the particle size and the  
25 shape of the particles. In addition, good water-absorbent resins must be nonirritant and inexpensive.

The most widely known water-absorbing systems

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include partially neutralized polyacrylic acids and their derivatives. Such acrylic super-absorbent resins have traditionally been produced essentially by two different methods of polymerization: solution polymerization, which  
5 yields a polymer mass which must subsequently be ground and classified to obtain a powder of suitable particle size, and inverse suspension polymerization, the direct result of which is a powder whose components are substantially spherical polymer particles.

10 Inverse suspension polymerization, however, has the disadvantage of providing, in the absence of agglomeration, superabsorbent polymer in the form of a powder of excessively fine particle size. This is the case, for example, with the polymerization of an alkali metal salt of  
15 acrylic acid or of a closely related monomer in inverse water-in-oil suspension, as described in published Japanese Patent Application No. 54-30710 utilizing a primary surfactant consisting of an ester of a fatty acid and of sorbitan with an HLB of between 3 and 6, or in published  
20 Japanese Patent Application No. 60-25045 using an anionic surfactant, which results in powders having particles between 10 and 100 micrometres in size.

It is known separately to agglomerate the initially formed individual particles to provide particles  
25 which are both of large size and of high specific surface without which the rate of water absorption would be insufficient. A number of agglomeration methods have been

proposed. There is, for example, the agglomeration of dry powders, by surface crosslinking with a crosslinking agent (European Patent Specification EP 349240, Nippon Shokubai) or by an aqueous solution of monomer containing a crosslinking agent (Japanese Patent Specification JP 1126314, Nippon Shokubai), which improves the rate of absorption of the polymer, but is a technically difficult operation, and also has the disadvantage of providing relatively fragile agglomerates.

10                   It has therefore generally been preferred to reaggregate powder resuspended in an inert hydrocarbon liquid with the aid of an agglomerating agent consisting of an inorganic powder (silica) and of a surfactant (European Patent Specification EP 224923 Seitetsu) or of a relatively  
15 small quantity of an acrylic aqueous solution introduced into the polymer suspension under polymerization conditions (International Patent Publication WO 90/08789, Dow Chemicals).

                  These processes are merely methods for the  
20 recovery of powders of unsatisfactory particle size. It is industrially somewhat unsatisfactory to have systematically to carry out two independent complete operations to achieve a single result. Thus attempts have been made to incorporate the agglomeration into the overall production of the  
25 superabsorbent polymer by making the agglomeration follow directly the inverse suspension polymerization, which gives the polymer in the form of individual particles. Thus,

European Patent Specification 522570 (Mitsubishi) describes the introduction of monomer directly into the slurry from first polymerization, the polymerization of which is next brought about by heating the mixture to approximately 60°C.

5 The method appears to function well, except in the case of small quantities of monomer. European Patent Specification 441507 (Sumitomo) describes a two-stage preparation in which, after having carried out the first stage of inverse suspension polymerization, the suspension of polymer  
10 particles is cooled to ambient temperature so as to inactivate the surfactant used to ensure the stability of the inverse suspension; after which a second monomer charge, in the form of an aqueous solution, is added to the suspension, the polymerization of which is brought about by raising the  
15 temperature to about 60/70°C. A narrow distribution of strongly bound large-sized agglomerates is thus obtained, but with the disadvantage of a high energy consumption and of poor output efficiency because of the slowness of the reactor cooling/heating cycles which are necessary.

20           According to the present invention there is provided a process for preparation of superabsorbent polymer in the form of a powder of agglomerated particles, which process comprises agglomerating using, as agglomerating agent, an aqueous solution of monomer, particles of super-  
25 absorbent polymer in suspension in a hydrocarbon liquid medium which is a non-solvent for the polymer and for the agglomerating agent, wherein:

- the aqueous solution of monomer is introduced into the mixture at the temperature of polymerization of the monomer,

- there is used between 50 % and 200 % by weight of agglomerating monomer based on the weight of the polymer to be agglomerated,

- the aqueous solution of monomer additionally contains a hydrophilic additive comprising a thickener and a surfactant with an HLB higher than or equal to 8.

10 The process according to the invention enables particles to be obtained with the required size distribution.

Within the meaning of the present specification, a temperature of polymerization is intended to mean a temperature at which the polymerization of the monomer is  
15 suitably carried out and which depends, among other things, on the polymerization initiator employed. In the case where this initiator is potassium persulphate, which is a preferred initiator for the invention, this temperature is above 50°C.

To carry out the invention, the starting material  
20 to be agglomerated may be a suspension, in the hydrocarbon liquid medium, of fine spherical particles which is a fine powder of superabsorbent polymer dispersed while heated with moderate agitation in hydrocarbon liquid medium, or the polymer slurry in the composition and temperature state which  
25 directly results from a preliminary inverse suspension polymerization.

The aqueous solution of unsaturated water-soluble

monomer agglomeration agent, which will have been prepared separately, is introduced with agitation and while the temperature of the reactor is maintained as accurately as possible at the temperature of polymerization, in practice  
5 between 60 and 75°C. For the monomer solution preparation, performed cold to prevent any untimely polymerization at this stage, the procedure is typically to dissolve and partially neutralize the monomer, to add polymerization initiator and, if appropriate, crosslinking agent, and an agglomerating  
10 agent intended to control the direct formation of clusters of polymer particles which will form the superabsorbent resin powder in its final form.

The rate of introduction of the monomer solution and the agitation in the reactor are controlled so that the  
15 temperature within the reactor departs as little as possible from the chosen target temperature, since the addition of cold monomer tends to lower it, and the exothermicity of the polymerization to increase it.

When the agglomeration polymerization is finished,  
20 which is ensured when the temperature of the mixture has become steady again after passing through an exothermic peak, the water and the solvent may be removed by distillation and the superabsorbent resin powder is collected directly in the form in which it is employed.

25 The unsaturated monomers, the polymerization initiators, the crosslinking agents, the nonreactive hydrocarbon liquids forming the dispersion medium, the

surface-active agents and the thickeners which are used according to the invention are materials which are known for use in disperse phase radical polymerization processes.

Acrylic acid and methacrylic acid are the preferred water-soluble unsaturated monomers for use according to the invention. Nevertheless, the process may be carried out with other unsaturated water-soluble monomers such as the methylpropanesulphonamides of these acids, their nonanionic derivatives such as acrylamide, methacrylamide and their N,N-dimethylsubstituted derivatives, 2-hydroxyethyl acrylate or methacrylate, N-methylolacrylamide or -methacrylamide, or their nitrogen-containing derivatives such as (dimethyl- or diethyl)amino(ethyl or propyl) acrylate or methacrylate and the corresponding quaternary ammonium salts.

The agglomeration polymerization is initiated by radical polymerization initiators, water-soluble ones being preferred since both the monomer and the polymer are themselves hydrophilic; potassium persulphate is particularly preferred.

Crosslinking agents, which can be employed for the partial crosslinking of the hydrophilic polymers produced, are generally compounds containing at least two unsaturated groups capable of copolymerizing with the unsaturated monomer (acrylic acid), of the polyol di/triacrylate type, or which are capable of reacting with its polymerization products, such as diol diglycidyl ethers.

The nonreactive hydrocarbon liquids employed as

dispersion media according to the invention are products that are chemically inert towards the monomers and the polymers formed. It is highly desirable that they should form an azeotrope with water, so that the latter may be removed by  
5 azeotropic distillation, and that their boiling point should be sufficiently low so that they may be evaporated from the final powder without thermal degradation. They are, for example, n-pentane, cyclohexane, n-heptane, toluene, ethylcyclohexane, isooctane and xylene.

10           It may happen that a spontaneous agglomeration of the polymer particles takes place under conditions similar to those of the invention. It is obviously not possible to rely on such a process in order to obtain the industrial result which is sought after. This result is achieved according to  
15 the invention by adding to the monomer agglomerating agent a highly hydrophilic agent with surfactant and viscosity-raising properties. This hydrophilic agent consists of the combination of a hydrophilic surfactant with an HLB higher than or equal to 8 and of a viscosity-raising or thickening  
20 agent.

          Hydrophilic surfactants which may be employed are, for example, nonionic agents like ethoxylated alkylphenols, sorbitan or ethoxylated sorbitol derivatives; among these, those containing 10 to 100 molecules, and more precisely 15  
25 to 50 molecules, of ethylene oxide per molecule are particularly valued; or conventional ionic surfactants such as sulphates or sulphonates, for example sodium

dodecylsulphate or dodecylbenzenesulphonic acid; or hydrophilic polymeric surface-active agents like polyvinyl alcohol or vinyl acetate/vinyl alcohol copolymers.

The choice of the hydrophilic viscosity-raising agents or thickeners may turn to the cellulose derivatives known as modified water-soluble celluloses, such as carboxymethyl cellulose, or to water-soluble acrylic polymers such as linear poly(meth)acrylic acids or their copolymers, for example with 2-hydroxyethyl acrylate, vinylpyrrolidone or its derivatives, linear (meth)acrylic acid/methyl vinyl ether/maleic acid or anhydride copolymers, their metal salts, polyethylene oxides and water-soluble polyurethanes.

It is to be noted that the use of a thickening or viscosity-raising agent in the charge of agglomerating agent is contrary to a prejudice of the prior art. What is desired from an agglomerating agent, whatever the mechanism by which it is consumed, is that it should bind onto or into the particles which it is intended to agglomerate and that it should not go into a stable suspension and polymerize in this form, the result of which would be the formation of a new population of individual polymer particles, which is obviously to be avoided. One of the unexpected teachings of the invention is that not only does a thickening agent in the charge of the agglomerating agent not promote its stabilization in the form of suspension, to the detriment of its contact with the polymer particles to be agglomerated, but that it is one of the characteristics of the process.

The weight ratio of the agglomerating agent to the polymer to be agglomerated is not without significance.

Below 50 % by weight of agglomerating agent the agglomeration is only very partial and the final powder contains an  
5 excessively high proportion of fine beads which have remained independent. Above 200 % by weight the process suffers from difficulties in stabilization: there is too much disperse phase in the hydrocarbon which forms the dispersion medium, and there is a severe risk of setting solid.

10 The following Examples will further illustrate the present invention.

In the accompanying Figures:

Figure 1 shows product according to Comparative Example 1, and

15 Figure 2 shows product according to the present invention of Example 2.

Example 1: Preparation of superabsorbent particles without agglomeration (comparison example).

This is a one-step polymerization process based on  
20 inverse suspension polymerization. The following sequences are carried out:

- a) preparation of the dispersion medium,
- b) preparation of the monomer solution,
- c) introduction and dispersion of the  
25 monomer in the dispersion medium and its polymerization,
- f) (final sequence): evaporation of the water and of the solvent and recovery of the powder obtained.

Sequence a)

1.07 grams of a polyethylene modified with maleic anhydride (Hi-Wax 1105A, marketed under this name by Mitsui Petrochemical Industries Co) and 0.55 grams of sucrose di/tristearate are dissolved in 275 grams of heptane at about 80°C and with stirring at 400 revolutions/minute and purging with nitrogen, in a one-litre reactor fitted with a device for introducing solid or liquid reactants, a bladed stirrer, a system for purging with inert gas, a temperature probe and a heating/cooling device consisting of a jacket in which a heat transfer fluid is circulated and can be assigned to a target temperature. This solution is kept at 80°C for the time needed for the surfactant system to dissolve completely in the heptane. After dissolving, the temperature is brought back to 60°C.

Sequence b)

In another one-litre reactor equipped like the preceding one, 92 grams of an aqueous solution containing 80 % by weight of acrylic acid are neutralized with 135.59 grams of 22.62 % sodium hydroxide lye, this being done slowly enough that the temperature does not exceed 30°C. To this solution are added 2 grams of carboxymethyl cellulose and then 0.414 grams of a solution containing 2 % by weight of ethylene glycol diglycidyl ether and 2.76 grams of an aqueous solution containing 2 % of potassium persulphate.

Sequence c)

While the reactor with the heptane-based solution

is kept stirred at 400 revolutions/minute and with nitrogen purging, the previously prepared aqueous phase is introduced rapidly into it and changes into an inverse suspension in the heptane. The rapid introduction of the aqueous phase into  
5 the reactor causes the temperature of the mixture to fall to about 40°C. This temperature is maintained for a stabilization period of 15 minutes. After this period the target temperature of the heat transfer fluid circulated in the jacket is raised to 70°C. The polymerization commences.  
10 The reactor is kept at this temperature level for 30 minutes.

Final sequence f)

The target temperature is now raised to 115-130°C to remove the water and heptane. After complete evaporation a superabsorbent polymer is obtained in the form of a powder  
15 consisting of individual beads (Figure 1) of superabsorbent polymer with a mean size of approximately 100 microns, whose absorptivity for water containing salt in a concentration of 0.9 % by weight is 75 grams per gram of polymer. The percentage of fines (particles smaller than 100 microns in  
20 size) is approximately 50 %, a value which is quite unacceptable.

Examples 2 to 7 are examples of processes comprising an agglomeration of individual fine particles. The following sequences are carried out:

25                    -        a), b) and c), for the preparation of the superabsorbent polymer as individual beads, which may be extemporaneous, and which are then linked directly into a

series with sequences d), e) and f) below, or else which correspond to a preliminary preparation of dry powder, in which case they have been followed by a sequence f) as above for the isolation of the powder,

5                   -       d)       preparation of a charge of agglomerating agent,

                  -       e)       introduction of the agglomerating agent charged into the powder of individual beads of polymer or into a dispersing medium within which these beads remain  
10 in suspension, and optionally its polymerization if a polymerizable monomer agglomerating agent is involved,

                  -       f)       a (second) sequence for evaporation of the solvents and recovery of the powder obtained.

Example 2: Reagglomeration of powder according to  
15 the invention.

Sequence a)

                  A reactor as described in the sequence a) of Example 1 is charged with 275 g of heptane. The temperature of the heat transfer fluid is set a target temperature of 80°C  
20 and 1.07 grams of Hi-Wax 1105A and 0.55 grams of sucrose di/tristearate are dissolved therein with stirring at 400 revolutions/minute and with nitrogen purging. This solution is kept at 80°C for the time needed for the dispersing system to dissolve in the heptane. The temperature is kept at 80°C  
25 and the superabsorbent powder obtained in Example 1 is introduced into the mixture, stirring being continued, in such quantity that there are 92 g of dry polymer, allowing

for the residual moisture in the powder.

Sequences b/c)

A quantity of water is introduced into the reactor such that, allowing for the moisture introduced by the  
5 superabsorbent, there are 138 g of water in the reactor (water content of the swollen superabsorbent polymer in suspension in the heptane medium equal to 60 % by weight of the total polymer + water). The temperature of the heat transfer fluid is set a target of 70°C.

10 Sequence d)

While the preceding sequence is in progress, 92 grams of aqueous solution containing 80 % by weight of acrylic acid are neutralized with 135.59 grams of 22.62 % sodium hydroxide lye in a reactor equipped like that in  
15 sequence a), this being performed slowly enough that the temperature does not exceed 30°C. To this solution of partially neutralized acrylic acid (75 moles %) are added 2 grams of carboxymethyl cellulose and 0.46 grams of an aqueous solution containing 10 % of nonylphenol ethoxylated with 50  
20 moles of ethylene oxide (Remcopal 31250 from Ceca S.A.), and then 2.76 grams of an aqueous solution containing 2 % by weight of potassium persulphate and 7 grams of an aqueous solution containing 2 % of ethylene glycol diglycidyl ether.

Sequence e)

25 The monomer charge prepared in sequence d) above is introduced dropwise into the reactor as it is at the end of sequence c). The introduction period is approximately 30

minutes, the temperature of the fluid in the jacket remaining set at 70°C, under nitrogen bubbling, the rate of stirring being maintained at 400-600 revolutions/minute. As a result of the introduction of this charge, which is relatively cold, 5 the reactor temperature drops slightly without, however, ever falling below 65°C, and then rises again both because of the heating by the jacket at 70°C and of the exothermicity of the polymerization reaction, which soon recommences. The rate of stirring is increased to 800 revolutions/minute and the 10 reactor is kept under these conditions for about twenty minutes.

Final sequence f)

The target temperature is now raised to 115-130°C to remove the water and heptane. After complete evaporation 15 a superabsorbent polymer is obtained in the form of a powder which appears under the microscope to be formed of agglomerates of polymer beads. The powder fraction passing through a 100-micron screen is less than 1 %. The salt water absorption is 60 g/g of polymer.

20 Example 3: Two-stage process, polymerization and agglomeration according to the invention.

To begin with, stages a), b) and c) are performed as in Example 1.

The sequences d) and e) are next linked in series 25 as in Example 2, and the operation is finished with a final sequence f), also as in Example 2.

A powder of superabsorbent polymer is thus

obtained in the form of a powder of agglomerates of beads (Figure 2), the undersize of which at 1 micrometre is lower than 1 %, and whose salt water absorption is 62 g/g of polymer.

5                    Example 4: Aqueous compositions according to the invention and temperature control according to Sumitomo.

The process is as in Example 3, except for the following differences.

The inverse suspension polymerization of the  
10 monomer resulting in the formation of a suspension of individual beads of monomer in the hydrocarbon solvent is carried out by performing the sequences a), b) and c) as in Example 1, but at the end of sequence c) the target temperature of the reactor is set at 40°C so as to bring the  
15 contents of the reactor to this temperature. When this temperature is reached, the heating control of the jacket is switched off. The following sequences are carried out.

Sequence d)

While the preceding sequence is in progress, 92  
20 grams of aqueous solution containing 80 % by weight of acrylic acid are neutralized with 135.59 grams of 22.62 % sodium hydroxide lye in a reactor equipped like that in sequence a), this being done slowly enough that the temperature does not exceed 30°C. To this solution of  
25 partially neutralized acrylic acid (75 moles %) are added 2 grams of carboxymethyl cellulose and 0.46 grams of an aqueous solution containing 10 % of nonylphenol ethoxylated with 50

moles of ethylene oxide (Remcopal 31250 from Ceca S.A.), and then 2.76 grams of an aqueous solution containing 2 % by weight of potassium persulphate and 2 grams of an aqueous solution containing 2 % of ethylene glycol diglycidyl ether.

5                   Sequence e)

The aqueous charge prepared according to sequence d) is introduced dropwise into the reactor, with nitrogen bubbling, the rate of stirring being maintained at 400-600 revolutions/minute. The temperature of the reactor contents  
10 decreases again to about 35°C. These conditions are maintained for approximately 15 minutes for stabilization and the heating control of the reactor is then brought back into action, the temperature of the heat transfer fluid being set a target of 70°C. The polymerization commences. These new  
15 conditions are maintained for about twenty minutes from the time when the temperature of the mixture has reached 70°C.

Final sequence f)

As in Example 1.

A powder which is substantially identical with  
20 that obtained in Example 3 is thus obtained, but at the expense of a greater experimental complexity, a longer production period and an appreciably higher consumption in the cooling/heating cycles in sequences c) and f).

Example 5: Aqueous compositions according to  
25 Sumitomo, and temperature control according to the invention.

The procedure is as in Example 4, except for the following differences.

Sequence a)

275 g of heptane are introduced into the device described in Example 1 and are heated to 80°C, and 0.74 g of sucrose di/tristearate and 1.07 g of polyethylene modified with maleic anhydride are dissolved therein with stirring at 400 revolutions/minute.

Sequence b)

92 g of an aqueous solution containing 80 % by weight of acrylic acid are separately neutralized with 135.59 g of 22 % sodium hydroxide lye. 1 g of carboxymethyl cellulose is added, followed by 2.76 g of an aqueous solution containing 2 % of potassium persulphate and 0.92 g of an aqueous solution containing 2 % of ethylene glycol diglycidyl ether.

15

Sequence c)

While the reactor is kept stirred at 400 revolutions/minute and with nitrogen purging at the rate of 80 litres/minute, the aqueous phase prepared previously is introduced into it a little at a time and changes into inverse suspension in the heptane. The temperature is raised to 70°C to induce polymerization; it is kept at this level for 30 minutes. The temperature is then brought back to 45°C.

Sequence d)

While the preceding operation is in progress, 92 g of aqueous solution containing 80 % by weight of acrylic acid is separately neutralized with 135.59 g of 22.6 % sodium hydroxide lye and then 2.76 g of an aqueous solution

containing 2 % of potassium persulphate and 0.92 g of an aqueous solution containing 2 % of ethylene glycol diglycidyl ether are then added. The temperature of this aqueous phase, which forms the monomer charge II, is then brought back to 5 10°C.

Sequence e)

The stirring in the reactor is raised to 800 revolutions/minute, the nitrogen purging being maintained at 80 litres/minute. The charge II is introduced into it a 10 little at a time. When the charge II has been introduced, the absorption is allowed to continue for 5 minutes at a temperature of 45°C. After this the temperature is raised to 70°C to start the second stage of polymerization. The polymerization is allowed to continue for 30 minutes.

15 Final sequence f)

The heptane and most of the water are removed by distillation.

The final product is a powder whose mean particle size is 150  $\mu\text{m}$ , whose undersize at 100  $\mu\text{m}$  is unacceptable, 20 with a value of more than 15 %, and whose absorption of 0.9 % salt water is 55 g/g.

Example 6

In this example the ability to conduct the operation at high temperature is exploited to the full. This 25 is an advantageous alternative form of the preceding Example.

Sequence a)

The procedure is as in Example 1, except for the

difference that at the end of the sequence the temperature is brought back to 70°C by setting the temperature of the heat transfer fluid in the reactor jacket at this temperature.

Sequence b)

5                   An aqueous solution of monomer is prepared as in Example 1.

Sequence c)

                  While the reactor with the heptane-based solution is kept stirred at 400 revolutions/minute and with nitrogen  
10 purging, the previously prepared aqueous phase is introduced into it rapidly and changes into inverse suspension in the heptane. The introduction of the aqueous phase into the reactor causes a brief drop in the temperature of the mixture, rapidly compensated by the fact that the jacket  
15 temperature is set a target of 70°C. The polymerization commences; its exothermicity can take the mixture to a higher temperature, brought back to 70°C by the same mechanism as soon as the polymerization exothermicity ceases. A polymer suspension is formed and stays automatically at 70°C.

20                   Sequence d)

                  While the preceding operation is in progress, a new charge of aqueous solution of monomer is prepared as described in sequence d) of Example 3.

Sequences e) and f)

25                   These are conducted like sequences e) and f) in Example 3.

                  A powder of superabsorbent polymer is thus

obtained in the form of a powder of agglomerates of beads, whose undersize at 1 micrometre is less than 1 %. Its salt water absorption is 65 g/g.

Example 7: Comparative Examples.

5           All the sequences take place as in the preceding example, with the exception of sequence d), in which the aqueous solution of monomer is prepared omitting the addition of the hydrophilic additive, that is to say of carboxymethyl cellulose and of nonylphenol ethoxylated with 50 moles of  
10 ethylene oxide.

A powder of superabsorbent polymer is thus obtained, consisting essentially of beads with an unacceptable 36 % undersize at 100 microns.

If the nonylphenol ethoxylated with 50 moles of  
15 ethylene oxide is omitted, a powder containing 30 % of fines is obtained. When it is the thickener that is omitted, the powder obtained contains 10 % of fines.



CLAIMS

1. A process for preparation of superabsorbent polymer in the form of a powder of agglomerated particles, which process comprises agglomerating using, as agglomerating  
5 agent, an aqueous solution of monomer, particles of superabsorbent polymer in suspension in a hydrocarbon liquid medium which is a non-solvent for the polymer and for the agglomerating agent, wherein:
  - the aqueous solution of monomer is  
10 introduced into the mixture at the temperature of polymerization of the monomer,
  - there is used between 50 % and 200 % by weight of agglomerating monomer based on the weight of the polymer to be agglomerated,
  - 15 - the aqueous solution of monomer additionally contains a hydrophilic additive comprising a thickener and a surfactant with an HLB higher than or equal to 8.
2. A process according to Claim 1, wherein the suspension of superabsorbent polymer to be agglomerated is  
20 produced by suspending a powder of superabsorbing polymer in a liquid hydrocarbon in which the polymer is not soluble.
3. A process according to Claim 2, wherein, before the agglomeration, the superabsorbent polymer, suspended in a liquid hydrocarbon, is swollen with water.
- 25 4. A process according to Claim 1, wherein the suspension of superabsorbent polymer to be agglomerated is a suspension as obtained by inverse suspension polymerization



of an aqueous solution of monomer in a hydrocarbon liquid in which the polymer and the agglomerating monomer are not soluble.

5. A process according to any one of Claims 1 to 4, wherein the aqueous solution of monomer for agglomeration is introduced into the mixture to be agglomerated at a temperature of 60 to 75°C.

6. A process according to any one of the preceding claims, wherein the said thickener is a modified water-soluble cellulose or a water-soluble acrylic polymer or copolymer.

7. A process according to any one of the preceding Claims, wherein the said surfactant is an ethoxylated alkylphenol, ethoxylated sorbitan or ethoxylated sorbitol derivative which contains 10 to 100 molecules of ethylene oxide per molecule.

8. A process according to any one of Claims 1 to 5, wherein the hydrophilic agent contains carboxymethyl cellulose as thickening agent and nonylphenol ethoxylated with 50 moles of ethylene oxide as hydroxylated surfactant.

9. A process according to Claim 1 substantially as described in any one of Examples 2, 3, 5 and 6.

10. Agglomerated particles of superabsorbent polymer prepared by the process claimed in any one of the preceding Claims.

ABSTRACT

PROCESS FOR PREPARING AGGLOMERATED SUPERABSORBENT  
POLYMER PARTICLES

According to the present invention, fine particles  
5 of superabsorbent polymer may be agglomerated by introducing  
an aqueous solution of monomer into a slurry of aqueous  
polymer dispersed within a hydrocarbon liquid, this  
introduction being performed directly at the temperature and  
under the conditions of polymerization of the monomer.

10 A superabsorbent product is thus obtained in a  
good yield, in the form of aggregates of particles whose  
undersize at 100 micrometres is below 1 %.

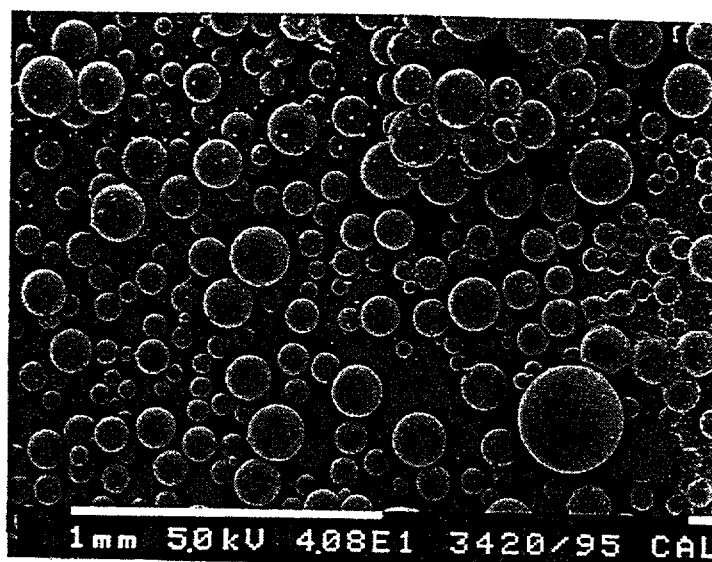


Fig. 1

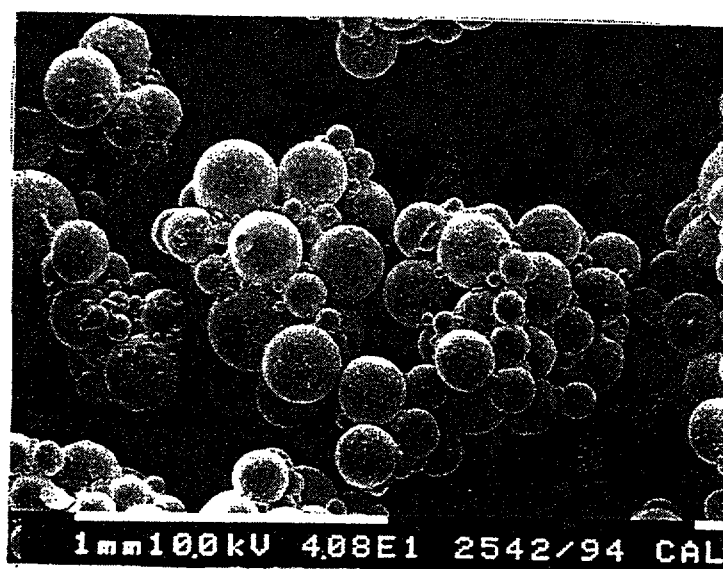


Fig.2

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## PROCESS FOR PREPARING AGGLOMERATED SUPERABSORBENT POLYMER PARTICLES

The present invention relates to the production of polymer resins with high absorptivity for water and aqueous fluids, in particular of absorbent resins in the form of agglomerated spherical particles.

5           Such absorbent resins are particularly useful in the manufacture of sanitary products, including disposable nappies for babies, sanitary towels and similar products. They are also useful in other applications, for example in agriculture, as soil conditioners or as water-retaining  
10 agents, and in civil engineering, as anti-condensation or dehydrating components in construction materials.

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compatibility with the other components of the sanitary  
15 product, low rewetting tendency, good mechanical strength of the water-swollen gel, which properties tend to depend on the chemical nature of the polymer, as well as upon having particle sizes of between 100 and 1,000 micrometres, with a narrow particle size distribution and in particular upon  
20 having as few small-sized particles as possible, which affect the handling and construction of the articles incorporating them. Also high rates of absorption, and good diffusion of liquids into, between and within the absorbent particles are characteristics that are related to the particle size and the  
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