

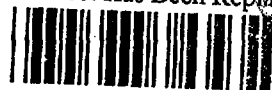
The present invention relates to polymers capable of absorbing large quantities of water or aqueous fluids, and, more specifically, to acrylic polymers produced by implementing processes involving polymerization in inverse suspensions.

At the present time, these materials are widely used in industry, in particular in the manufacture of sanitary products designed to absorb and retain body fluids.

The production of superabsorbent polyacrylate powders in inverse suspensions has been described in French Patent No. 2,367,083 (Kao Soap). It consists in polymerizing an acrylate in aqueous suspension preliminary placed in suspension in an aliphatic solvent through the use of an emulsifying agent having an HLB of between 3 and 6 and in the absence of a cross-linking agent. The performances of the polymer powders were then improved through the use of an emulsifying agent having an HLB of between 8 and 12 (EP 36463, Seitsu Kagaku Co., Ltd.). The most apparent difference in outcome between these two methods lies in the fact that they yield polymer powders, the first in the form of spheres, the second in the form of particles having more uneven shapes.

One major improvement entailed implementing the process in two stages, as described in European Patent No. EP 0441507: i.e., in a first step, by forming a gel by polymerization of an acrylic solution in inverse suspension, then by causing it to absorb a second monomer filler, which is polymerized within the gel itself as previously formed.

These methods do not make it possible to produce polymer

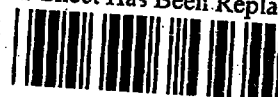


powders which properly fulfill the needs of certain major sectors of the industry, since the absorbent powders thus obtained have a excessively-long gelling time, or because, although they have an acceptable gelling time, this property is achieved at the expense of the other physical properties or of their extractible products content.

The present invention remedies these difficulties by means of a process for preparation of absorbent polymer powders having both a low gelling time, high capillary suction, high gel strength, and low extractibles content. The process according to the invention entails double polymerization (the expression "process entailing double polymerization" designates a process including a first step involving polymerization of a first monomer filler (filler I) in an aqueous solution placed in inverse suspension in an organic solvent using a surfactant whose HLB is high (HLB of between 8 and 12), and a second step during which the polymer gel obtained in the first step is made to absorb a second monomer filler (filler II), which is then polymerized within this gel).

The originality of the process according to the present invention lies in the combination of the following elements:

- presence of a crosslinking agent in the first polymerization filler,
- pronounced increase of the quantity of acrylic monomer filler absorbed by the gel during the second step of the process, and
- addition of a surfactant having a low HLB into the reaction



medium, effected very precisely after absorption of the second monomer filler and before the polymerization thereof.

The surfactant to be used in this case after absorption of the filler II and before the polymerization thereof must have an HLB of approximately 2 to 5. Esters of fatty acids and glycerol, sorbitol, or sucrose fulfill this characteristic. Sucrose di-tristearate is preferred.

In the double-polymerization processes according to prior art, the respective quantities of monomer, and more precisely, of acrylic monomer, used in the first and second steps, and which can be represented by the ratio "filler II/filler I", were restricted to an approximate value by weight of 1:2. It was impossible to go beyond this value, since caking of the reactor contents then occurred. According to the invention, this filler ratio of 1 to 1.2 and its use are possible, provided that a crosslinking agent is added to filler I. It is possible to use for this purpose a compound capable of crosslinking the polymers of α,β unsaturated carboxylic acids, or the derivatives thereof. These products are well known to the specialist, who will easily find long lists of them, for example in European Patent Application No. EP 0176664. Preferred crosslinking agents are bisacrylic derivatives, most notably N,N-methylenebisacrylamide and diglycidyl ether-type compounds, in particular ethylene glycol diglycidyl ether. The addition of a crosslinking agent of this kind to filler II is also advantageous.

In two-step polymerization processes involving inverse



suspension according to conventional prior art, it was necessary to effect absorption of filler II at low temperature. If this not done, the surface-active agent used during the first step to place the acrylic aqueous solution in inverse suspension remained functional and promoted placement of filler II in inverse suspension, to the detriment of its absorption by the previously-formed gel. This proved to be a major constraint impeding implementation of the process on an industrial scale. In this regard, the process according to the invention is much less sensitive. It is possible to work at temperatures approaching ambient temperature, and indeed temperatures as high as 40° C, as long as the surfactant to be used in the first step is judiciously selected. This is a considerable advantage for industrial-scale production, since, after the first polymerization, the contents of the reactor are normally at about 80° C, and the cooling process is lengthy. The production cycle is shortened considerably and, in consequence, productivity is significantly improved, since the product must be cooled only to 40° C, rather than to 20° C as in prior art.

The process is further improved by increasing the acrylic material content of the gel; i.e., by increasing the ratio of the aqueous phase to the organic phase during the first step. This increase cannot be effected according to prior art, since the inverse suspension produced during the first step shows signs of instability as soon as the aqueous phase/organic phase ratio reaches 0.4 to 0.6. It is found that, according to the invention



process, polymerization is more effectively controlled by virtue of the use of a crosslinking agent. Henceforth, it is possible to proceed using high aqueous phase/organic phase ratios ranging from 0.7 to 1.1.

By virtue of the new process described, it is possible to obtain superabsorbent polymers exhibiting a combination of unique properties:

- a gelling time of between 15 and 40 seconds,
- a gel strength of more than 2,800 Pascals,
- capillary suction under 2 kPa of more than 30 ml/g,
- capillary suction under 5 kPa of more than 20 ml/g,
- an absorption capacity exceeding 50/g,
- an extractibles percentage of less than 10%,
- a fines content of less than 10%, and
- retention greater than 28 g/g.

These are new products, which are also an object of the present invention. They can be used immediately in products such as those intended for feminine hygiene and adult incontinence.

Examples

In the following examples, distinction is made among the following sequences:

- a) preparation of the solvent phase,
- b) preparation of the aqueous monomer phase (filler I),
- c) placement in suspension of the monomer and polymerization I,
- d) preparation of the aqueous monomer phase (filler II),



- e) absorption of filler II and of polymerization II
- f) separation of the polymer.

Great value is placed on the properties of the superabsorbent powders thus produced using methods known to the specialist, which are briefly recapitulated below.

Saline solution-absorption capacity: 1 gram of superabsorbent powder is dispersed in 200 grams of a 0.9% sodium chloride solution and the mixture is stirred for two hours. The product is filtered on a slightly inclined (15°) sieve with 75 μ m mesh and is weighed after 30 minutes. If p is the weight of the swelled powder remaining on the filter, the absorption capacity is measured by p-1.

Gelling Time: In a 200 ml beaker (inner ϕ = 55 mm) equipped with a magnetic stirring apparatus rotating at 600 revolutions/minute, 100 ml of a 0.9% sodium chloride solution are added at a temperature of 20° C, followed quickly by 3 grams of superabsorbent powder. The time required for disappearance of the vortex formed in the liquid under the effect of stirring is measured. This time expressed in seconds is the gelling time.

Gel Strength: The method as practiced consists in placing 58 grams of a 0.9% aqueous sodium chloride solution in a beaker equipped with a magnetic stirring apparatus, adding 2 grams of superabsorbent powder, and continuing to stir until, as affected by the rheological change of its content, the surface of the beaker becomes horizontal following the disappearance of the vortex initially formed because of stirring. The modulus of elasticity of



the gel is then measured, here expressed in N/m^2 using a "neo-crud-meter," Model M-302, sold by the Electric Corporation of Japan.

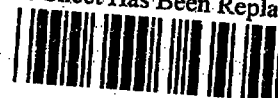
Pressurized Capillary Suction: The principle at work here is the absorption of a saline solution by a superabsorbent powder placed between two non-woven sheets and subjected through these sheets to a pressure of either 2 or 5 kPa. The experimental device and the operating procedure followed are described, for example, in French Patent No. FR 2602775.

Proportion of Extractibles: This measure is taken by absolute end point potentiometric quantitative analysis of the proportion of polyacrylic acid, sodium polyacrylate, and various monomers that can be extracted using synthetic urine consisting of an aqueous solution containing 15 grams of a 1% Triton^(R) x 100 solution (Rohm & Haas), 50 grams sodium chloride, 1.8 grams dihydrated calcium chloride, 3.6 grams hexahydrated magnesium chloride, and 6,000 milliliters distilled water. Return quantitative analysis is then performed in the solution obtained by maceration of 1.2 grams superabsorbent powder in 225 milliliters synthetic urine for 16 hours at ambient temperature and while stirring mechanically at 500 rotations/minute, then the product is filtered on a 50 μm -mesh sieve.

Example 1 (conforming to prior art according to EP 0441507).

Sequence a)

In a one-liter reactor equipped with a device for adding solid or liquid reagents, a stirring apparatus, a neutral gas current-



sweeping system, a temperature sensor, and a heating/cooling device, 0.97 gram sorbitan monolaurate (HLB = 8.6), sold by Nippon Oil and Fats Co. under the name LP20 R was dissolved in 385 grams heptane at 80° C while stirring at 800 rotations/minute and under a nitrogen current of 0.2 liter/minute. The mixture was cooled to 30° C.

Sequence b)

In a separately operation, 92 grams of an aqueous solution containing 80% by weight acrylic acid was neutralized with 152.6 grams 20.1% soda lye. 2.2 grams of an aqueous solution containing 5% potassium persulfate were added. This operation was carried out at a temperature of approximately 15° C.

Sequence c)

With the reactor continuing to be stirred at 800 rotations/minute and under a nitrogen current at the rate of 0.2 liter/minute, the previously-prepared aqueous phase was gradually added, this phase becoming an inverse suspension in heptane. The temperature was raised to 70° C to trigger polymerization. It was kept at that level for 30 minutes, before being reduced to 10° C.

Sequence d)

During the preceding operation, 46 grams of aqueous solution containing 80% by weight acrylic acid was separately neutralized using 76.3 grams 20.1% lye soda. 1.1 grams of an aqueous solution containing 5% potassium persulfate was then added. This aqueous phase forming monomer filler II was then prepared at a temperature of approximately 10° C.



Sequence e)

While continuing to stir at 800 rotations/minute and while maintaining the nitrogen current at the rate of 0.2 liter/minute, the filler II was added over about 15 minutes. Stirring was continued for 5 minutes, after which the temperature was raised to 70° to initiate the second polymerization phase. Polymerization was allowed to continue for 30 minutes.

Final sequence f)

The heptane and the largest part of the water were removed by distillation. 8.3 grams of an aqueous solution containing 2% ethylene glycol diglycidyl ether (compound sold under the name E100 by Nippon Oil and Fats Co.) were then added to the reactor contents and the mixture was dried.

In this way, 97.2 grams of a superabsorbent powder with particle size of less than 800 μm were obtained. The yield expressed in comparison to the acrylic acid was 72%.

Example 2 (comparative example)

Sequence a)

Identical to example 1.

Sequence b)

Identical to example 1.

Sequence c)

Identical to example 1.

Sequence d)

During the preceding operation, 92 grams of an aqueous solution containing 80% acrylic acid by weight were neutralized in



a separate operation using 139.4 grams 20.1 % soda lye; 5.5 grams of an aqueous solution containing 1% potassium persulfate were then added. As in the preceding example, preparation of this aqueous phase constituting the monomer filler II was then undertaken at a temperature of approximately 10° C.

Sequence e)

With stirring continuing in the reactor at 800 rotations/minute and under a nitrogen current at a rate of 0.2 liter/minute, the filler II was added over about 15 minutes, and stirring continued for five minutes. At that point, 7.36 grams of a 10% sucrose di/tristearate solution was then added. This solution is sold by Mutsubishi Chemical Food Ind. Co. under the name S370. Next, as in the preceding example, the temperature was raised to 70° C to initiate the second polymerization phase. Polymerization was allowed to continue for 30 minutes.

Final sequence f)

Identical to Example 1.

In this way, 129 grams of a superabsorbent powder were produced. Yield in relation to the acrylic acid was 71.3%.

The table below allows comparison of the results of the present test to those of the preceding one.



TEST	Example 1	Example 2
Absorption capacity (g/g)	57	56
Retention 30 (g/g)	27	26
Gelling time (s)	5	6
Gel strength (Pascals)	2700	2500
Extractibles (%)	15	17
Suction under 2 kPa (ml/g)	22	21
Suction under 5 kPa (ml/g)	17	17
Average diameter (μm)	237	240
< 100 μm (%)	18.7	16

Examples 3 and 4

The results obtained in Example 2 were improved by reducing appreciably the quantity of organic solvent in which filler 1 was placed in inverse suspension. It is possible to produce these conditions by adding a crosslinking agent to filler I. The sequences implemented were as follows:

Sequence a)

The same as in Example 2, but the speed of rotation of the stirrer was decreased to 500 rotations/minute, the quantity of n-heptane was only 264 grams, and the quantity of sorbitan monolaurate was 0.5 gram.

Sequence b)

Same as in Example 2, but, in addition, 0.92 gram of a 2% ethylene glycol diglycidyl ether (E100) was added.



Sequence c)

Same as in Example 2. However, at the end of the procedure the reactor temperature was 10° C for Example 3 and 40° C for Example 4.

Sequence d)

Same as in Example 2, except that filler II contained, in addition, 0.92 gram of a 2% ethylene glycol diglyceridyl ether solution (E100). Following the neutralization procedure, the temperatures were reduced to 10° C for Example 3 and 40° C for Example 4.

Sequence e)

This sequence was performed as in Example 2, including the addition of sucrose di/tristearate.

Final sequence f)

Identical to Example 2.

In this way, 155 grams of superabsorbent powder were obtained in Example 3, and 164.4 grams in Example 4, respectively, results corresponding to respective acrylic acid yields of 87% and 90.1%.

These results are shown in the table below and compared to the results in Example 1.



TEST	1	3	4
Temperature II ($^{\circ}$ C)	10	10	40
SAP (grams)			
- quantity obtained	97.2	155	164.4
- theoretical quantity	135.7	180.9	180.9
Absorption capacity (g/g)	57	56	57
Retention 30 (g/g)	27	30	30
Gelling time (s)	5	25	21
Gel strength (Pascals)	2700	2850	3000
Extractibles (%)	15	8	6.4
Suction under 2 kPa (ml/g)	22	32	37
Suction under 5 kPa (ml/g)	17	21	23
Average diameter (μ m)	237	255	220
Reaching < 100 μ m (%)	18.7	7.5	8.4

Example 5 (verification example)

The conditions used for Example 4 were repeated, with the basic difference that, during Sequence e, the addition of sucrose di/tristearate was omitted. As soon as polymerization was triggered by raising the temperature, the reactor contents congealed and the test had to be stopped.

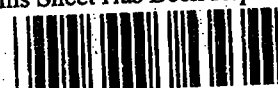
Example 6

Variant of Example, except that, in Sequence a, the speed of rotation was decreased to 300 rotations/minute and that the quantity of sorbitan monolaurate was 0.67 gram. The test procedure was quite comparable to that used in Example 4, as regards both the quality of absorbent powder and the yield, as shown by the figures



given below.

TEST	No. 4	No. 6
Quantity obtained	154.4	155.7
Yield (%)	91	86
Absorption capacity (g/g)	57	55
Retention 30 (g/g)	30	28
Gelling time (s)	21	28
Gel strength (Pascals)	3000	3000
Extractibles (%)	6.4	5.7
Suction under 2 kPa (ml/g)	37	36
Suction under 5 kPa (ml/g)	23	28
Average diameter (μm)	220	240
< 100 μm (%)	8.4	8.0



CLAIMS



1. In a procedure for producing a polyacrylic acid polymer in superabsorbent powder form for aqueous fluids, according to a process comprising a first step involving polymerization of a first monomer acrylic acid filler in an aqueous phase in inverse suspension in an organic solvent in the presence of an emulsifying agent having an HLB of between 8 and 12, then a second step involving polymerization of the polymer gel obtained in the first step, improvement consisting of:

- addition of a crosslinking agent in the first aqueous phase of the acrylic acid,

- use of a second acrylic acid filler in a ratio by weight of 1 to 1.2 in relation to the first acrylic acid filler, and

- addition to the reactive medium, after absorption of the second monomer filler and before triggering polymerization, of a surfactant having an HLB of between 2 and 5.

2. Process according to claim 1, wherein the emulsifying agent having an HLB of between 2 and 5 is sucrose di-tristearate.

3. Process according to claim 1, wherein the crosslinking agent is a bis acrylic derivative or a diglycidyl ether.

4. Process according to claim 3, wherein the crosslinking agent is N,N-methylenebisacrylamide.

5. Process according to claim 3, wherein the crosslinking agent is ethylene glycol diglycidyl ether.

6. Process according to any of claims 1 to 5, wherein, in the first step, during which a first monomer acrylic acid filler is





placed in aqueous phase in inverse suspension in an organic solvent, the ratio by weight of the aqueous phase to the organic phase ranges between 0.7 and 1.1.

7. Superabsorbent powder obtained by a process according to any of the preceding claims and possessing the following characteristics:

- a gelling time of between 15 and 40 seconds,
- a gel strength of more than 2,800 Pascals,
- capillary suction under 2 kPa of more than 30 ml/g,
- capillary suction under 5 kPa of more than 20 ml/g,
- an absorption capacity exceeding 50/g,
- an extractibles percentage of less than 10%,
- a fines content of less than 10%, and
- retention greater than 28 g/g.

