

DESCRIPTION

The present invention relates to the production of acrylic polymer powders capable of absorbing large quantities of water or of aqueous fluids.

It is known now to produce materials which possess a high water absorption capacity by solution or inverse suspension polymerisation of monomers possessing ethylenic unsaturation, more particularly of acrylic monomers. The powders which are thus obtained swell strongly in the presence of water, giving gels having high mechanical strength. These properties are utilised for, inter alia, the manufacture of sanitary articles for the absorption and retention of body fluids.

These products however contain not insignificant amounts of monomer. This is a serious disadvantage because these monomers are toxic or at least aggressive towards the mucous membranes and the skin. Various more or less satisfactory solutions have been proposed for reducing the residual monomer content of the hydrophilic acrylic monomers, namely: treatment with isopropanol (EP 0262380, Cassella), with hydroxylamine (U.S. 4929717, Stockhausen), with an amino acid such as lysine (U.S. 4766173, Nalco) or with azo compounds or peroxides (JP 1-0103644, Sanyo). Sanyo in particular teaches that the monomer content can be reduced to a level of 500 ppm either by introducing an



oxidation-reduction couple into the mass undergoing polymerisation, or by treating the polymer formed, but prior to its final drying, with 0.01 to 100 ppm of hydrogen peroxide relative to the polymer (expressed as dry weight), 0.01 ppm being a lower limit below which no significant effect on the residual monomer is observed any longer, and 100 ppm being an upper limit which cannot be exceeded without adversely affecting the absorption capacity of the final product.

10 An important improvement in the production of such absorbent powders is described in European Patent EP 0,441,507. It consists in carrying out the polymerisation of the acrylic monomer in at least two stages. In a first stage, an inverse suspension
15 polymerisation is carried out in a conventional manner, and this polymerisation leads to the formation of a gel. In a second stage, a new charge of monomer is caused to become absorbed on this gel and the polymerisation of this new charge is brought about
20 within the previously formed gel. This absorption/polymerisation sequence can, where necessary, be repeated. In this manner, one obtains polymeric resins which are valued because of their significantly larger particle size than that of the
25 resins obtained by simple inverse suspension polymerisation, their rate of swelling in the presence of water and the significantly improved modulus of elasticity, plasticity and resistance to deswelling



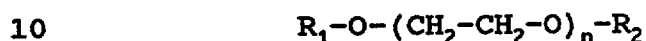
under pressure, of the gel which they form in the presence of water.

It has been found that provided this process comprises a final sequence of isolation of the polymer
5 comprising a first removal of water by azeotropic distillation and a subsequent drying, it is possible to reduce the residual monomer content of the finished product to a level which is as low as 50 ppm by introducing hydrogen peroxide between the azeotropic
10 distillation and the drying. A comparable result is not achieved if action is taken at a different stage of the process.

In processes for obtaining acrylic superabsorbents by two-stage polymerisation, nonionic
15 surfactants are generally used, such as the esters of fatty acids with sorbitan, with polyglycerol or with sucrose, or the polyoxyethylene-alkylphenyl ethers. However, it has been noted that it is industrially very advantageous to be able to carry out the absorption
20 phase of the multi-stage process without it being necessary to cool the reactor very greatly. Carrying out this absorption at temperatures of 35 to 45°C very significantly improves the economics of the process, but for this it is necessary to employ special
25 surfactants for the stage of the first polymerisation in inverse suspension. These are either surfactants of the polyethylene glycol/dodecyl glycol block copolymer type, formed from a polyethylene glycol chain provided



at one and/or the other of its ends with a plurality of hydrophobic chains consisting of dodecyl glycol radicals and especially polyethylene glycol/dodecyl glycol block copolymers, using which it is possible to carry out the absorption of the second charge of monomer, by the polymeric gel formed in the first place, at temperatures of the order of 35°C, or surfactants of a polymerisable type, corresponding to the general formula:



where R_1 is a hydrocarbon chain having at least 9 carbon atoms,

where R_2 is a polymerisable group, namely an acryloyl, methacryloyl or maleoyl radical,

15 and where the degree of condensation n in respect of ethylene oxide is between 30 and 70, these being surfactants by virtue of which the stage of adsorption of the second charge of monomer can be carried out at a temperature of 45°C. The maleic acid
20 monoester of nonylphenyl oxyethylenated with 50 molecules of ethylene oxide is a preferred surfactant of this type.

It has also been shown that in these multi-stage processes it is valuable to vary the
25 neutralisation of the aqueous phases of acrylic monomer and to use, for the phase to be polymerised in inverse suspension in the first place, a monomeric acrylic acid which is over-neutralised relative to the degree of



neutralisation envisaged for the final polymer, and for the phase to be polymerised after absorption by the gel thus formed, a monomeric acrylic acid which is under-neutralised. The product which results therefrom is a powder consisting no longer of smooth spheres but of spheroidal particles having an irregular surface, the shape of which is not dissimilar from that of truffles, of a high particle size of between 100 and 500 μm , with the proportion passing a 100 μm screen being very low, and in every case less than 0.5 % by weight, this being very helpful at the manufacturing level because the process directly produces large particles which are the only ones that can be used for the common applications, and because a post-agglomeration sequence becomes unnecessary. From the point of view of usage, the irregular geometry of the particles ensures better fixation in the fibrous medium and greater ease of use. These products are however not devoid of residual monomers and it is very valuable to apply to them the process of the invention, in order to bring the content to 50 ppm or less. The powders which thus result, and which consist of spheroidal particles, having an irregular surface, of polyacrylic acid neutralised to a degree of between 65 and 95 % and having a mean diameter of between 100 and 500 μm , with less than 0.5 % passing through a 100 μm screen, and a residual monomer content which is at most equal to 50 ppm, are novel and form part of the invention.



The useful amounts of hydrogen peroxide are between 0.08 and 0.19 % relative to the dry polymer. The hydrogen peroxide is introduced after dilution preferably to hydrogen peroxide strength 1 to 20% into the reactor after having carried out the azeotropic dehydration and before the final drying of the polymer. The examples which follow will permit a better understanding of the invention.

EXAMPLES

- 10 In the examples which follow, one distinguishes the following sequences:
- a) separation of the solvent phase,
 - b) preparation of the aqueous monomer phase (charge I),
 - 15 c) bringing the monomer into suspension, and polymerisation I,
 - d) preparation of the aqueous monomer phase (charge II),
 - e) absorption of charge II and polymerisation
 - 20 II and
 - f) isolation of the polymer.

Example 1 (prior art)

The example corresponds to obtaining polyacrylic acid neutralised to the extent of 75 %, in accordance with the ordinary process of inverse suspension polymerisation; accordingly it comprises neither sequence d nor sequence e.

Sequence a: in a one-litre reactor equipped



with a device for introducing solid or liquid reactants, a propeller stirrer or anchor stirrer, a temperature probe, a system for flushing with neutral gas and a heating and cooling device, 1,38 g of
5 polyethylene modified with maleic anhydride, a product marketed by Mitsui Petrochemical Industries Co under the name Hi-Wax 1105A, and 0.92 g of sucrose distearate/tristearate are dissolved in 376 g of heptane at about 80°C, with stirring at 325 rpm.

10 Sequence b: separately, 92 g of an 80 % by weight aqueous solution of acrylic acid are neutralised, whilst keeping the temperature below 30°C, with 141.6 g of 21.66 % strength sodium hydroxide solution. 0.276 g of hydroxyethylcellulose is added,
15 followed by 11 g of a 0.95 % aqueous solution of potassium persulphate.

Sequence c: whilst continuing to stir the reactor at 400 rpm and flushing it with nitrogen at the rate of 80 litres/minute, the previously prepared
20 aqueous phase is introduced a little at a time, and passes into inverse suspension in the heptane. The temperature is raised to 70°C to bring about the polymerisation and is kept at this level for about 30 minutes. The temperature is then brought to 20°C.

25 Final sequence f: first of all, the agglomeration of the polymer particles is brought about by adding 0.55 g of colloidal silica (Tokusil P) diluted in 45 g of heptane. The temperature is brought



to 60°-70°C, with stirring at 1500 rpm. Thereafter, the heptane and the greater part of the water are removed by distillation. 9.2 g of a 2 % aqueous solution of ethylene glycol diglycidyl ether are then added to the contents of the reactor and the drying is continued.

The powder which is thus obtained has 2 % passing through a 100 μ m screen, and has an unacceptable acrylic monomer content of 100 ppm, due to the modest amounts of potassium persulphate used in sequence b.

Example 2 (prior art)

The example corresponds to obtaining a polyacrylate, neutralised to the extent of 75 %, in accordance with the two-stage process, namely a first polymerisation in inverse suspension, absorption and a second polymerisation in the gel.

Sequence a: in the apparatus described in Example 1, 0.92 g of Hi-Wax 1105A modified polyethylene and 0.736 g of sucrose distearate/tristearate are dissolved in 376 g of heptane at 80°C, while stirring at 400 rpm.

Sequence b: separately, 92 g of an 80 % by weight aqueous solution of acrylic acid are neutralised with 176.8 g of 17.35 % sodium hydroxide solution. 0.276 g of hydroxyethylcellulose is added, followed by 5.5 g of a 1 % strength aqueous solution of potassium persulphate and 0.92 g of a 2 % strength aqueous solution of ethylene glycol diglycidyl ether. This



aqueous phase is brought to 38°C.

Sequence c: whilst continuing to stir the reactor at 400 rpm and flushing it with nitrogen at the rate of 80 litres/minute, the previously prepared aqueous phase is introduced a little at a time, and passes into inverse suspension in the heptane. The temperature is raised to 70°C to bring about the polymerisation and is kept at this level for about 30 minutes. The temperature is then brought to 20°C.

Sequence d: while the preceding operation is taking place, 92 g of an 80 % by weight aqueous solution of acrylic acid are separately neutralised with 176.8 g of 17.35 % strength sodium hydroxide solution, after which 5.5 g of a 1 % strength aqueous potassium persulphate solution and 0.92 g of a 2 % strength aqueous ethylene glycol diglycidyl ether solution are added. This aqueous phase, which constitutes monomer charge II, is then brought to 20°C.

Sequence e: stirring in the reactor is brought to 800 rpm, whilst continuing the flushing with nitrogen at 80 litres/minute. Charge II is introduced a little at a time, after which the temperature is raised to 70°C to bring about the second polymerisation phase. The polymerisation is allowed to continue for about 30 minutes.

Final sequence f: first of all, the agglomeration of the polymer particles is brought about by adding 0.55 g of colloidal silica (Tokusil P)



diluted in 45 g of heptane. The temperature is brought to 60°C-70°C, with stirring at 1500 rpm. Thereafter the heptane and a greater part of the water are removed by distillation. 9.2 g of a 2 % aqueous ethylene glycol diglycidyl ether solution are added to the contents of the reactor and the drying is continued.

The powder which is obtained contains 1 % passing through a 100 μ m screen and has a high free monomer content of 414 ppm.

10 Example 3

This is a comparative example which only differs from Example 2 in that during the sequence d of preparation of the second aqueous charge of acrylic monomer 5.5 g of 1 % strength hydrogen peroxide are introduced at the same time as the potassium persulphate and the ethylene glycol diglycidyl ether.

The powder thus obtained has 1 % passing through a 100 μ m screen and its free acrylic monomer content has remained very high (490 ppm).

20 Example 4

This example according to the invention only differs from Example 2 in that, between the dehydration stage and the drying stage of sequence f, 0.552 g of 20 % strength hydrogen peroxide are introduced at the same time as the 9.2 g of 2 % strength ethylene glycol diglycidyl ether.

This gives a powder of which about 1 % passes through a 100 μ m screen and in which the free acrylic



monomer content has now dropped to 30 ppm.

Example 5

Here, the advantages of a process for obtaining a polyacrylic superabsorbent by inverse suspension polymerisation, absorption and polymerisation in the gel, in which the absorption of the second monomer charge has been carried out at 35°C, have been combined with the introduction of hydrogen peroxide between the polymer dehydration stage and the polymer drying.

Sequence a: in the apparatus described in Example 1, 0.92 g of Hi-Wax 1105A modified polyethylene is dissolved in 265.6 g of heptane at 80°C, while stirring at 400 rpm.

Sequence b: separately, 92 g of an 80 % by weight aqueous solution of acrylic acid are neutralised with 139.4 g of a 22 % strength sodium hydroxide solution. 0.276 g of hydroxyethylcellulose is added, followed by 5.5 g of a 1 % strength aqueous solution of potassium persulphate, 0.92 g of a 2 % aqueous solution of ethylene glycol diglycidyl ether and 0.18 g of a maleate ester of nonylphenol containing 50 mol of ethylene oxide (Aerosol MEM-NP 50 from Cyanamid). It should be noted that this emulsifier is introduced into the system in solution in the aqueous charge, which is rather unusual if it is desired to bring about the formation of an inverse suspension.

Sequence c: while continuing to stir the



reactor at 400 rpm and flushing it with nitrogen at a rate of 80 litres/minute, the previously prepared aqueous phase is introduced a little at a time, and passes into inverse suspension in the heptane. The temperature is raised to 70°C to bring about the polymerisation and is kept at this level for about 30 minutes. The temperature is then brought to 15°C.

Sequence d: while the preceding operation is taking place, 92 g of an 80 % by weight aqueous solution of acrylic acid are separately neutralised with 139.4 g of a 22 % strength sodium hydroxide solution, after which 5.5 g of a 1 % strength aqueous potassium persulphate solution and 0.92 g of a 2 % strength aqueous ethylene glycol diglycidyl ether solution are added. This aqueous phase, which constitutes monomer charge II, is then brought to 15°C.

Sequence e: the stirring in the reactor is increased to 800 rpm whilst continuing the flushing with nitrogen at 80 litres/minute. Charge II is introduced a little at a time, after which the temperature is raised to 70°C to bring about the second polymerisation phase. The polymerisation is allowed to proceed for about 30 minutes.

Final sequence f: a solution prepared from 1.84 g of a 2 % strength aqueous solution of ethylene glycol diglycidyl ether and 0.552 g of 20 % strength hydrogen peroxide is added to the contents of the reactor, after which the drying of the product is



carried out.

1 % of the powder thus obtained passes through a 100 μ m screen. The residual monomer content of the powder is 41 ppm.

5 Example 6

This example gathers together the advantage of the combination of an over-neutralisation of the first monomer charge and an under-neutralisation of the second charge, the use of a surfactant of the block
10 polymer type which permits carrying out the absorption of the second monomer charge by means of the gel formed during the first polymerisation at a relatively high temperature of 35°C, and the reduction in the residual monomer content according to the invention.

15 Sequence a: using the apparatus of Example 1, 0.92 g of Hi-Wax 1105A modified polyethylene and 0.46 g of a polyethylene glycol/dodecyl glycol block copolymer, namely Dapral E348 from AKZO (the molecule having about three dodecyl glycol radicals at one end
20 of a methoxypolyethylene glycol chain for about 22 ethylene glycol chain members) are dissolved in 285.1 g of heptane at 80°C, while stirring at 400 rpm.

Sequence b: separately, 92 g of an 80 % by weight aqueous solution of acrylic acid are neutralised
25 with 160.65 g of a 24.17 % strength sodium hydroxide solution. 0.276 of hydroxyethylcellulose is added,



followed by 2.75 g of a 2 % strength aqueous solution of potassium persulphate and 0.92 g of a 2 % strength aqueous solution of ethylene glycol diglycidyl ether.

Sequence c: whilst continuing to stir the
5 reactor at 400 rpm and flushing it with nitrogen at the rate of 80 litres/minute, the previously prepared aqueous phase is introduced a little at a time and passes into inverse suspension in the heptane. The temperature is raised to 70°C to bring about the
10 polymerisation and is kept at this level for about 30 minutes. The temperature is then brought to 42°C.

Sequence d: whilst the preceding operation is taking place, 92 g of an 80 % by weight aqueous solution of acrylic acid are separately neutralised
15 with 135.75 g of 16.6 % strength sodium hydroxide solution after which 2.75 g of a 2 % strength aqueous solution of potassium persulphate and 0.92 g of a 2 % strength aqueous solution of ethylene glycol diglycidyl ether are added. This aqueous phase, which constitutes
20 monomer charge II, is then brought to 15°C. The stirring in the reactor is increased to 800 rpm, whilst continuing the flushing with nitrogen at 80 litres per minute. Charge II is introduced a little at a time, after which the temperature is raised to 70°C to bring
25 about the second polymerisation phase. The polymerisation is allowed to proceed for about 30 minutes.

Sequence f: after the azeotropic dehydration,



0.92 g of a 2 % strength aqueous solution of ethylene glycol diglycidyl ether and 0.552 g of 20 % strength hydrogen peroxide are introduced into the reactor after which the drying of the product is carried out.

- 5 The powder which is thus obtained consists of spheroidal particles having an irregular surface, with virtually no material passing through a 100 μm screen; the free monomer content of the powder is 45 ppm.



CLAIMS

1. Process for the production of powders which are superabsorbent for water and aqueous liquids and consist of partially neutralised polyacrylic acid having a very low free monomer content, which process comprises at least the following sequences:
- a) preparation of the solvent phase,
 - b) preparation of the aqueous phase of acrylic acid monomer (charge I),
 - 10 c) bringing the monomer into inverse suspension, and polymerisation I,
 - d) preparation of the aqueous phase of acrylic acid monomer (charge II),
 - e) absorption of charge II and polymerisation
 - 15 II and
 - f) isolation of the polymer,
- characterised in that the sequence of isolation of the polymer comprises at least one azeotropic dehydration operation and one drying operation and that hydrogen peroxide is introduced onto or into the polymer between the said dehydration and drying operations.
- 20
2. Process for the production of superabsorbent powders according to Claim 1, characterised in that charge I of monomeric acrylic acid is neutralised to a degree greater than that of the final polyacrylic polymer, whilst charge II of monomeric acrylic acid is neutralised to a lower degree.
- 25



3. Process according to Claim 2, characterised
in that the charges of monomeric acrylic acid in phases
b and d are prepared in equal amounts, that the degree
of neutralisation of charge I is between 90 and 100 %
5 and that the degree of neutralisation of charge II is
between 60 and 50 %.

4. Process according to one or other of Claims 1
to 3, characterised in that the monomeric acrylic acid
of the first charge is brought into inverse suspension
10 with the aid of surfactants of the block copolymer
type, which result from the reaction of epoxyalkanes
with polyalkylene glycols or with their monoesters.

5. Process according to Claim 4, characterised
in that the surfactant is a polyethylene glycol/dodecyl
15 glycol block copolymer.

6. Process according to Claim 4 or 5,
characterised in that the absorption of the second
monomer charge is carried out at a temperature of about
35°C.

20 7. Process according to one or other of Claims 1
to 3, characterised in that the monomeric acrylic acid
of charge I is brought into inverse suspension with the
aid of a polymerisable emulsifier corresponding to the
general formula:



where R_1 is a hydrocarbon chain having at least 9 carbon
atoms,

where R_2 is a polymerisable group, namely an acryloyl,



methacryloyl or maleoyl radical and
where the degree of condensation n in respect of
ethylene oxide is between 30 and 70.

8. Process according to Claim 7, characterised
5 in that the surfactant is the maleic acid ester of
nonylphenol oxyethylenated with 50 molecules of
ethylene oxide, and that it is dissolved in the aqueous
phase.

9. Process according to Claim 6 or 7,
10 characterised in that the absorption of the second
monomer charge is carried out at a temperature greater
than or equal to 45°C.

10. Polyacrylic acid powder neutralised to a
degree of between 65 and 85 %, having a mean diameter
15 of between 100 and 500 μm , and with less than 0.5 %
passing through a 100 μm screen, characterised in that
it consists of spheroidal particles having an irregular
surface and that its residual monomer content is at
most 50 ppm.