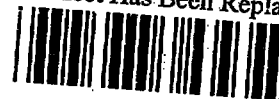


DESCRIPTION

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 to produce materials endowed with a high capacity for water absorption by inverse suspension polymerisation of monomers containing ethylenic unsaturation, more particularly of acrylic monomers. The powders which are thus obtained swell strongly in the presence of water, giving gels of high mechanical strength. These properties are exploited, inter alia, for the manufacture of sanitary articles for absorption and retention of body fluids.

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 polymerisation is carried out in conventional manner, this polymerisation resulting in the formation of a gel. In a second stage a new monomer charge is absorbed in this gel and its polymerisation is induced within the actual gel formed previously. If appropriate, this absorption/polymerisation sequence can be repeated. In this way polymeric resins are obtained with a particle



size which is appreciably larger than the resins from single inverse suspension polymerisation. Their rate of swelling in the presence of water, the elastic modulus, the plasticity and the resistance to collapse under
5 pressure of the gel formed are also appreciably improved.

The absorbent qualities of the final polymer depend on the degree of neutralisation of the monomeric acrylic acid and it is now well known that for the
10 hygiene application the optimum degree of neutralisation must be near 75 %, in particular bearing in mind the necessary compatibility of the superabsorbent with the skin. Thus, in the multistage process a first inverse suspension polymerisation of a
15 first aqueous charge of 75% neutralised acrylic acid is induced, and subsequent charges of aqueous acrylic acid, also 75% neutralised are absorbed by the gel thus formed.

It has now just been found that it is not
20 inconsequential to use monomer solutions with different degrees of neutralisation, provided that the overall degree of neutralisation of the final polymer is obeyed. In particular, it has appeared extremely advantageous to form a superabsorbent polymer 75%
25 neutralised overall using the two-stage process, using the combination of two neutralised monomer charges, in the case of the first to a degree of between 90 and 100 %, in the case of the second to a degree of between



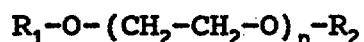
60 and 50 %. The result of this particular operating procedure is unexpected: on the one hand, the polymer particles obtained at the end of the operation are no longer spherical (Figure 1) but lumpy spheroidal ones, of shapes which sometimes resemble those of truffles (Figure 2), and, on the other hand, their size, which is between approximately 100 and 500 μm , is substantially larger than that reached with conventional processes, with greatly reduced proportions of undersize at 100 μm . It is very valuable to produce directly the large particles which are the only ones that can be employed for the common applications, since this saves on a postagglomeration sequence. According to the prior art it was known to make particles of this size, but at the cost of a decrease in the monomer charge; this has an effect on the yield of the operation, and the particles which are thus obtained are excessively polydisperse. The process according to the invention now permits an economical access to large particles, in addition to a narrower particle size distribution. There is also an appreciable advantage in use, the nonuniform geometry of the particles providing them with better binding into the fibrous medium and hence greater ease of processing.

The surfactants which can be employed in the invention are the surfactants of the prior art, in particular the nonionic surfactants such as the fatty

acid esters of sorbitan, of polyglycerine and of sucrose, or polyoxyethylene alkylphenyl ethers.

However, it is also highly advantageous to produce the inverse suspension of the first monomer charge by using surfactants of polyethylene glycol/dodecyl glycol block copolymer type which are formed by a polyethylene glycol chain provided at either or both of their ends with a number of hydrophobic chains consisting of dodecyl glycol residues. The absorption of the second monomer charge by the polymer gel formed in the first place can then be proceeded with without any need to cool the reactor intensely and this absorption stage can be performed at temperatures which are not lower than 35°C, thereby very appreciably improving the profitability of the process.

It is also possible to employ surfactants of polymerisable type corresponding to the general formula



where R_1 is a hydrocarbon chain containing at least 9 carbon atoms,
where R_2 is a polymerisable group or acryloyl, methacryloyl or maleoyl residue,
and where the degree of condensation n of ethylene oxide is between 30 and 70. With such surfactants the stage of absorption of the second monomer charge may be performed at a temperature of 45°C. The maleic monoester of nonylphenol oxyethylenated with 50 molecules of ethylene oxide is a preferred surfactant



of this type.

EXAMPLES

The sequences which are distinguished in the examples which follow are:

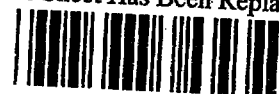
- 5 a) of preparation of the solvent phase,
- b) of preparation of the monomer aqueous phase
 (charge I)
- c) of placing the monomer in suspension and
polymerisation I,
- 10 d) of preparation of the monomer aqueous phase
 (charge II),
- e) of absorption of the charge II and polymerisation
 II,
- f) of isolation of the polymer.

15 Example 1 (prior art)

The example corresponds to the two-stage preparation of a 75% neutralised polyacrylate by successive use of acrylic acid solutions, both 75% neutralised.

20 Sequence a.

- 0.92 g of polyethylene modified with maleic anhydride, a product marketed by Mitsui Petrochemical Industries Co under the name of Hi-Wax 1105A, and which will be used as protective colloid, and 0.736 g of
- 25 sucrose di/tristearate are dissolved in 376 g of heptane at 80°C and with stirring at 400 revolutions/minute in a one-litre reactor fitted with a



device for introducing solid or liquid reactants, a stirrer, a system for purging with neutral gas, a temperature probe and a heating/refrigerating device. The mixture is brought back to 38°C.

5 Sequence b.

Separately, 92 g of an aqueous solution containing 80 % by weight of acrylic acid are neutralised with 176.8 g of 17.35% soda lye. 0.276 g of hydroxyethyl cellulose are added, followed by 5.5 g of
10 an aqueous solution containing 1 % of potassium persulphate, and 0.92 g of an aqueous solution containing 2 % of ethylene glycol diglycidyl ether. This operation is conducted at a temperature of approximately 15°C.

15 Sequence c.

With the reactor being stirred at 400 revolutions/minute and with nitrogen purging at a rate of 80 litres/minute, the aqueous phase prepared previously, which changes into inverse suspension in
20 heptane, is introduced therein little by little. The temperature is raised to 70°C to induce polymerisation; it is maintained at this value for 30 minutes. The temperature is then returned to 20°C.

Sequence d.

25 While the above operation takes place, 92 g of aqueous solution containing 80 % by weight of acrylic acid are separately neutralised with 176.8 g of 17.35% soda lye, followed by the addition of 5.5 g of



an aqueous solution containing 1 % of potassium persulphate and of 0.92 g of an aqueous solution containing 2 % of ethylene glycol diglycidyl ether. The preparation of this aqueous phase, which constitutes the monomer charge II, was performed at a temperature of approximately 15°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 therein little by little, after which the temperature is raised to 70°C to initiate the second stage of polymerisation. The polymerisation is left to proceed for half an hour.

Final sequence f.

The heptane and most of the water are removed by distillation. 9.2 g of an aqueous solution containing 2 % of ethylene glycol diglycidyl ether are then added to the content of the reactor and drying is continued.

A powder consisting of spherical particles (Figure 1) the undersize of which at 100 μm reaches 1 % is thus obtained; a photomicrograph of it is given in Figure 1.

Example 2

In this example, in accordance with the invention, a polyacrylate with a degree of



neutralisation of 75% is produced by using a first solution of 100% neutralised acrylic acid, followed by absorption/polymerisation of a second solution, 50% neutralised.

5 Example 1 is reproduced, the only difference being that in sequence b the 92 g of 80% polyacrylic acid are neutralised with 176.8 g of 23.13% soda lye and that in sequence d the 92 g of 80% polyacrylic acid are neutralised with 177.7 g of 11.56% soda lye.

10 A powder made up of nonuniform spheroids (Figure 2) is thus obtained with a narrow particle size distribution whose undersize at 100 μ m is practically zero; a photomicrograph of it is given in Figure 2.

Example 3

15 In this example the advantage of the combination of an overneutralisation of the first monomer charge and of an underneutralisation of the second charge is combined with the use of a polyethylene glycol/dodecyl glycol block copolymer,
20 Dapral E348, marketed by AKZO (molecule containing approximately three dodecyl glycol residues with one end of a methoxypolyethylene glycol chain containing approximately 22 ethylene glycol chain units), by virtue of which the absorption of the second monomer
25 charge by the gel formed during the first polymerisation can be carried out at the relatively high temperature of 35°C.



The essential differences in the operating procedure when compared with Example 1 are indicated below.

Sequence a.

- 5 The organic phase consists of 285.1 g of heptane, of 0.92 g of polyethylene modified with maleic anhydride, a product marketed by Mitsui Petrochemical Industries Co under the name of Hi-Wax 1105A and of 0.46 g of Dapral E348.

10 Sequence b.

- Charge I here consists of 92 g of aqueous solution containing 80 % by weight of acrylic acid, 160.65 g of 24.17% soda lye, 2.75 g of an aqueous solution containing 2 % of potassium persulphate and
15 0.92 % of an aqueous solution containing 2 % of ethylene glycol diglycidyl ether.

Sequence c.

 After polymerisation the temperature of the content of the reactor is returned to 36°C.

20 Sequence d.

- Charge II here consists of 92 g of an aqueous solution containing 80 % by weight of acrylic acid, 135.75 g of 16.6% soda lye, 2.75 g of an aqueous solution containing 2 % of potassium persulphate and
25 0.92 g of an aqueous solution containing 2 % of ethylene glycol diglycidyl ether, returned to a temperature of 15°C before use in the next sequence.

 A powder is thus obtained, consisting of



spheroids with a nonuniform surface without appreciable
undersize at 100 μm , by a process the profitability of
which is very appreciably improved in comparison with
those of the prior art which require an energetic
5 cooling of the reactor in order to tackle sequence d.



CLAIMS

1. Process for the production of superabsorbent powders for water and aqueous liquids consisting of partially neutralised polyacrylic acid, process comprising the sequences
- a) of preparation of the solvent phase,
 - b) of preparation of the monomeric acrylic acid aqueous phase (charge I),
 - c) of placing the monomer in inverse suspension and polymerisation I,
 - d) of preparation of the monomeric acrylic acid aqueous phase (charge II),
 - e) of absorption of charge II and polymerisation II,
 - f) of isolation of the polymer,
- characterised in that the monomeric acrylic acid charge I is neutralised to a degree higher than that of the final polyacrylic acid and that the monomeric acrylic acid charge II is neutralised to a lower degree.
2. Process according to Claim 1, characterised in that the charges of monomeric acrylic acid in stages b and d are prepared in equal quantities, that the degree of neutralisation of charge I is between 90 and 100 % and that that of charge II is between 60 and 50 %.
3. Process according to Claim 2, characterised in that the degree of neutralisation of the final polyacrylic acid is taken close to 75 %.
4. Process according to one or other of





Claims 1 to 3, characterised in that the acrylic acid monomer of the first charge is placed in inverse suspension with the aid of block polymer surfactants of the polyethylene glycol/dodecyl glycol copolymer type.

5 5. Process according to Claim 4, characterised in that the block copolymer is a molecule containing approximately three dodecyl glycol residues with one end of a methoxypolyethylene glycol chain containing approximately 22 ethylene glycol chain
10 units.

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

15 7. Process according to one or other of Claims 1 to 3, characterised in that the acrylic acid monomer of the charge is placed in inverse suspension with the aid of a polymerisable surfactant corresponding to the general formula



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

where R_2 is a polymerisable group or acryloyl, methacryloyl or maleoyl residue,

25 and where the degree of condensation n of ethylene oxide is between 30 and 70.

8. Process according to Claim 7, characterised in that the polymerisable surfactant is





the maleic ester of nonylphenol oxyethylenated with 50 molecules of ethylene oxide and in that it is dissolved in the organic solvent phase.

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

10. Polyacrylic acid powder neutralised to a degree of between 65 and 85 %, with a mean diameter of
10 between 100 and 500 μm , and practically free from undersize at 100 μm , characterised in that it consists of spheroidal particles with a nonuniform surface.

