

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 which possess a high water absorption capacity by 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, inter alia, for the manufacture of sanitary articles for the 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 a conventional manner in a hydrocarbon solvent, and this polymerisation leads to the formation of a gel. In a second stage, a new charge of monomer is caused to become absorbed into this gel and the polymerisation of this new charge is brought about within the previously formed gel. This absorption/polymerisation sequence can, where necessary, be repeated. In this manner, polymeric



resins of significantly larger particle size than the resins from simple inverse suspension polymerisation are obtained. Their rate of swelling in the presence of water, the elastic modulus, the plasticity and the resistance of the gel formed to deswelling under pressure are also significantly improved.

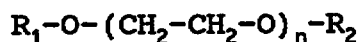
However, to achieve this result, it is necessary to ensure that the second charge of monomer does indeed polymerise within the first gel formed and does not polymerise afresh in the form of an inverse suspension in the hydrocarbon phase. It is thus necessary to render the surfactant, which is always present in the reactor after the first polymerisation stage, incapable of dispersing the second charge of monomer. This is the reason why, according to the prior art, it is necessary to cool the mass resulting from the first polymerisation before introducing the second charge of monomer. This cooling stage, which is an essential characteristic of the process, is also extremely restrictive on an industrial scale because it considerably lengthens the manufacturing time and adversely affects the economics of the process.

The present invention constitutes an important improvement in the processes for obtaining absorbent powders by two-stage radical polymerisation in inverse suspension, in which the absorption of the second charge of monomer takes place at a temperature equal to or greater than 45°C. and which consists in



effecting the bringing into inverse suspension of the first charge of monomer with the aid of certain surfactants which are also polymerisable by radical polymerisation and which disappear from the medium, as
5 suspending agents, during the first stage of polymerisation.

The choice of suitable surfactants of this type is an extremely delicate matter, especially as regards the result of the first polymerisation, and the
10 invention resides in the use of compounds corresponding to the general formula:



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

15 where R_2 is acryloyl, methacryloyl or maleoyl, and where the degree of condensation n of ethylene oxide is between 30 and 70.

Amongst the particularly valuable products belonging to this family of polymerisable surfactants,
20 there may be mentioned the maleic acid monoester of nonylphenol oxyethylenated with 50 molecules of ethylene oxide, the acrylic acid monoester of nonylphenol oxyethylenated with 45 molecules of ethylene oxide and the methacrylic acid monoester of
25 nonylphenol oxyethylenated with 50 molecules of ethylene oxide.

In general, the two-stage inverse suspension polymerisation processes according to the invention

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comprise the following sequences, which are detailed in the examples:

a) preparation of the hydrocarbon solvent phase,

5 b) preparation of the aqueous monomer phase (charge I),

c) bringing the monomer into suspension, and polymerisation I,

d) preparation of the aqueous monomer phase
10 (charge II),

e) absorption of the charge II and polymerisation II,

f) isolation of the polymer.

What is involved is an operating process
15 which in its essentials is at the present time well known to a man skilled in the art and which is concerned with obtaining polymers of water-soluble unsaturated monomers such as acrylic acid, methacrylic acid and their nonionic derivatives such as acrylamide, 20 methacrylamide and their N,N-dimethyl-substituted derivatives, 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate; N-methylol-acrylamide or N-methylol-methacrylamide, or their nitrogen-containing derivatives such as (dimethyl or diethyl)amino(ethyl or 25 propyl) acrylate or methacrylate and the corresponding quaternary ammonium salts. Acrylic acid is the preferred unsaturated monomer. The polymerisation is initiated by radical polymerisation initiators, which



are preferably water-soluble because both the monomer and the polymer are themselves hydrophilic; potassium persulphate is particularly suitable for the present case. The various auxiliaries used to obtain

5 hydrophilic polymers by suspension polymerisation are also well known to a man skilled in the art, and these include the protective colloids which accompany the emulsifiers as an accessory for physically stabilising the reactants brought into suspension, for example
10 modified celluloses, polyethylenes or their copolymers which have been oxidised or modified with maleic anhydride; they also include crosslinking agents for the partial crosslinking of the hydrophilic polymers produced, these crosslinking agents consisting of
15 compounds which possess at least two unsaturated groups which are copolymerisable with the unsaturated monomer (acrylic acid), typical examples being diacrylates and triacrylates of polyols, or capable of reacting with
20 its polymerisation products, such as the diglycidyl ethers of diols. It is also known that it is possible to use, as the solvent for bringing into inverse suspension, various aliphatic, cycloaliphatic or aromatic hydrocarbon solvents, the solvent preferred for the purpose being heptane.

25 According to the invention, the polymerisable surfactant is introduced during sequence b, and since it disappears from the reaction medium at the end of sequence c, there is no need to carry out more than



modest cooling of the reactor, to a temperature equal to or greater than 45°C, so that sequence e), namely the absorption of the monomer, takes place at a temperature which is not excessive but which however
5 does not have to be below 35°C.

It is not impossible that after carrying out this absorption sequence the suspension may appear to lack stability. This is remedied, where necessary, by adding a dispersant to the composition, this dispersant
10 not being subject to any special restriction. In particular, it is possible to use, as a complementary emulsifier, the known emulsifiers of the prior art, to the extent that the sequences d to f are not repeated.

Carrying out the process has the effect of an
15 unexpected and very substantial gain in productivity, the extent of which becomes apparent when considering that whilst bringing the absorption temperature of the second charge from 18°C to 35°C, an operation which involves cooling the reactor, after the first
20 polymerisation, to only 45°C, in the laboratory results in only an apparently negligible gain in time, the increase in productivity on an industrial scale is, in contrast, about 30 %.

The examples which follow will permit a
25 better understanding of the invention and specify the conditions thereof.

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EXAMPLE 1**Sequence a**

In a one litre reactor equipped with a device for introducing solid or liquid reactants, a stirrer, a
5 system for flushing with neutral gas, a temperature probe and a heating and cooling device, there are introduced 265.6 g of heptane which are heated to 80°C, and in which there are dissolved, with stirring at
10 400 rpm, 0.92 g of a polyethylene modified with maleic anhydride, this being a product which is marketed by MITSUI PETROCHEMICAL INDUSTRIES Co. under the name of HI-Wax 1105A and which serves as a protective colloid.

Sequence b

Separately, 92 g of an 80 % by weight aqueous
15 solution of acrylic acid are neutralised with 139.4 g of 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 % strength aqueous solution of ethylene
20 glycol diglycidyl ether and 0.46 g of maleic acid ester of nonylphenol containing 50 moles of ethylene oxide (Aerosol MEM-NP 50 of Cyanamid). It should be noted that this emulsifier is introduced into the aqueous
charge, which is rather unusual when it is desired to
25 bring about the formation of an inverse suspension.

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; it is
5 kept at this level for 30 minutes. The temperature is then brought back to 45°C.

Sequence d

Whilst the preceding operation is taking place, 92 g of an 80 % by weight aqueous solution of
10 acrylic acid are separately neutralised with 139.4 g of a 20 % 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
15 phase, which constitutes monomer charge II, is then brought to 10°C.

Sequence e

The stirring in the reactor is increased to 800 rpm whilst continuing the flushing with nitrogen at
20 80 litres/minute. The charge II is introduced a little at a time. After the charge II has been introduced, the absorption is allowed to continue for 5 minutes at a temperature set at around 35°C. After this the temperature is raised to 70°C to bring about the second
25 polymerisation phase. The polymerisation is allowed to proceed for 30 minutes.

Final sequence f

The heptane and the greater part of the water

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are removed by distillation. After this, 1.84 g of a 2 % strength aqueous solution of ethylene glycol diglycidyl ether are added to the contents of the reactor and the product is dried under nitrogen.

5 A powder having a mean particle size of 370 μm , with no material passing through a 100 μm screen, is thus obtained. This result is not significantly different if the absorption sequence is carried out at 50°C.

10 EXAMPLE 2 (COMPARATIVE EXAMPLE)

The operations of Example 1 are repeated except that in sequence b, instead of 0.46 g of Aerosol MEM-NP 50, 0.46 g of the acrylic acid monoester of nonylphenol oxyethylenated with 20 molecules of
15 ethylene oxide is introduced as the emulsifier.

The polymerisation takes place very differently from sequence c; the contents of the reactor set solid and it is impossible to continue the operation.

20 EXAMPLE 3 (COMPARATIVE EXAMPLE)

This is a comparative example carried out with an emulsifier according to the prior art, which functions correctly if the absorption sequence is carried out strictly at a low temperature (20°C). An
25 attempt to reproduce the operation at an absorption temperature of 35°C is unsuccessful.

Sequence a

Using the device described in Example 1,



265.6 g of heptane are introduced and heated to 80°C, and 0.74 g of sucrose distearate/tristearate and 0.92 g of polyethylene modified with maleic anhydride are dissolved therein, with stirring at 400 rpm.

5

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 and 0.92 g of a 2 % strength aqueous solution of ethylene glycol diglycidyl ether.

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All the subsequent sequences c and d are carried out as in Example 1. The final product is a powder whose mean particle size is 150 μm , and of which the amount passing through a 100 μm screen is unacceptable, having a value greater than 15 %.

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CLAIMS

1. Process for the production of powders which are superabsorbent for water and aqueous liquids, by polymerisation of water-soluble unsaturated monomers, comprising the following operations:

a) preparation of the hydrocarbon solvent phase,

b) preparation of the aqueous monomer phase (charge I),

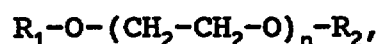
c) bringing the monomer into suspension in the hydrocarbon solvent, and polymerisation I,

d) preparation of the aqueous monomer phase (charge II),

e) absorption of charge II and polymerisation II and

f) isolation of the polymer,

characterised in that the surfactant used for bringing the monomer into suspension is a surfactant which is polymerisable by radical polymerisation and which disappears from the medium by polymerisation or copolymerisation at the end of operation c), this surfactant corresponding to the general formula



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

where R_2 is acryloyl, methacryloyl or maleoyl and

where the degree of condensation n in respect



of ethylene oxide is between 30 and 70.

2. Process according to Claim 1,
characterised in that the polymerisable surfactant is
the maleic acid ester of nonylphenol oxyethylenated
5 with 50 molecules of ethylene oxide, and that it is
dissolved in the aqueous phase during the preparation
of the aqueous monomer phase (charge I).

3. Process according to Claim 1,
characterised in that the polymer constituting the
10 superabsorbent powder is an acrylic acid polymer.

4. Process according to Claim 1,
characterised in that the absorption of the second
monomer charge is carried out at a temperature
initially equal to or greater than 45°C.

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