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(54) Titre : PREPARATION D'UN COPOLYMERE GREFFE POLYACRYALATE/CHLORURE DE VINYLE RESISTANT AUX IMPACTS

(54) Title: PREPARATION OF AN IMPACT-RESISTANT POLYACRYLATE/VINYL CHLORIDE GRAFT COPOLYMER

(57) Abrégé/Abstract:

A new process far preparing a thermoplastic material based on vinyl chloride homo- or copolymers and polyacrylates is disclosed. The process comprises adding a polyacrylate latex to an aqueous suspension of vinyl chloride or vinyl chloride with a copolymerizable monomer, in the presence of an initiator and a suspending agent, at a temperature of at least 30° and polymerizing vinyl chloride onto the polyacrylate at a temperature greater than 30°C. The polyacrylate latex is prepared by polymerizing in an aqueous emulsion an acrylate or a mixture of acrylates having a polymer glass transition temperature of less thaw -20°C, in the presence of a copolymerizable crosslinking compound having at least two nonconjugated double bonds. Compared with process known in the prior art, the process of the invention produces polymer particles having narrower particle size distribution and more reproducible bulk density. The caking on the reactor walls during the polymerization process is also substantially reduced. The mouldings obtained from the polymers prepared by the process of the invention are characterized by good processibility, high impact strength and good surface quality.

## ABSTRACT

A new process for preparing a thermoplastic material based on vinyl chloride homo- or copolymers and polyacrylates is disclosed. The process comprises adding a polyacrylate latex to an aqueous suspension of vinyl chloride or vinyl chloride with a copolymerizable monomer, in the presence of an initiator and a suspending agent, at a temperature of at least 30° and polymerizing vinyl chloride onto the polyacrylate at a temperature greater than 30°C. The polyacrylate latex is prepared by polymerizing in an aqueous emulsion an acrylate or a mixture of acrylates having a polymer glass transition temperature of less than -20°C, in the presence of a copolymerizable crosslinking compound having at least two nonconjugated double bonds. Compared with process known in the prior art, the process of the invention produces polymer particles having narrower particle size distribution and more reproducible bulk density. The caking on the reactor walls during the polymerization process is also substantially reduced. The mouldings obtained from the polymers prepared by the process of the invention are characterized by good processibility, high impact strength and good surface quality.

The invention relates to a process for the preparation of thermoplastic materials consisting of vinyl chloride homo- or copolymers and impact strength modifying polyacrylate-based polymers. Compared with the prior art, an improvement in the particle size distribution, the reproducibility of the bulk density and especially in the amount of caking on the wall during polymerization was achieved.

The processes, according to the prior art, for the preparation of vinyl chloride graft copolymers in suspension on elastomeric polymer particles prepared in emulsion still have some disadvantages.

The preparation of graft polymers by polymerization of vinyl chloride on polyalkyl acrylates, which serve as impact strength modifiers, is known. German Patents 1,082,734, 1,090,856 and 1,090,857 describe processes in which graft polymers containing about 2 to 25% by weight of acrylate rubber are obtained. In the preparation of such graft polymers, the reactor walls exhibit deposits which can be removed only with difficulty. The particle size distribution (measured using an air-jet sieve) still shows a fine fraction below 40 µm and a coarse fraction above 250 µm. The fine fraction leads to turbidity and hence to pollution of the wastewater when the suspension polymer is separated off from the aqueous phase, and to dust problems during handling of the dry powder. The coarse fractions impair the surface quality on modern high performance processing machines.

German Offenlegungsschrift 2,162,615 discloses the preparation of graft polymers of vinyl chloride on polymers of the acrylate type, the final polymers containing 30 to 60% by weight of acrylate units. The acrylates are polymerized in the presence of small amounts of a polyfunctional ethylenically unsaturated monomer in emulsion. An emulsifier having a low HLB value (2 to 12) or a high one (> 40), such as, for example, the sodium salt of bis-(tridecyl) sulphosuccinate (HLB = 4 to 7) or an alkylsulphate salt having a short alkyl chain, such as sodium 2-ethylhexylsulphate (HLB about 50), should be used for the emulsion polymerization. Vinyl chloride, a suitable suspending agent and an initiator soluble in the monomer are added to the aqueous emulsion of the rubber particles. The pH should be adjusted to from 3 to 9. To prevent the formation of wall deposits, a highly viscous methylhydroxypropylcellulose is preferably used. The vinyl chloride graft polymerization is carried out in suspension.

The disadvantage of this process is the use of a suspending agent which has a high molecular weight and is therefore difficult to handle. Furthermore, the bulk density of the graft polymers is insufficient for the conventional processing methods and, when processed on, for example, extruders, in admixture with polyvinyl chloride, mouldings having comparatively low impact strength, a poor surface and a low output rate are obtained.

European Patent Publication 0,313,507 discloses a process in which a polymer having 70 to 40% by weight of polymerized units of vinyl chloride and 30 to 60% by weight of polymerized units of at least one acrylate and optionally other monomers copolymerizable with acrylates is obtained. In a first step, acrylates and optionally other monomers are reacted in aqueous emulsion with the addition of a monomer having at least two ethylenically unsaturated, nonconjugated double bonds, in the presence of an initiator and of a water-soluble salt of a fatty acid containing 12 to 18 C atoms as an emulsifier, at an initial pH above 9, to give a polymer having a glass transition temperature of less than 0°C. In addition to the fatty acid salt, polymerization is carried out in the presence of at least one alkali metal or ammonium salt of an alkylsulphonic acid having 8 to 20 C atoms and/or of an alkyl acryloylsulphonate having 3 to 16 C atoms in the alkyl radical.

In a second step, water, the suspending agent, a precipitating agent for the emulsifiers used in the emulsion polymerization, an initiator, optionally further auxiliaries and vinyl chloride are introduced into the polymerization vessel and the aqueous polyacrylate dispersion is added.

The addition of a second emulsifier and precipitating agent presents problems during normal operation. Furthermore, this necessitates greater expense with regard to storage and filling.

A process has now been found which eliminates or at least substantially reduces the disadvantages of the abovementioned processes. The preparation, according to the invention, of the final polymer is carried out in two stages, where, in a first stage, the elastomeric impact modifier is polymerized in an emulsion polymerization and, in a second stage, the monomer forming the matrix to be modified is polymerized in suspension in the presence of the elastomeric particles, and, in the second stage, the monomer forming the matrix is introduced with the initiator, the suspending agent system and optionally additives and is heated to a temperature of $\geq$ 30°C and the emulsion latex is then added. For reasons relating to production technology, the emulsion latex generally has a temperature of 30 to 40°C.

Thus, according to one aspect, the invention provides a process for preparing a thermoplastic material based on vinyl chloride homo- or copolymers and polyacrylates, which process comprises: adding a polyacrylate latex to an aqueous suspension of vinyl chloride or vinyl chloride with a copolymerizable monomer, in the presence of an initiator and a suspending agent, wherein the suspension has a temperature of at least 30°C, and polymerizing vinyl chloride onto the polyacrylate at a temperature greater than 30°C, to a predetermined conversion of vinyl chloride.

In the first stage, at least one acrylate is polymerized in aqueous emulsion in the presence of crosslinking compounds copolymerizable with the acrylates and having at least two nonconjugated double bonds.

The polymerization in aqueous emulsion takes place in the presence of emulsifying salts.

Suitable acrylates are those which have a glass transition temperature of less than -20°C in the polymer. Mixtures of acrylates or mixtures of acrylates with copolymerizable monomers can also be used.

The following may be mentioned as examples of acrylates: alkyl esters having 2 to 10 C atoms in the alkyl chain, such as, for example, butyl acrylate, 2-ethylhexyl acrylate, octyl acrylate and similar alkyl acrylates, or arylalkyl acrylates, such as, for example, phenylpropyl acrylate, or acrylic acid polyether esters, such as, for example, phenoxyethoxyethyl acrylate.

The following may be mentioned as examples of crosslinking substances: (meth)acrylates of polyhydric alcohols, such as, for example, ethylene glycol dimethacrylate, butylene glycol dimethacrylate, pentaerythritol tetraacrylate, etc., or allyl methacrylate, or the allyl esters of polybasic acids, such as, for example, diallyl phthalate, diallyl maleate or diallyl fumarate.

The crosslinking compounds are used in amounts of 0.1 to 5.0 parts by weight, based on the organic phase of the first stage, and the amount should be chosen so that the gel content of the particles is 90% or more.

Examples of suitable monomers copolymerizable with the acrylates are styrene, vinyl acetate, methacrylates having 1 to 10 C atoms and vinyl ether.

Emulsifying compounds which may be used are the alkali metal salts or the ammonium salt of fatty acids having 12 to 18 C atoms or of alkylsulphonic acids having 12 to 18 C atoms or of alkylarylsulphonic acids or of sulphuric acid alkyl half-esters having 12 to 18 C atoms in the chain.

Sodium laurate, sodium laurylsulphonate, sodium dodecylbenzenesulphonate and sodium laurylsulphate may be mentioned as examples. These are usually used in amounts of 0.3 to 2.5% by weight, based on the monomer of the first stage.

Conventional compounds, such as ammonium peroxydisulphate, hydrogen peroxide or azo compounds, such as, for example, azobisisobutyronitrile, etc., are used as initiators in the emulsion polymerization, in amounts of from 0.05 to 0.5% by weight, based on the monomer.

If necessary, reducing compounds and metal salts capable of forming a redox system with the initiator are added, such as, for example, alkali metal sulphites, alkali metal aldehyde sulphoxylates, organic acids, such as ascorbic acid, and metal salts, such as, for example, iron sulphate and copper sulphate.

The emulsion polymerization can be carried out batchwise, continuously or semicontinuously, the method of semicontinuous polymerization being preferred.

Here, some of the water, of the monomers, of the emulsifier and of the initiator (or of the redox system) is introduced at the polymerization temperature of 40 to 90°C and, after the polymerization has started, the remaining amount of the reaction mixture is added continuously or batchwise.

The polymerization is ended at a conversion of $> 99.9\%$. In the second stage, vinyl chloride or vinyl chloride with up to 20% by weight of copolymerizable monomers is polymerized in aqueous suspension onto the elastomeric particles prepared in the first stage.

To obtain the advantageous properties of the final polymer, it is necessary first to prepare a suspension of vinyl chloride in the aqueous phase and thereafter to add the emulsion latex. Surprisingly, it has been found that the amount of deposits on the reactor walls is dramatically reduced only at feed temperatures above 30°C.

Examples of suitable copolymerisable monomers are vinyl esters (for example vinyl acetate and vinyl laurate), vinyl halides (for example vinylidene chloride), unsaturated acids and anhydrides thereof (for example fumaric acid and maleic acid), (meth)acrylic acid and esters thereof (mono- and diesters) and imides of maleic acid and its N-derivatives.

Suitable suspending agents are the conventionally used ones, such as, for example, hydroxyethylcellulose, hydroxypropylcellulose, methyl hydroxypropylcellulose, polyvinyl alcohols, partially hydrolysed polyvinyl acetates, copolymers of maleic acid with alkyl vinyl ethers and polyvinylpyrrolidone, either individually or as a mixture. It is also possible to add fatty esters of monohydric or polyhydric alcohols, such as, for example, fatty ethoxylates, sorbitan esters, fatty alcohol ethoxylates, in amounts of from 0.05 to 1.0%.

The suspension polymerisation is carried out in the presence of free radical initiators which are soluble in vinyl chloride. Examples of these are diacyl peroxides, such as dilauroyl peroxide or dibenzoyl peroxide; dialkyl peroxides, such as dicumyl peroxide; peroxyesters, such as tert-butyl perpivalate or dialkyl peroxydicarbonates having isopropyl, butyl, myristyl, cyclohexyl, etc. as alkyl groups; organic sulphoperacids, such as acetylcyclohexylsulphonyl peroxide, or azo initiators, such as azobisisobutyronitrile. The conversion of vinyl chloride should be 75 to 95%, based on vinyl chloride used. At the desired final conversion, the residual monomer is removed, the solid is separated off from the aqueous dispersion, for example by centrifuging, and the solid thus obtained is dried in, for example, pneumatic dryers.

In checking the wall deposits, a striking feature is the fact that only a few, easily removable caked deposits adhere to the wall of the polymerization reactor in the procedure according to the invention after the polymerization, even after several batches. In a procedure not according to the invention, in which the polyacrylate latex was added before the vinyl chloride, or after the vinyl chloride but at temperatures below 30°C, depending on the reactor size caked deposits up to several centimetres thick which are difficult to remove and which, as described, substantially hinder heat removal during the polymerization are observed after only one polymerization batch.

The modified PVC powder obtained by the process according to the invention is distinguished by a narrow particle size distribution, high bulk density in conjunction with advantageous porosity and good monomer removal.

For polyacrylate contents of up to about 10%, the polymers are processed to mouldings with the addition of conventional processing auxiliaries, pigments and optionally other additives by, for example, extrusion, calendering, injection moulding, etc.

In the case of polyalkyl acrylates contents of up to 40%, mixing with a non-toughened polyvinyl chloride in amounts of 3 to 10%, preferably 5 to 7%, is usually carried out, followed by processing in the above-mentioned manner.

The mouldings from the polymers prepared by the polymerization process according to the invention are distinguished by good processibility, high impact strength and good surface quality.

The invention is illustrated below by Examples 1 to 3 and Comparative Examples 1 to 4.

The stated values were determined by the following methods:

Gel content of the polyacrylates: the fraction which is insoluble in tetrahydrofuran;

separation by centrifuging:

$$\frac{\text{Gel [g]}}{\text{Polymer [g]}} \text{ (x 100)}$$

| | |
|---|---|
| Swelling index of the polyacrylate gel: | $\frac{\text{Swollen gel [g]}}{\text{Dried gel [g]}}$<br>(The gel content and swelling index were determined using freeze-dried material) |
| Residual monomer contents: | Head-space gas chromatography |
| K value of the powder: | DIN 53,726 |
| Bulk density: | DIN 53,468 |
| Flowability: | Funnel method (diameter 2 to 16 mm) |
| Particle size distribution: | With air-jet sieve according to DIN 53,734 |
| Plasticiser absorption: | DIN 53,417 |
| Surface of the moulding: | Visual assessment |
| Impact strength: | DIN 53,453, notched standard small bar |

## Example 1

a) Preparation of the polyacrylate dispersion

| | Initially taken mixture parts = kg | Metering parts = kg |
|---|---|---|
| Demineralised water | 200 = 60 | 100 = 30 |
| Butyl acrylate | - | 99 = 29.7 |
| Allyl methacrylate | - | 1 = 0.3 |
| Ammonium persulphate | 0.04 = 0.012 | 0.06 = 0.01 |
| Lauric acid | 0.36 = 0.108 | 0.54 = 0.16 |
| Sodium hydroxide | 0.083= 0.025 | 0.123 = 0.03 |

In a 150 l polymerisation reactor equipped with a paddle stirrer, the atmospheric oxygen was displaced by evacuation and flushing with nitrogen gas and 57 kg of demineralised water, 0.108 kg of lauric acid and 0.025 kg of sodium hydroxide were introduced and were heated to 80°C.

After the solid constituents had dissolved, 12 g of ammonium persulphate dissolved in 3 kg of demineralised water were added, followed by 0.30 kg of the butyl acrylate/allyl methacrylate mixture. The polymerisation having been started, after 5 minutes the remaining 29.7 kg of the monomer mixture and at the same time a solution of 0.162 kg of lauric acid, 0.037 kg of NaOH and 0.018 kg of ammonium persulphate in 30 kg of demineralised water were added in the course of four hours. Polymerisation was continued for a further two hours.

The following values were determined:

| | |
|---|---|
| Residual monomer content: | < 500 ppm (i.e. conversion > 99.95%) |
| Gel content of the solid: | 95% |
| Swelling index: | 5 |
| Solids content: | 25.1% |

b) Polymerisation of vinyl chloride onto the polyacrylate

For the subsequent suspension polymerisation, the following were introduced into a 235 l polymerisation reactor with an impeller stirrer and heating/cooling jacket:

| | |
|---|---|
| Demineralised water: | 112.1 parts = 89.4 kg |
| Methylhydroxypropylcellulose: (viscosity 50 mPa.s, 2% strength by weight solution) | 0.16 part = 0.128 kg |
| Sorbitan monolaurate | 0.12 part = 0.096 kg |
| Lauroyl peroxide | 0.10 part = 0.080 kg |

The atmospheric oxygen was displaced by evacuation and flushing with nitrogen gas. The following were then added:

Vinyl Chloride: 94 parts = 75 kg

and after heating to 35°C:

Polybutyl acrylate latex (19.07 kg)

Solidscontent: 6 parts = 4.79 kg

Aqueous fraction: 17.9 parts = 14.28 kg

The mixture was then heated to the polymerization temperature of 60°C and polymerization was carried out at this temperature to a vinyl chloride pressure of 3.5 bar. Thereafter, the mixture was cooled, the residual monomer was removed and the solid was separated from the aqueous phase by filtration. The filtrate was clear.

The reactor wall was free from caked deposits.

The solid was dried in a fluidized-bed dryer. The following values were determined:

Polyacrylate content: 6.7% by weight (corresponds to a vinyl chloride conversion of 89%)

Sieve analysis: Fraction < 63 µm: 3%
Fraction > 250 µm: 2%

Bulk density: 680 g/l

Flowability: 2 mm

Plasticiser absorption: 8 g/100 g

A further 20 experiments were carried out in the reactor without cleaning before caked deposits made cleaning necessary, although heat removal was still sufficient.

<u>Comparative Example 1</u>

The polybutyl acrylate latex was prepared as described in Example 1. In the subsequent vinyl chloride graft polymerization, in contrast to Example 1 the latex was added before the vinyl chloride. Working up was also the same. The filtrate was slightly cloudy.

The reactor wall showed substantial deposits. After three experiments, cleaning was necessary since the heat removal was so greatly impaired by the severe deposits that the internal temperature in the subsequent experiment could no longer have been kept constant.

The following values were determined:

| | |
|---|---|
| Polyacrylate content: | 6.7% by weight |
| Sieve analysis: | Fraction < 63 µm: 9% |
| | Fraction > 250 µm: 12% |
| Bulk density: | 640 g/l |
| Flowability: | 2 mm |
| Plasticiser absorption: | 6 g/100 g |

Comparative Example 2

The polybutyl acrylate latex was prepared as described in Example 1. In the subsequent vinyl chloride graft polymerization, the only difference compared with Example 1 was that the latex was added to the vinyl chloride-containing batch at 25°C. The reactor wall showed fewer caked deposits than in Comparative Example 1 but more than in Example 1. Six polymerization experiments could thus be carried out without intermediate cleaning.

The following values were determined:

| | |
|---|---|
| Polyacrylate content: | 6.7% by weight |

| | |
|---|---|
| Sieve analysis: | Fraction < 63 µm: 5% |
| | Fraction > 250 µm: 3% |
| Bulk density: | 680 g/l |
| Flowability: | 2 mm |
| Plasticiser absorption: | 7 g/100 g |

## Example 2

The procedure was as in Example 1, except that 11 parts (solid) of the polybutyl acrylate latex were added at 32°C to 89 parts of vinyl chloride in demineralised water/suspending agent. The cellulose content was 0.20% ≙ 0.16 kg.

After drying, a powder having the following values was obtained:

| | |
|---|---|
| Polyacrylate content: | 12.2% by weight |
| Sieve analysis: | Fraction < 63 µm: 4%<br>Fraction > 250 µm: 2% |
| Bulk density: | 650 g/l |
| Flowability: | 2 mm |
| Plasticiser absorption: | 6 g/100 g |

A further 12 experiments were carried out without cleaning before the caked deposits became too severe.

## Comparative Example 3

The procedure was as in Example 2, except that the latex was added at 20°C.

| | |
|---|---|
| Polyacrylate content: | 12.2% by weight |
| Sieve analysis: | Fraction < 63 µm: 5%<br>Fraction > 250 µm: 4% |
| Bulk density: | 630 g/l |

The flowability and the plasticiser absorption were as in Example 2.

A further 4 experiments could be carried out without cleaning.

Example 3

The procedure was as in Example 1, except that 35 parts (solid) of polybutyl acrylate latex were added at 32°C to 89 parts of vinyl chloride in demineralised water/suspending agent. The cellulose content was 0.40%.

After drying, a powder having the following values was obtained:

| | |
|---|---|
| Polyacrylate content: | 38% by weight |
| Sieve analysis: | Fraction < 63 μm: 8% |
| | Fraction > 250 μm: 3% |
| Bulk density: | 520 g/l |
| Flowability: | 2 mm |
| Plasticiser absorption: | 35 g/100 g |

A further 4 experiments were carried out without intermediate cleaning.

Comparative Example 4

The procedure was as in Example 3, except that the latex was added before the vinyl chloride.

After drying, a powder having the following values was obtained:

| | |
|---|---|
| Polyacrylate content: | 38% by weight |
| Sieve analysis: | Fraction < 63 μm: 17% |
| Bulk density: | 380 g/l |
| Flowability: | 12 mm |
| Plasticiser absorption: | 50 g/100 g |

Cleaning had to be carried out after each polymerisation experiment.

The powders of Examples 1 to 3 and of Comparative Examples 1 to 4 were processed in an extruder with the addition of commercial formulation components. The polyacrylate contents were necessarily adjusted by the addition of a commercial suspension PVC (K value 68) to 6.7%, based on PVC plus polyacrylate = 100.

Profiles were produced and their surfaces were visually assessed and test specimens for the notched impact test were produced from them.

| | Surface | $a_k$ kg/m$^2$ |
|---|---|---|
| Example | | |
| 1 | glossy | 40 |
| 2 | glossy | 42 |
| 3 | glossy, slightly matt | 38 |
| Comp. Example | | |
| 1 | glossy | 34 |
| 2 | glossy | 38 |
| 3 | glossy | 38 |
| 4 | matt/striped | 15 |

CLAIMS:

1. A process for preparing a thermoplastic material based on a vinyl chloride homo- or copolymer and a polyacrylate, which process comprises:

(A) polymerizing in an aqueous emulsion a monomer selected from the group consisting of an acrylate, a mixture of acrylates and a mixture of an acrylate and another copolymerizable monomer using an initiator in the presence of an emulsifying salt and a copolymerizable crosslinking compound having at least two non-conjugated double bonds, at a conversion rate of the monomer of greater than 99.9% to form a polyacrylate latex, wherein the crosslinking compound is employed in such an amount that is from 0.1 to 5.0 parts by weight based on an organic phase of the emulsion and that a gel content of particles of the polyacrylate latex is at least 90% and wherein the initiator is employed in an amount of 0.05 to 0.5% by weight based on the monomer;

(B) adding the polyacrylate latex to an aqueous suspension of vinyl chloride alone or together with another copolymerizable monomer, in the presence of an initiator and a suspending agent, wherein the suspension has a temperature of at least 30°C; and

(C) polymerizing vinyl chloride alone or together with the copolymerizable monomer onto the polyacrylate at a temperature greater than 30°C, to a predetermined conversion of vinyl chloride alone or together with the copolymerizable monomer.

2. A process according to claim 1, wherein the polyacrylate has a polymer glass transition temperature of less than about -20°C.

3. A process according to claim 1 or 2, wherein the polymerization of step (A) is carried out at a temperature of from about 40 to about 90°C.

4. A process according to any one of claims 1 to 3, wherein vinyl chloride or a mixture thereof containing up to 20% (based on the mixture) of the copolymerizable monomer is polymerized onto the polyacrylate in step (C).

5. A process according to claim 4, wherein the copolymerizable monomer is selected from the group consisting of vinyl esters, vinyl halides, unsaturated acids and anhyrides thereof, (meth)acrylic acid and esters thereof and imides of maleic acid and N-derivatives thereof.

6. A process according to any one of claims 1 to 5, wherein the polymerization of step (C) is terminated at a conversion of vinyl chloride of from about 75 to about 95%.

7. A process according to any one of claims 1 to 6, wherein the initiator used in the suspension polymerization is a free radical initiator soluble in vinyl chloride.

8. A process according to any one of claims 1 to 7, wherein the suspending agent employed in step (B) is at least one member selected from the group consisting of hydroxyethylcellulose, hydroxypropylcellulose, methyl hydroxypropylcellulose, polyvinyl alcohol, partially hydrolysed polyvinyl acetate, a copolymer of maleic acid and an alkyl vinyl ether and polyvinylpyrrolidone.

9. A process according to any one of claims 1 to 8, wherein the resulting thermoplastic material contains the polyacrylate in an amount of up to 10% by weight.

10. A process according to any one of claims 1 to 8, wherein the resulting thermoplastic material contains the

polyacrylate in an amount of more than 10 but not more than 40% by weight.

11. A process according to any one of claims 1 to 10, wherein the polyacrylate latex is added to the aqueous suspension when the aqueous suspension has a temperature of from 30°C to 35°C.

12. A process according to any one of claims 1 to 11, wherein the polymerization of step (C) is conducted at a temperature of about 60°C.

13. A process according to any one of claims 1 to 12, wherein the polyacrylate latex has a temperature of from 30°C to 40°C when the polyacrylate latex is added to the aqueous suspension in step (B).

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