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(71) Applicant (for all designated States except US): **ORGANIK KIMYA SANAYI VE TIC. A.S.** [TR/TR]; Organik Building, Mimarosin Mah, Cendere Yolu No: 146, 34075 Kemerburgaz/Eyup, Istanbul (TR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **PEREZ-LORENZO, Guillermo** [ES/ES]; Areal 136, 7C., E-36201 Vigo (ES). **ALTINOK, Sibel** [TR/TR]; Acarkent, 3.üncü cadde 16.sok C66, 34820 Kavacik-Beykoz, Istanbul (TR).

(74) Agent: **HOCK, Joachim**; Müller-Bore & Partner, Grafingerstraße 2, 81671 München (DE).

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(54) Title: PROCESS OF PREPARING AN EMULSION CONTAINING CORE-SHEATH-SHELL POLYMER PARTICLES

(57) Abstract: The present invention relates to a process of preparing an emulsion containing core-sheath-shell polymer particles which, when dried, contain a microvoid which causes opacity in compositions in which they are contained. The particles can serve as binding or opacifying agents in paints, coating, impregnating, and molding compositions primarily, also extended to paper coatings and to some extent in leather, textiles and water based construction materials.



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Process of preparing an emulsion containing core-sheath-shell polymer particles

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The present invention relates to a process of preparing an emulsion containing core-sheath-shell polymer particles which, when dried, contain a microvoid which causes opacity in compositions in which they are contained. The particles can serve as binding or opacifying agents in paints, coating, impregnating, and molding compositions primarily, also extended to paper coatings and to some extent in leather, textiles and water based construction materials.

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US 4,594,363 discloses a process for making core-sheath polymer particles containing voids, said particles useful for opacifying, comprising (A) emulsion polymerization a core from a core monomer system comprised of at least one ethylenically unsaturated monomer containing acid functionality; (B) encapsulating said core with a hard sheath by emulsion polymerizing a sheath monomer system in the presence of said core, said sheath permitting penetration of fixed or permanent bases; and (C) swelling at elevated temperature the resultant core-sheath polymer particles with fixed or permanent base so as to produce a dispersion of particles which, when dried, contain a microvoid which causes opacity in compositions in which they are contained, provided that either (1) said sheath comprises at least about 1% acid functional monomer or (2) said swelling takes place in the presence of solvent.

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US 4,920,160 describes the use of fixed bases like sodium and potassium hydroxide but differs from US 4,594,363 in that neither acid in sheath/shell steps, nor solvent to help swelling of the core are needed.

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US 2009/256701 A1 discloses a process for making core-sheath polymer particles containing voids, said process *inter alia* strictly requiring the use of a non-homo-polymerizing monomer.

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The most extensive technology jump in said field of core-sheath polymeric opacifying particles is reflected in US 6,020,435. The polymeric opacifying particles disclosed therein exhibit much higher opacity values (at about 8 – 10) than those resulting from the process disclosed in US 4,594,363 (at about 1 – 3). The process of US 6,020,435 provokes a major depletion in free radicals contained in the medium before the swelling additions are performed, said depletion being obtained by the addition of an effective amount of polymerization inhibitors such as N,N-diethylhydroxylamine, N-nitrosodiphenylamine, 2,4-dinitrophenylhydrazine, p-phenylenediamine, phenathiazine, alloocimene, triethyl phosphite, 4-nitrosophenol, 2-nitrophenol, p-aminophenol, 4-hydroxy-TEMPO (also known as 4-hydroxy-2,2,6,6, tetramethylpiperidinyloxy, free radical), hydroquinone, p-methoxyhydroquinone, tert-butyl-p-hydroquinone, 2,5-di-tert-butyl-p-hydroquinone, 1,4-naphthalenediol, 4-tert butyl catechol, copper sulfate, copper nitrate, cresol and phenol. Almost all examples given in US 6,020,435 use 4HT (4-hydroxy-2,2,6,6, tetramethyl-piperidinyloxy), a sophisticated living radical, though a stable solid material when stored at temperatures below 5-8°C.

Apart from toxicity and even mutagenic hazards involved when using those chemicals, they are all quite expensive materials. Moreover, the use of such polymerization inhibitors like 4-hydroxy-TEMPO requires undesired manual operations, including the preparation of a fresh solution of the solid inhibitor material by manually dissolving the material and pouring it into the reaction vessel. Therefore, the high opacity values of the resulting opacifying particles are obtained on account of using intricate, toxic, expensive chemical compounds and undesired operations besides the actual reaction vessel.

It is therefore an object of the present invention to provide a process of preparing core-sheath-shell opacifying polymeric particles having at least the same or comparable performances like those particles disclosed by the process of US 6,020,435, in particular similar opacity values, in which those particles should not have the odor problems associated with the use of volatile base swelling agents, should be obtained without using such intricate, toxic, expensive chemical

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compounds, in particular without such polymerization inhibitors, and are obtainable in a safer and much more efficient and thus cheaper way than those of US 6,020,435.

- 5 This object and others which will become apparent from the following disclosure are achieved by the present invention which relates to a process of preparing an emulsion containing core-sheath-shell polymer particles which, when dried, contain a microvoid which causes opacity in compositions in which they are contained, without using any polymerization inhibitors or scavengers, i.e.
- 10 excluding the use of any polymerization inhibitors or scavengers, said particles being useful as opacifying agents, said process comprising the steps of:
- (i) emulsion polymerizing a core (A) from a core monomer system comprising, as polymerized units, from 5 to 100 percent by weight, based on the weight of the
- 15 core, of hydrophilic monoethylenically unsaturated monomer containing acid functionality, and from 0 to 95 percent by weight, based on the weight of the core, of at least one nonionic monoethylenically unsaturated monomer;
- (ii) encapsulating said core (A) with a sheath polymeric layer (B) by emulsion
- 20 polymerizing a sheath monomer system (E1) comprising, as polymerized units, at least 20 % by weight, preferably at least 40 % by weight, of a hydrophilic monoethylenically unsaturated monomer, at least 20 % by weight, preferably at least 40 % by weight, of a hydrophobic monoethylenically unsaturated monomer, and 1% to 20 % by weight of a hydrophilic monoethylenically unsaturated
- 25 monomer containing acid functionality, each based on the total weight of the sheath polymeric layer, in the presence of said core, said sheath permitting penetration of volatile, fixed or permanent bases;
- (iii) encapsulating said core-sheath particles with a polymeric shell (C) by
- 30 emulsion polymerizing a shell monomer system (E2) comprising, as polymerized units, from 1 to 10 percent by weight, of hydrophilic monoethylenically unsaturated monomer containing acid functionality, and from 90 to 99 percent by weight, of at

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least one nonionic monoethylenically unsaturated monomer, each based on the total weight of the polymeric shell;

(iv) neutralizing and swelling at elevated temperature the resultant core-sheath-shell polymer particles with a volatile, fixed or permanent base, said swelling
5 taking place in the presence of a monomer-solvent-system comprising from 5-50 % by weight of the at least one nonionic monoethylenically unsaturated monomer of said shell monomer system (E2), said monomer acting as a solvent, which, in turn, assists in the penetration of the base through the created polymer layers
10 down to the core, wherein said monomer-solvent-system can be added before, after or during the addition of the base, and

(v) after the swelling step, reducing the level of said at least one nonionic monoethylenically unsaturated monomer of said monomer-solvent-system in step
15 (iv) by polymerizing the monomer to less than 10,000 ppm, based on polymer solids, so as to produce an emulsion of particles which, when dried, contain a microvoid which causes opacity in compositions in which they are contained,

wherein a water soluble polymerization catalyst in a total amount of 0.05 to 0.45 %
20 by weight, based on the total amount of monomers in E1 *plus* E2, is either fed in parallel with the sheath monomer system E1 into the polymerization reactor or is fed into the polymerization reactor right before emulsion polymerization of E1 in step (ii) starts.

25 The present invention further relates to an emulsion containing said core-sheath-shell polymer particles obtained by the above process, and to core-sheath-shell polymer particles containing voids, obtained by at least partially drying said emulsion. The swollen core-sheath-shell polymer particles contain voids which, when the particles are in the form of an aqueous emulsion, are filled with liquid
30 water. On drying the voids become filled with air, thus conferring on the particles their opacifying properties.

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The main polymerization reaction according to the present invention resides in encapsulating the acidic, alkali swellable core polymer (or seed) with a sheath that serves as a bridge to further encapsulate said core-sheath with a shell. In

accordance with the present invention, a catalyst, within certain tailored limits, is
5 dosed together with sheath monomer system E1 or shot-in right before E1 addition starts and that catalyst is all and the only catalyst present in reacting the monomer systems E1 and E2, with no further catalysts being added or shot at any moment of the reaction after that catalyst has been added. Thus, no inhibitors or scavengers are added at any moment of the whole reaction from beginning to
10 end. To that extent, reacting or not said at least one nonionic monoethylenically unsaturated monomer of said monomer-solvent-system in step (iv), preferably styrene monomer, that has acted as solvent in the swelling step, is not a fundamental part of the process for preparing the polymeric particles as such.

15 If the polymerization process is run according to the present invention, after the monomer systems E1 (sheath) and E2 (shell) have been polymerized within the given ranges, then both the monomer-solvent-system, preferably styrene monomer, and the swelling neutralizing agent (preferably NaOH, KOH) are present together in order to perform the swelling of particles by neutralizing the
20 core. If one of them is not present, no swelling takes place and, consequently, no opacifying properties are developed. But if both are present, the shell becomes permeable to the base which can diffuse through the shell and the sheath, neutralizing the core, provoking its expansion, and thus the particles swell. As mentioned, in step (iv) the monomer-solvent-system can be added before, after or
25 during the addition of the base.

Usually, the swollen particles have a diameter from about 300 nm to about 1000 nm, depending on the intended application (paints, paper, etc.). When used as opacifying agent for paints, diameters from about 300 nm to 500 nm are preferred.

30 If this product is dried, water will evaporate as free monomer of the monomer-solvent-system, preferably styrene monomer, also will, and an opacifying agent is obtained which has all desired properties. When not performing above step (v), the product smells of monomer, i.e. styrene, which of course is not desired.

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Therefore, in step (v) at the end of the process, free monomer which “smells”, is removed by polymerization. Therefore, when setting the limits for catalyst amounts, surfactant amounts, ratio core-to-shell, level of functional acid monomer, etc., it is always referred to these amounts as a percentage on monomers in the monomer systems E1+E2, or, in other words, “based on (actual) monomers to be polymerized” (i.e. monomers present in E1+E2).

The process of the present invention differs from that of US 4,594,363 at least in the following points:

- 10 - total amount of water soluble polymerization catalyst in the range of 0.05 to 0.45 % by weight, based on the total amount of monomers in E1 *plus* E2, the catalyst being either fed in parallel with the sheath monomer system E1 into the polymerization reactor or is fed into the polymerization reactor right before emulsion polymerization of E1 in step
15 (ii) starts, while US 4,594,363 uses in Examples 2A to 3E catalyst amounts of 1.42 % by weight, calculated as percentage on monomers to be polymerized, and the catalyst are also dosed with the shell monomer supply;
- 20 - the sheath monomer system of US 4,594,363 does not mandatorily provide for comprising, as polymerized units, at least 20 % by weight of a hydrophilic monoethylenically unsaturated monomer, at least 20 % by weight of a hydrophobic monoethylenically unsaturated monomer, and 1% to 20 % by weight of a hydrophilic monoethylenically unsaturated monomer containing acid functionality, each based on the total weight of
25 the sheath polymeric layer; instead a system of 20 % by weight butyl (meth)acrylate, 80 % by weight methyl (meth)acrylate *plus* acid is adopted;
- 30 - the shell monomer system (E2) for making up the polymeric shell (C) mandatorily comprises hydrophilic monoethylenically unsaturated monomer containing acid functionality, while none of the Examples of US US 4,594,363 do;

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- the process of the present invention provide for opacifying particles with high opacity values of between 8 to 10, while the particles obtained by US 4,594,363 show much lesser opacity values, i.e. between 1 to 3.

5 By refining certain process parameters, the process of the present invention is capable of producing swollen multi-stage emulsion polymers having much higher opacity values as those obtained by the process of US 4,594,363.

10 The process of the present invention differs from that of US 6,020,435 at least in the following points:

- no use at all of any polymerization inhibitors or scavengers;
- total amount of water soluble polymerization catalyst in the range of 0.05 to 0.45 % by weight, based on the total amount of monomers in E1 *plus* E2, the catalyst being either fed in parallel with the sheath
15 monomer system E1 into the polymerization reactor or is fed into the polymerization reactor right before emulsion polymerization of E1 in step (ii) starts, while in US 6,020,435 uses in Examples 17 to 49 catalyst amounts between 0.64 and 1.33 % by weight, calculated as percentage on monomers to be polymerized, and the catalyst are also dosed with
20 the shell monomer supply;
- the sheath monomer system of US 6,020,435 does not mandatorily provide for comprising, as polymerized units, at least 20 % by weight of a hydrophilic monoethylenically unsaturated monomer, at least 20 % by weight of a hydrophobic monoethylenically unsaturated monomer, and
25 1% to 20 % by weight of a hydrophilic monoethylenically unsaturated monomer containing acid functionality, each based on the total weight of the sheath polymeric layer; instead a system of 9 % by weight butyl (meth)acrylate, 89 % by weight methyl (meth)acrylate *plus* 2 % by weight of (meth)acrylic acid is adopted;
- the shell monomer system (E2) for making up the polymeric shell (C) mandatorily comprises hydrophilic monoethylenically unsaturated monomer containing acid functionality, while none of the Examples of
30 US 6,020,435 do.

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By refining certain process parameters, the process of the present invention is capable of producing swollen multi-stage emulsion polymers having opacity values as high as those obtained by the process of US 6,020,435, however avoiding the use of intricate, toxic, expensive chemical compounds, in particular not using any polymerization inhibitors or scavengers. The overall process of the present invention is much more efficient and cheaper than that of US 6,020,435.

Apart from several other differences, the process disclosed in US2009/256701 A1 strictly requires the use of a non-homo-polymerizing monomer. To the contrary, the process of the present invention does not in any way prescribe the use of such type of monomers, neither any other chemical substance similar to, nor any other alternative chemical playing a similar role in the process. Furthermore, the process of the present invention does not prescribe or requires any special chemical to be used "instead of" that claimed chemical substance mandatorily to be used in US2009/256701 A1. The process of the present invention, in fact, requires no additional chemical substance to perform the art it teaches. As presented in the experimental part given hereinbelow, the opacifying polymer obtained by the process disclosed in US2009/256701 A1 has a very low opacity, contrary to the high opacity values provided by the opacifiers obtained by the present invention.

"Emulsion polymer", as used herein, refers to a water-insoluble polymer which is prepared by emulsion polymerization techniques.

"Polymer emulsion", as used herein, refers to an aqueous composition having discrete, water-insoluble polymer particles dispersed therein.

As used herein, acrylate and methacrylate are referred to as "(meth)acrylate," acrylic acid and methacrylic acid are referred to as "(meth)acrylic acid."

The stages of the multi-stage polymer particles of the present invention include core stage polymer (A), sheath stage polymer (B), and shell stage polymer (C).

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The core, sheath and shell may themselves be comprised of more than one stage. The core of the multi-stage polymers of the present invention are emulsion polymers comprising, as polymerized units, from 5 to 100 percent by weight, based on the weight of the core, of at least one hydrophilic monoethylenically unsaturated monomer containing acid functionality, and from 0 to 95 percent by weight, based on the weight of the core stage polymer, of at least one nonionic monoethylenically unsaturated monomer.

Cores containing at least five percent by weight, based on the total weight of the core polymer, of at least one hydrophilic monoethylenically unsaturated monomer containing acid functionality will generally result in a suitable degree of swelling. Preferably, the core comprises, as polymerized units, hydrophilic monoethylenically unsaturated monomer containing acid functionality at a level of from 5 to 100, more preferably, from 20 to 60, and most preferably, from 30 to 50 percent by weight based on the total weight of the core. The hydrophilic core polymer may be made in a single stage or step of the sequential polymerization or may be made by a plurality of steps in sequence.

Suitable hydrophilic monoethylenically unsaturated monomers containing acid-functionality useful for making the core polymer include monoethylenically unsaturated monomers containing at least one carboxylic acid group including acrylic acid, methacrylic acid, acryloxypropionic acid, (meth)acryloxypropionic acid, itaconic acid, aconitic acid, maleic acid or anhydride, fumaric acid, crotonic acid, monomethyl maleate, monomethyl fumarate, monomethyl itaconate and the like. Acrylic acid and methacrylic acid are preferred.

Suitable nonionic monoethylenically unsaturated monomers for making the hydrophilic core polymer include styrene, α -methyl styrene, p-methyl styrene, t-butyl styrene, vinyltoluene, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, (meth)acrylonitrile, (meth)acrylamide, (C₁ -C₂₀) alkyl or (C₃ -C₂₀) alkenyl esters of (meth)acrylic acid, such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, benzyl (meth)acrylate, lauryl (meth)acrylate, oleyl

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(meth)acrylate, palmityl (meth)acrylate, stearyl (meth)acrylate and the like.

In a preferred embodiment of the invention, the core (A) is polymerized from a core monomer system comprising 30-40 % by weight (meth)acrylic acid and 60-70 % by weight methyl (meth)acrylate.

The core, whether obtained by a single stage process or a process involving several stages, has an average particle size of from 50 nm to 300 nm, preferably from 100 nm to 250 nm, diameter in unswollen condition. If the core is obtained from a seed polymer, the seed polymer preferably has an average particle size of from 30 nm to 100 nm.

The multi-stage polymer particles of the present invention contain an intermediate stage, i.e. a sheath polymeric layer (B). The sheath polymeric layer (B) partially or fully encapsulates the core (A) and itself is partially or fully encapsulated by the shell (C). The sheath polymeric layer (B) is prepared by conducting an emulsion polymerization in the presence of the core.

The hydrophilic monoethylenically unsaturated monomers containing acid functionality and the nonionic monoethylenically unsaturated monomers useful for making the core are also useful for making the sheath polymeric layer.

Preferably, the sheath polymeric layer is polymerized from a sheath monomer system (E1) comprising at least 20 % by weight, more preferably at least 40 % by weight, of styrene, at least 20 % by weight, more preferably at least 40 % by weight, of methyl (meth)acrylate, and 1% to 20 % by weight of (meth)acrylic acid.

Usually, the sheath monomer system (E1) is polymerized at least to about 90% before the shell monomer system (E2) begins to be polymerized. The total amount of sheath polymeric layer (B) is by weight from 1 to 5 times the weight of the core. The core-sheath particle after step (ii) whether obtained by a single stage process or a process involving several stages, has usually an average particle size of from

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100 nm to 300 nm, preferably from 150 nm to 250 nm, diameter in unswollen condition.

The shell (C) of the multi-staged polymer of this invention is the product of emulsion polymerizing a shell monomer system (E2) comprising, as polymerized units, from 1 to 10 percent by weight, of hydrophilic monoethylenically unsaturated monomer containing acid functionality, and from 90 to 99 percent by weight, of at least one nonionic monoethylenically unsaturated monomer, each based on the total weight of the polymeric shell.

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The nonionic monoethylenically unsaturated monomers suitable for the core are also suitable for the shell. Styrene is preferred. The shell also contains, as polymerized units, from 1 to 10, preferably from 1 to 5, percent by weight based on the weight of the shell, of one or more monoethylenically unsaturated monomers containing acid-functionality including acrylic acid, methacrylic acid, acryloxypropionic acid, (meth)acryloxypropionic acid, itaconic acid, aconitic acid, maleic acid, maleic anhydride, fumaric acid, crotonic acid, monomethyl maleate, monomethyl fumarate, monomethyl itaconate and the like. Acrylic acid and methacrylic acid are preferred.

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The shell may also optionally contain less than 20 percent by weight, preferably from 0.1 to 3 percent by weight, based on the total weight of the shell, of polyethylenically unsaturated monomer like alkylene glycol diacrylates and dimethacrylates, such as for example, ethylene glycol diacrylate, ethylene glycol dimethacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate propylene glycol diacrylate and triethylene glycol dimethylacrylate; 1,3-glycerol dimethacrylate; 1,1,1-trimethylol propane dimethacrylate; 1,1,1-trimethylol ethane diacrylate; pentaerythritol trimethacrylate; 1,2,6-hexane triacrylate; sorbitol pentamethacrylate; methylene bis-acrylamide, methylene bis-methacrylamide, divinyl benzene, vinyl methacrylate, vinyl crotonate, vinyl acrylate, vinyl acetylene, trivinyl benzene, triallyl cyanurate, divinyl acetylene, divinyl ethane, divinyl sulfide, divinyl ether, divinyl sulfone, diallyl cyanamide, ethylene glycol divinyl ether, diallyl phthalate, divinyl dimethyl silane, glycerol trivinyl ether, divinyl adipate;

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dicyclopentenyl (meth)acrylates; dicyclopentenylloxy (meth)acrylates; unsaturated esters of glycol monodicyclopentenyl ethers; allyl esters of α,β -unsaturated mono- and dicarboxylic acids having terminal ethylenic unsaturation including allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl itaconate and the like.

In a preferred embodiment of the present invention, the shell monomer system (E2) comprises, as polymerized units, from 1 to 10 percent by weight, of (meth)acrylic acid, and from 90 to 99 percent by weight, of styrene.

The core-sheath-shell particle after step (iii) whether obtained by a single stage process or a process involving several stages, has usually an average particle size of from 250 nm to 1000 nm, diameter in unswollen condition. When intended for use as opacifying agent for paints, an average particle size of from 300 nm to 450 nm is preferable.

The presence of acid-functional monoethylenically unsaturated monomer in the shell (C) may serve several functions:

(1) stabilizing of the final multi-stage emulsion polymer particle; and

(2) compatibilizing the shell with the previously formed stage of the multistage emulsion polymer particle.

As used herein, the term "sequentially emulsion polymerized" or "sequentially emulsion produced" refers to polymers (including homopolymers and copolymers) which are prepared in aqueous medium by an emulsion polymerization process in the presence of the dispersed polymer particles of a previously formed emulsion polymer such that the previously formed emulsion polymers are increased in size by deposition thereon of emulsion polymerized product of one or more successive monomer charges introduced into the medium containing the dispersed particles of the preformed emulsion polymer.

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The method of this invention contemplates that the core, the sheath polymeric layer, and/or the shell may be made in a single stage or step of the sequential polymerization or may be made by a plurality of steps in sequence following the polymerization.

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According to the present invention, a water soluble polymerization catalyst in a total amount of 0.05 to 0.45 % by weight, based on the total amount of monomers in E1 *plus* E2, is employed. When performing the process of the present invention on an industrial scale, i.e. in reactors with capacities of about 10 000 to 50 000 kg, the water soluble polymerization catalyst is preferably employed in a total amount of 0.10 to 0.30 by weight, based on the total amount of monomers in E1 *plus* E2. The reason for that resides in the enhanced efficiency of such catalysts under real plant conditions when compared to their employment under laboratory conditions or in pilot plants.

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The catalyst is either fed in parallel with the sheath monomer system E1 into the polymerization reactor or is fed into the polymerization reactor right before emulsion polymerization of E1 in step (ii) starts. The water soluble polymerization catalyst is preferably a water-soluble free radical initiator utilized in the aqueous emulsion polymerization. Suitable water-soluble free radical initiators include hydrogen peroxide; tert.-butyl peroxide; diazo initiators like V-50 from Wako Pure Chemical Industries, Ltd.; alkali metal persulfates such as sodium, potassium and lithium persulfate; ammonium persulfate; and mixtures of such initiators with a reducing agent. Reducing agents include: sulfites, such as alkali metal metabisulfite, hydrosulfite, and hyposulfite; sodium formaldehyde sulfoxylate; and reducing sugars such as ascorbic acid and isoascorbic acid.

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In step (ii) and/or step (iii) one or more nonionic or anionic emulsifiers, or surfactants, may be used, either alone or together. Examples of suitable nonionic emulsifiers include tert-octylphenoxyethylpoly(39)-ethoxyethanol, dodecyloxypoly(10)ethoxyethanol, nonylphenoxyethyl-poly(40)ethoxyethanol, polyethylene glycol 2000 monooleate, ethoxylated castor oil, fluorinated alkyl esters and alkoxylates, polyoxyethylene (20) sorbitan monolaurate, sucrose

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monococoate, di(2-butyl)phenoxy poly(20)ethoxyethanol, hydroxyethylcellulose polybutyl acrylate graft copolymer, dimethyl silicone polyalkylene oxide graft copolymer, poly(ethylene oxide) poly(butyl acrylate) block copolymer, block copolymers of propylene oxide and ethylene oxide, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylated with 30 moles of ethylene oxide, N-polyoxyethylene(20)lauramide, N-lauryl-N-polyoxyethylene(3)amine and poly(10)ethylene glycol dodecyl thioether. Examples of suitable anionic emulsifiers include sodium lauryl sulfate, sodium dodecylbenzenesulfonate, potassium stearate, sodium dioctyl sulfosuccinate, sodium dodecyl diphenyl oxide disulfonate, nonylphenoxyethyl poly(l)ethoxyethyl sulfate ammonium salt, sodium styrene sulfonate, sodium dodecyl allyl sulfosuccinate, linseed oil fatty acid, sodium or ammonium salts of phosphate esters of ethoxylated nonylphenol, sodium octoxynol-3-sulfonate, sodium cocoyl sarcocinate, sodium 1-alkoxy-2-hydroxypropyl sulfonate, sodium alpha-olefin (C₁₄-C₁₆)sulfonate, sulfates of hydroxyalkanols, tetrasodium N-(1,2-dicarboxy ethyl)-N-octadecylsulfosuccinamate, disodium N-octadecylsulfosuccinamate, disodium alkylamido polyethoxy sulfosuccinate, disodium ethoxylated nonylphenol half ester of sulfosuccinic acid and the sodium salt of tert-octylphenoxyethoxy poly(39)ethoxyethyl sulfate. The one or more surfactants are generally used at a level of from 0 to 3 percent based on the weight of the multi-stage polymer. The one or more surfactants can be added prior to the addition of any monomer charge, during the addition of a monomer charge or a combination thereof. In certain monomer/emulsifier systems for forming the shell, the tendency to produce gum or coagulum in the reaction medium may be reduced or prevented by the addition of about 0.05% to about 2.0% by weight, based on total weight of the shell polymer, of emulsifier without detriment to the deposition of the polymer formed on the previously formed particles.

By carrying out the emulsion polymerization while maintaining low levels of emulsifier, the subsequent stages of polymer-formation deposit the most-recently formed polymer on the existing dispersed polymer particles resulting from the preceding step or stage. As a general rule, the amount of emulsifier should be kept below that corresponding to the critical micelle concentration for a particular

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monomer system, but while this limitation is preferable and produces a unimodal product, in some systems the critical micelle concentration of the emulsifier may be exceeded somewhat without the formation of an objectionable or excessive number of dispersed micelles or particles. It is for the purpose of controlling the number of micelles during the various stages of polymerization so that the deposition of the subsequently formed polymer in each stage occurs upon the dispersed micelles or particles formed in the previous stages, that the concentration of emulsifier is kept low.

- 10 The viscosity-average molecular weight of the polymer formed in a given stage may range from 100,000, or lower if a chain transfer agent is used, to several million molecular weight. If it is desired to produce a core having a molecular weight in the lower part of the range, such as down to as low as about 20,000, it is frequently most practical to do so by avoiding any polyethylenically unsaturated monomers and using a chain transfer agent instead, such as 0.05% to 2% or more thereof, examples being alkyl mercaptans, such as sec-butyl mercaptan.

The weight ratio of core to the sheath is generally in the range of from 1:0.5 to 1:10, preferably in the range of from 1:1 to 1:5. The weight ratio of core to shell is generally in the range of from 1:5 to 1:20, preferably in the range of from 1:8 to 1:15. Preferably, the weight of the polymeric shell (C) constitutes more than 50% of the total monomer weight of the particles. When trying to decrease the dry density of the final product, is preferred to have as little shell as possible while still encapsulating the core.

25 In order to minimize the dry density of the final product, it is preferable to deposit only as much shell polymer as is needed to fully encapsulate the core. When the hydrophilic core polymer is fully encapsulated, it does not titrate with alkali metal bases under normal analytical conditions of about 1 hour and at room temperature. The extent of encapsulation can be determined by removing samples during the course of the shell polymerization and titrating with sodium hydroxide.

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In step (iv) suitable swelling agents include those which, in the presence of the multistage emulsion polymer and monomer, are capable of permeating the shell and swelling the core. Swelling agents may be aqueous or gaseous, volatile or fixed bases or combinations thereof.

5

Suitable swelling agents in step (iv) of the present invention include volatile bases such as ammonia, ammonium hydroxide, preferably aqueous ammonium hydroxide, and volatile lower aliphatic amines, such as morpholine, trimethylamine, and triethylamine, and the like; fixed or permanent bases such as
10 potassium hydroxide, lithium hydroxide, zinc ammonium complex, copper ammonium complex, silver ammonium complex, strontium hydroxide, barium hydroxide and the like. Sodium hydroxide and potassium hydroxide are preferred.

15

The amount of swelling agent can be less than, equal to or greater than the amount needed to provide for complete neutralization of the core. Preferably, the amount of swelling agent is in the range of from 75 to 150 percent, based on the total amount of acid contained in the core *plus* sheath *plus* shell, i.e. relative to the core, sheath and shell in total.

20

Swelling is generally very efficient under conditions of elevated temperature and in the presence of monomer-solvent-system. Under these conditions, swelling is generally complete within 30 minutes, preferably within 20 minutes, most preferably within 10 minutes of adding the one or more swelling agents.

25

Preferably, the elevated temperature in the neutralization and swelling step (iv) is from about 50 °C to about 120 °C, preferably from about 80 °C to about 95 °C.

30

The core polymer of the multistage emulsion polymer swells when the core is subjected to a basic swelling agent that permeates the shell to at least partially neutralize the hydrophilic-functionality of the core, preferably to a pH of at least about 6 to at least about 10, and thereby results in swelling by hydration of the hydrophilic core polymer. The swelling, or expansion, of the core may involve partial merging of the outer periphery of the core into the pores of the inner

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periphery of the shell and also partial enlargement or bulging of the shell and the entire particle overall.

In accordance with the present invention, said swelling takes place in the presence of a monomer-solvent-system comprising from 5-50 % by weight, preferably 15-30 % by weight, more preferably 20-30 % by weight, of the at least one nonionic monoethylenically unsaturated monomer in said shell monomer system (E2), said monomer acting as a solvent, which, in turn, assists in the penetration of the base through the created polymer layers down to the core. Said monomer-solvent-system of step (iv) can be added before, after or during the addition of the base. Preferably, said monomer is styrene.

The presence of said monomer in step (iv) is helpful in facilitating the swelling of the multistage polymer, whether by plasticizing the shell, aiding in the transport through the shell or a combination thereof. However, the presence of monomer is detrimental when trying to maximize swelling and minimize the dry bulk density of the swollen multistage emulsion polymer. Accordingly, and in order to avoid any smell of the final product caused by the presence of said monomer, after swelling the multistage emulsion polymer in the presence of both monomer-solvent system and swelling agent, the level of said monomer of the monomer-solvent system is reduced to less than 10,000 ppm, preferably to less than 5,000 ppm based on polymer solids. This is accomplished by polymerizing the monomer of the monomer-solvent-system used in step (iv). Preferably, in said step (v) of the present invention, said monomer-solvent-system is polymerized by redox catalyst initiation after the swelling step is completed. Those redox catalysts are well known in the art. A typically used system is tBHP/SSF. Since the polymerization takes place in the shell, the resulting polymer, preferably polystyrene, becomes a constituent of the shell (C) of the particles.

The process of the present invention is capable of producing swollen multi-stage emulsion polymer particles having opacity values as high as those obtained by the process of US 6,020,435, however avoiding the use of intricate, toxic, expensive

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chemical compounds, in particular not using any polymerization inhibitors or scavengers.

The performance of these swollen multi-stage emulsion polymer particles as opacifiers has been judged as follows: As reference the best (and almost only) product in the market called Ropaque UltraE supplied by Rohm and Haas Company has been taken. A typical acrylic polymer emulsion that produces, upon drying, a clear transparent film has been taken. Always the same amount, solids on solids, of the trial product have been blended therein and the same has been done with the reference product, accounting for any small differences in solids content as to have always the same dry film thickness and the same ratio opacifier-on-polymer on dry bases. Samples are applied on black&white standard Leneta chart. Upon drying (60 °C oven, 20 min) the opacity of the samples has been compared. The reference product is given a value of 10 and no opacity (transparent film) is given a value of 0.

When the swollen multistage emulsion polymers are at least partially dried to produce voided polymer particles, these voided polymer particles impart favorable properties, such as gloss, brightness and opacity to paper coating formulations to which they are added.

The voided polymer particles produced by the method of the present invention are useful in coating compositions, such as aqueous-based paint and paper coatings. The voided polymer particles produced by the method of this invention impart improved gloss, brightness and opacity to paper coating formulations to which they are added. Also, the voided polymer particles produced by the method of this invention impart opacity to aqueous coating compositions, such as paints, to which they are added.

The present invention will be further illustrated in the following examples without any limitation thereto.

EXAMPLE 1

The process was performed as follows: Firstly, reaction water was added into the polymerization reactor which was then heated to 90-92°C. Following this, seed particles were introduced which were prepared by conventional means. These seed particles were composed of 65% by weight methyl methacrylate and 35 % by weight methacrylic acid. The mean particle size has been 147 nm, solids content 30%. When adding the seed particles, the temperature decreased to 78-82°C.

- 5
- 10 Subsequently, feeding of the Preemulsion-I (E1), i.e. the sheath monomer system, was started; in the first 15 minutes the flow rate has been $\frac{1}{2}$ of normal rate (i.e. about 0.5 g/min for 15 min), then normal flow rate during 45 min (i.e. about 1.2 g/min for 45 min). The reaction temperature was between 80-83°C, reaction period: 60 min. The catalyst was co-fed with the sheath monomer system (E1).
- 15 Both catalysts and E1 finished at the same time. After the feeding was completed, it was waited 15-30 minutes till the temperature was stable at 80 – 82°C.

- Following this, the feeding of the shell monomer system (E2), i.e. Preemulsion-II, was started at 80-82°C. The temperature then gradually increased to 84-85°C,
- 20 after 10-20 minutes increased to 92-94°C. The reaction period was 70 min. Then, in 15-30 min after E2 was finished, the temperature went down to 88-90°C.

- Following this, the Preemulsion-III (E3), i.e. the monomer-solvent-system, was added in 5 minutes. Then it was waited 10 minutes till the temperature was stable
- 25 at around 85-87°C. Subsequently, the feeding of the neutralizing agent (caustic solution) was started, taking about 60 minutes. The emulsion was kept at 85-89°C during all the addition. After neutralization, the mixture was kept 15 minutes while mixing. Then, the redox catalyst was added at 84-88°C (first t-BHP, then SSF). A temperature increase of 5-8°C to 90-95°C was observed. After ten minutes the
- 30 emulsion was cooled down. Below 40°C a biocide (Acticide® MV commercially available from Thor GmbH) was added. After final work-up, the respective sample was taken out for analytical studies. In the following, the reactor charges for within the individual steps are given:

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Component	Quantity (g)
Water	340,000
Seed (30% solids, particle size 147nm)	68,000
Preemulsion-I (E1)	
Water	17,000
Rhodacal DS-10(15%)	0,500
Methacrylic Acid	3,000
Methyl Methacrylate	20,000
Styrene	20,000
Preemulsion-II: (E2)	
Water	92,000
Rhodacal DS-10 (15%)	2,670
Methacrylic Acid	4,000
Styrene	200,000
Allyl Methacrylate	0,400
Linseed oil	1,000
Preemulsion-III (E3)	
Water	16,000
Rhodacal DS-10 (15%)	0,670
Styrene	50,000
Catalyst	
Sodium Persulfate	0,800
Water	24,200
Neutralizing Agent	
Sodium Hydroxyde (50%)	8,800
Water	167,200
Post treatment	
t-Butylhydroxyperoxyde(tBHP)	0,800
Water	6,200
Sodium sulfoxylate (SSF)	0,800

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Water	11,200
Biocide	1,000
DiW	2,000
Flush water	20,00
Total product	1078

The analytical specifications gave the following results:

Analytical Specifications		Results
Aspect:	white opaque emulsion	OK
Wet	white	white
Dry film	white powder	white powder
Solids(%)	29-31	30.6
Viscosity Sp rpm	max 500, LVT 2/60	85
pH	7.5-8.5	8.2
Gel,82 mesh (g/l):	<0.05	<0.06
Powdering	soft, equal to standard	OK
Opacity	equal to standard (10)	10
Mechanical stability	good	OK
Dry density	0.550-610 g/cm ³	0.592
Ps (nm)	380-480	444

5

EXAMPLE 2

The process was performed as follows: Firstly, reaction water was added into the polymerization reactor which was then heated to 90-92°C. Following this, the catalyst was added (shot) followed by seed particles prepared by conventional means. These seed particles were composed of 65% by weight methyl methacrylate and 35 % by weight methacrylic acid. The mean particle size has been 147 nm, solids content 30%. When adding the seed particles, the temperature decreased to 78-82°C.

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Subsequently, feeding of the Preemulsion-I (E1), i.e. the sheath monomer system, was started; in the first 15 minutes the flow rate has been ½ of normal rate (i.e. about 0.5 g/min for 15 min), then normal flow rate during 45 min (i.e. about 1.2 g/min for 45 min). The reaction temperature was between 80-84°C, reaction period: 60 min. After the feeding was completed, it was waited 15-30 minutes till the temperature was stable at 80 – 82°C.

Following this, the feeding of the shell monomer system (E2), i.e. Preemulsion-II, was started at 80-82°C. The temperature then gradually increased to 84-85°C, after 10-20 minutes increased to 92-94°C. The reaction period was 70 min. Then, in 15-30 min after E2 was finished, the temperature went down to 88-90°C.

Following this, the Preemulsion-III (E3), i.e. the monomer-solvent-system, was added in 5 minutes. Then it was waited 10 minutes till the temperature was stable at around 85-87°C. Subsequently, the feeding of the neutralizing agent (caustic solution) was started, taking about 60 minutes. The emulsion was kept at 85-89°C during all the addition. After neutralization, the mixture was kept 15 minutes while mixing. Then, the redox catalyst was added at 84-88°C (first t-BHP, then SSF). A temperature increase of 5-8°C to 90-95°C was observed. After ten minutes the emulsion was cooled down. Below 40°C a biocide (Acticide® MV commercially available from Thor GmbH) was added. After final work-up, the respective sample was taken out for analytical studies. In the following, the reactor charges for within the individual steps are given:

Component	Quantity
Water	340,000
Seed (30% solids, particle size 147nm)	68,000
Preemulsion-I (E1)	
Water	17,000
Rhodacal DS-10(15%)	0,500
Methacrylic Acid	3,000

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Methyl Methacrylate	20,000
Styrene	20,000
Preemulsion-II: (E2)	
Water	92,000
Rhodacal DS-10 (15%)	2,670
Methacrylic Acid	4,000
Styrene	200,000
Allyl Methacrylate	0,400
Linseed oil	1,000
Preemulsion-III (E3)	
Water	16,000
Rhodacal DS-10 (15%)	0,670
Styrene	50,000
Catalyst	
Sodium Persulfate	1,00
Water	24,200
Neutralizing Agent	
Sodium Hydroxyde (50%)	8,800
Water	167,200
Post treatment	
t-Butylhydroperoxyde(tBHP)	0,800
Water	6,200
Sodium sulfoxylate (SSF)	0,800
Water	11,200
Biocide	1,000
DiW	2,000
Flush water	20,00
Total product	1078

The analytical specifications gave the following results:

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Analytical Specifications		Results
Aspect:	white opaque emulsion	OK
Wet	white	white
Dry film	white powder	white powder
Solids(%)	29-31	30
Viscosity Sp rpm	max 500, LVT 2/60	50
pH	7.5-8.5	8.2
Gel, 82 mesh (g/l):	<0.05	<0.05
Powdering	soft, equal to standard	OK
Opacity	equal to standard (10)	10
Mechanical stability	good	OK
Dry density	0.550-610 g/cm ³	0.573
Ps (nm)	380-480	436

EXAMPLE 3

- 5 As in Example 1, where catalyst is fed with E1, no other catalyst, no inhibitors. Trials T-340, T-325, T-328 and T-329 contain, respectively 1.2 g, 1.0 g, 0.8 g and 0.6 g of catalyst (corresponding to 0.5%, 0.42%, 0.33%, 0.25% based on E1+E2 monomers). The resulting opacities are, respectively: 6; 9; 10; 10.

10 **EXAMPLE 4**

- As in Example 2, where catalyst is shot right before E1, no other catalysts, no inhibitors. Trials T-338, T-333, T-327, T-336 contain same gradation of catalyst as in Example 1 (corresponding to 0.5%, 0.42%, 0.33%, 0.25% based on E1+E2 monomers). The resulting opacities are 6.5; 9.5; 10; 10.
- 15

- 25 -

COMPARATIVE EXAMPLE 1

In the same recipe given in Example 2, apart from the existing catalyst (0.42% shot right before E1) a second catalyst (Catalyst-2, 0.13% based on E1+E2 monomers) has been added, which has been dosed parallel with E2. When E2 and Catalyst-2 are finished, 0.5 g (or 1.15%) of the inhibitor 4-Hydroxy Tempo are added in E3. Remaining part of the reaction is the same as in Example 2. The results are that the reference commercial product, this Comparative Example 1, inventive Example 1 and inventive Example 2 show the same opacity, all of them ranging at 9.5-10.

COMPARATIVE EXAMPLE 2

Examples 2A and 2B of US 4,594,363 have been reproduced. These reactions were carried as close to an exact reproduction as technically possible, using same raw materials and processes. Both reactions run smoothly, showing neither physical nor chemical problems. Resulting products were as expected in terms of solids%, pH, viscosity, absence of coagulum, etc. The opacity values obtained were, in the scale from 0 to 10 explained above, approximately 1.5 and 1.0 respectively. Even allowing for small differences in materials and processing, the differences in opacity compared to the above inventive Examples 1 and 2 are huge.

CONCLUSION

Inventive Examples 1 and 2 are identical in every aspect, except for the catalyst. In Example 1 (Trial 363), the catalyst is fed in parallel with E1 and both feeds end up at the same time. In Example 2 (Trial 333), the catalyst is shot in the reactor right before E1 starts. Neither there are added further catalysts, nor inhibitors nor scavengers to disturb the process in any way. In both Example 1 and Example 2 the amount of catalyst referred to monomers to be polymerized (monomers in E1+monomers in E2) is equal or lower than 0.45%, actually 0.33% and 0.42

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respectively. In this context, it should be noted that Examples 1 and 2 represent processes carried out under laboratory conditions (adopted for charges of 1 to 5 kg) similar to those of pilot plant conditions adopted for charges of 100 kg to 2000 kg. However, as mentioned above, when performing the process of the present invention on an industrial scale, i.e. in reactors with capacities of about 10 000 to 50 000 kg, preferably, the water soluble polymerization catalyst is used in a total amount of 0.10 to 0.30 by weight, based on the total amount of monomers in E1 *plus* E2,. Thus, this does mean that Examples 1 and 2 are outside the preferred range for the total catalyst amount.

The obtained products exhibit opacity values of 10. The product of Comparative Example 1 exhibits opacity values as good as those of inventive Examples 1 and 2, however using much higher catalyst amount and unwanted polymerization inhibitor.

According to the present invention, no catalyst with E2 is used, and the total amount of catalyst has to be equal or lower than 0.45%. By doing it this way, no sophisticated polymerization inhibitors are needed at all, which results in a simpler, cleaner and cheaper product and process, avoiding any undesired manual operations of preparing fresh polymerization inhibitors solutions.

Comparison versus US2009/256701 A1

Example 1 in US2009/256701 A1 was strictly followed. Only exception was the recommended surfactant, Alipal CO-436, which was substituted for Disponil FES 32 of Cognis A.G. which is very similar to AlipalCO-436 in composition and characteristics. Anyhow, in paragraph [0040] of US2009/256701 A1, the only part where surfactants are mentioned, basically any kind of surfactant is allowed.

In the seed production, paragraphs [0044] to [0047] of US2009/256701 A1 were followed, resulting on seeds of particle sizes ranging from 53 nm to 85 nm (Example 1 ranges are said to be 58nm to 65 nm) as measured with a particle size analyzer from Malvern Instruments, Zetasizer, Nano S.

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In the polymer core production, paragraphs [0049] to [0051] of US2009/256701 A1 were followed, resulting in cores of 141 and 151 nm (Example 1 only refers to one core at 166 nm). Since the equipment to measure particle sizes is not disclosed, the applicant preferred to prepare to close to the referred value to look for differences and trends. Based on these two cores, paragraphs [0053] to [0056] were strictly followed, particularly so for the stage of adding ammonia and α -methyl-styrene. Amounts of free monomer (styrene) we found to be 0.037% and 0.047% respectively, well in line with Example 1 result of 0.05%.

However, opacity is very low. When opacity is checked accordingly with the methodology explained above, the opacifying polymer obtained gives values ranging from 0 to 1, as opposed to opacity values from 9 to 10 provided by the opacifiers obtained by the present invention.

Another way of measuring the opacifying power of these particles is by measuring the dry density on the particles. The size of the void in the particle is the one and main important factor to get light scattering which tantamount to opacity. The size of the void can be determined by measuring the dry density of the particles. The particles resulting from the two reproductions of Example 1 gave dry density values of 1.0164 g/cm³ and 0.9865 g/cm³, way above the typical values of examples according to the present invention as indicated above of 0.592 g/cm³ and 0.573 g/cm³ and close to the theoretical dry density of the particle if no void is formed, i.e. 1.07 g/cm³.

Claims

1. A process for preparing an emulsion containing core-sheath-shell polymer
5 particles, without using any polymerization inhibitors or scavengers, said particles
being useful as opacifying agents, said process comprising the steps of:
- (i) emulsion polymerizing a core (A) from a core monomer system comprising,
as polymerized units, from 5 to 100 percent by weight, based on the weight of the
10 core, of hydrophilic monoethylenically unsaturated monomer containing acid
functionality, and from 0 to 95 percent by weight, based on the weight of the core,
of at least one nonionic monoethylenically unsaturated monomer;
- (ii) encapsulating said core (A) with a sheath polymeric layer (B) by emulsion
15 polymerizing a sheath monomer system (E1) comprising, as polymerized units, at
least 20 % by weight of a hydrophilic monoethylenically unsaturated monomer, at
least 20 % by weight of a hydrophobic monoethylenically unsaturated monomer,
and 1% to 20 % by weight of a hydrophilic monoethylenically unsaturated
monomer containing acid functionality, each based on the total weight of the
20 sheath polymeric layer, in the presence of said core, said sheath permitting
penetration of volatile, fixed or permanent bases;
- (iii) encapsulating said core-sheath particles with a polymeric shell (C) by
emulsion polymerizing a shell monomer system (E2) comprising, as polymerized
25 units, from 1 to 10 percent by weight, of hydrophilic monoethylenically unsaturated
monomer containing acid functionality, and from 90 to 99 percent by weight, of at
least one nonionic monoethylenically unsaturated monomer, each based on the
total weight of the polymeric shell;
- 30 (iv) neutralizing and swelling at elevated temperature the resultant core-sheath-
shell polymer particles with a volatile, fixed or permanent base, said swelling
taking place in the presence of a monomer-solvent-system comprising from 5-50

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% by weight of the at least one nonionic monoethylenically unsaturated monomer of said shell monomer system (E2), said monomer acting as a solvent, which, in turn, assists in the penetration of the base through the created polymer layers down to the core, wherein said monomer-solvent-system can be added before, after or during the addition of the base, and

(v) after the swelling step, reducing the level of said at least one nonionic monoethylenically unsaturated monomer of said monomer-solvent-system in step (iv) by polymerizing the monomer to less than 10,000 ppm, based on polymer solids, so as to produce an emulsion of particles which, when dried, contain a microvoid which causes opacity in compositions in which they are contained,

wherein a water soluble polymerization catalyst in a total amount of 0.05 to 0.45 % by weight, based on the total amount of monomers in E1 *plus* E2, is either fed in parallel with the sheath monomer system E1 into the polymerization reactor or is fed into the polymerization reactor right before emulsion polymerization of E1 in step (ii) starts.

2. The process of claim 1, wherein the total amount of polymerization catalyst is from 0.10 to 0.30 % by weight, based on the total amount of monomers in E1 *plus* E2.

3. The process of claim 1 or 2, wherein in step (iv) the monomer-solvent-system comprises from 15-30 % by weight of the at least one nonionic monoethylenically unsaturated monomer.

4. The process of any one of claims 1 to 3, wherein said core (A) is polymerized from a core monomer system comprising 30-40 % by weight (meth)acrylic acid and 60-70 % by weight methyl (meth)acrylate.

5. The process of any one of claims 1 to 4, wherein said sheath polymeric layer (B) is polymerized from a sheath monomer system (E1) comprising at least 20 % by weight, preferably at least 40 % by weight, of styrene, at least 20 % by

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weight, preferably at least 40 % by weight, of methyl (meth)acrylate, and 1% to 20 % by weight of (meth)acrylic acid.

6. The process of any one of claims 1 to 5, wherein the sheath monomer system (E1) is polymerized at least to 90% before the shell monomer system (E2) begins to be polymerized.

7. The process of any one of claims 1 to 6, wherein the total amount of sheath polymeric layer (B) is by weight from 1 to 5 times the weight of the core.

10

8. The process of any one of claims 1 to 7, wherein the shell monomer system (E2) comprises, as polymerized units, from 1 to 10 percent by weight, of (meth)acrylic acid, and from 90 to 99 percent by weight, of styrene.

15 9. The process of any one of claims 1 to 8, wherein the weight of said polymeric shell (C) constitutes more than 50% of the total monomer weight of the particles.

10 10. The process of any one of claims 1 to 9, wherein the shell monomer system (E2) is polymerized at least to 90% before step (iv) is started.

25 11. The process of any one of claims 1 to 10, wherein the volatile, fixed or permanent base is selected from the group consisting of ammonia, amines, potassium hydroxide, lithium hydroxide, sodium hydroxide, calcium hydroxide, sodium carbonate, sodium silicate, and transition metal amino compounds, preferably selected from potassium hydroxide or sodium hydroxide.

30 12. The process of any one of claims 1 to 11, wherein the elevated temperature in the neutralization and swelling step (iv) is from about 50 °C to about 120 °C, preferably from about 80 °C to about 95 °C.

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13. The process of any one of claims 1 to 12, wherein said at least one nonionic monoethylenically unsaturated monomer of said monomer-solvent-system in step (iv) is styrene.

5 14. The process of any one of claims 1 to 13, wherein in step (v) said monomer-solvent-system is polymerized by redox catalyst initiation after the swelling step is completed.

10 15. Emulsion containing core-sheath-shell polymer particles obtained by the process of any one of claims 1 to 14.

16. Core-sheath-shell polymer particles containing voids, obtained by at least partially drying the emulsion of claim 15.

15

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/001189

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F285/00 C08F2/22 C08J9/00 C09D5/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F C08J C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/156701 A1 (JOSEP HEUTS MARTIN PETER [US] ET AL) 18 June 2009 (2009-06-18) paragraphs [0005], [0021] - [0023], [0031], [0034], [0036], [0037], [0039]; claim 1; figure 1 and 2; example 1 -----	1,15,16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

13 July 2012

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Clement, Silvia

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/001189

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009156701 A1	18-06-2009	CN 101296949 A	29-10-2008
		EP 1940885 A2	09-07-2008
		US 2009156701 A1	18-06-2009
		WO 2007050326 A2	03-05-2007
