example when used in coatings for alkali sensitive substrates such as oak. Furthermore, the molecular weight of the oligomer must be relatively low to prevent that the viscosity of the alkaline solution will become too high or the dispersant action of the solubilized first stage polymer will be lost resulting in the formation of a product with a broad particle size distribution, lacking transparency and substantial formation of coagulum. Low molecular weight hydrophilic components are a disadvantage for the resulting coating properties.

[0007] EP 1008 635 B1 (Bardman et al.) describes a core-shell polymer where a first polymer contains from 0.5% to 7%. preferably from 1% to 5%, of a copolymerized monoethylenicallyunsaturated ionic monomer, based on the weight of the first polymer. A second polymer is polymerized in the presence of the first polymer. In this second polymer 0.25% to 6% (based on the weight of said second polymer) of copolymerized multi-ethylenically unsaturated monomer has to be present in the second stage. This patent uses a reactor pre-charge with a low concentration of inorganic salts, but there is no mention of the type of surfactant needed to obtain the desirable combination of properties. Even though a particle size from 30 to 500 nm is mentioned, all examples have particle sizes above 90 nm, so the dispersions do not have the required in can clarity. The use of chain-transfer agents is mentioned, but the patent is silent about the molecular weight range needed to have a good balance between minimal film-formation temperature and hardness.

SUMMARY OF THE ~~INVENTION~~DISCLOSURE

[0008] The problem of the disclosure~~invention~~ is to provide a process for the preparation of an aqueous dispersion of a vinyl polymer and to provide an aqueous dispersion obtainable by said process which dispersion has good film forming properties on one hand and good coating properties on the other hand and which does not have one or more of the abovementioned disadvantages of the prior art.

[0009] According to the disclosure~~invention~~ this problem has been solved by providing a process for the preparation of an aqueous dispersion of hydroplasticisable multiphase vinyl polymer particles comprising,

(1) a first polymerization step comprising

(1a) preparing an emulsion (1A) in water of a first monomer mixture (1a1), a surfactant (1a2) and a water soluble inorganic salt (1a3),

wherein the first monomers mixture (1a1) comprises

1) carboxylic acid functional monomers,

2) optional crosslinking monomers other than 1

3) vinyl monomers other than 1) and 2) and

4) optional chain transfer agents,

wherein surfactant (1a2) is a sulfur based anionic surfactant containing less than 60 wt% ethylene oxide and wherein the water soluble inorganic salt (1a3) content at the start of polymerization (1b) is between 0.01 and 3 g/kg water,

(1b) emulsion polymerizing the obtained emulsion 1A forming a hydroplasticisable first stage polymer particle dispersion (1B) said first stage polymer having a Tg from 10 to 125°C,

(2) a second polymerization step comprising

(2a) adding to dispersion 1B a second monomer mixture (2a1) comprising

1) monomers chosen from the same group as in the first monomer mixture (1a1)

2) optional monomers (2a2) comprising 2 or more ethylenically unsaturated groups for pre-crosslinking, preferably in an amount less than 2 wt%,

wherein carboxylic acid functional monomers in the second monomer mixture is present in an amount such that the acid value of the resulting second polymer is less than 23 KOH/g and

wherein the amount of monomer mixture (2a1) is between 10 and 90 wt% of the total weight of monomer mixtures (1a1) plus (2a1)

(2b) polymerizing second monomer mixture (2a1) to form a second stage polymer in the first particle dispersion (1B) to form a multiphase particle dispersion (2B),

(3) optionally hydroplasticising the multiphase particle dispersion (2B) by addition of base, preferably a volatile base, to a pH between 6.5 and 10.

(4) optionally adding a separate crosslinking agent for reaction with crosslinking monomers in monomer mixtures (1a1) or (2a1) or with unsaturated groups (2a2)

[0010] In the conditions as specified in the process according to the disclosure~~invention~~, a well defined particle size and particle size distribution are obtained in the first polymer dispersion, typically below 80 nm but even below 50 nm (expressed as the Z-average mean as measured by photon correlation spectroscopy), which particles can then be grown in the second polymerization step to the desired final particle size. The resulting polymer dispersion 2B has a good stability, a small particle size and very good in can clarity even at relatively high solid contents.

[0011] It is noted that in the second polymerisation step the second monomer mixture is added to dispersion 1B comprising hydroplasticisable first polymer and polymerised. This implies that in the second polymerisation step the first stage polymer is not yet hydroplasticed, i.e. not neutralised before the second stage polymerisation. The pH during the second stage polymerisation therefore is low; typically below 7, preferably less than 6.5, more preferably less than 6. The vinyl polymer dispersion can be but does not need to be hydro-plasticized by the addition of base at the end of the polymerization process. After neutralization step 3 the pH is 7 to 10, preferably 7 – 9. One advantage of the disclosure~~invention~~ is that it allows to formulate the aqueous dispersion to a coating composition by mixing in coating additives at lower viscosity before hydroplasticising. A further advantage of the coating composition that has not been (fully) neutralised and has a pH of below 8, 7.5 or even below 7 is that it can advantageously be used on substrates that are sensitive to high pH, as for example certain wood substrates.

[0012] Typically, in the polymerization step (2b) the multiphase particles in the multiphase particle dispersion (2B) have an average particle size of less than 80 nm and preferably a transparency value of at least 35 at a solids content of at least 35 wt%. The transparency value being defined as measured using a LICO 200 as described in more detail below. The solids content here and hereafter (unless specified differently) is the dry non/volatile weight of the polymer components specified above as determined by ISO 3251.

[0001] It is noted that EP338486 and US 4,894,397 (Morgan et al.) describes an emulsion polymerization process in which in the first stage a hydrophilic low molecular weight polymer is made and in which in the second stage a hydrophobic second polymer is formed into the first stage polymer followed by addition of a base thus producing an inverted core-shell emulsion. However, the document is silent about obtaining good film forming properties while preserving good coating properties. Further, it is not described how to achieve good particle size control and the polymer dispersions obtained have a low solids content and-or a lack of transparency. The comparative examples show that the process according to Morgan results in polymer dispersions having a significantly larger particle size than the dispersions of the disclosure~~invention~~, resulting in a lower in can clarity and poorer film forming properties.

[0001a] In an embodiment, there is provided a process for the preparation of an aqueous dispersion of hydroplasticisable multiphase vinyl polymer particles comprising,

(1) a first polymerization step comprising

(1a) preparing an emulsion (1A) in water of a first monomer mixture (1a1), a surfactant (1a2) and water soluble inorganic salt (1a3),

wherein the first monomers mixture (1a1) comprises

1) carboxylic acid functional monomers,

2) optional crosslinking monomers other than 1

3) vinyl monomers other than 1) and 2) and

4) optional chain transfer agents,

wherein surfactant (1a2) is a sulfur based anionic surfactant containing less than 50 wt% ethylene oxide and

wherein the water soluble inorganic salt (1a3) content at the start of polymerization (1b) is between 0.01 and 3 gr/kg water,

(1b) emulsion polymerizing the obtained emulsion 1A forming a hydroplasticisable first stage polymer particle dispersion (1B) said first stage polymer having a Tg calculated from the Fox equation from 10 to 125°C,

wherein the first particle dispersion (1B) has a particle size below 50 nm (Z average mean as measured by dynamic light scattering).

(2) a second polymerization step comprising

(2a) adding to dispersion 1B a second monomer mixture (2a1) comprising

1) monomers chosen from the same group as in the first monomer mixture (1a1)

2) optional monomers (2a2) comprising 2 or more ethylenically unsaturated groups for pre-crosslinking, preferably in an amount less than 2 wt%,

wherein carboxylic acid functional monomers in the second monomer mixture is present in an amount such that the acid value of the resulting second polymer is less than 23 mg KOH/g and

wherein the amount of monomer mixture (2a1) is between 10 and 90 wt% of the total weight of monomer mixtures (1a1) plus (2a1)

(2b) polymerizing second monomer mixture (2a1) to form a second stage polymer in the first particle dispersion (1B) to form a multiphase particle dispersion (2B)

(3) optionally hydroplasticising the multiphase particle dispersion (2B) by addition of base, preferably a volatile base, to a pH between 6.5 and 10, preferably 9,

(4) optionally adding a separate crosslinking agent for reaction with crosslinking monomers in monomer mixtures (1a1) or (2a1) or with unsaturated groups (2a2).

[0001b] In an embodiment, there is provided a multiphase vinyl polymer particle dispersion obtainable according to the method as defined herein, wherein the multiphase particles have an average particle size of less than 80 nm.

[0001c] In an embodiment, there is provided a coating composition comprising the multiphase vinyl polymer particle dispersion as defined herein and one or more further coating additives.

[0001d] In an embodiment, there is provided a process for preparing a coating composition comprising providing a hydroplasticisable dispersion 2B obtained by a process comprising,

(1) a first polymerization step comprising

(1a) preparing an emulsion (1A) in water of a first monomer mixture (1a1), a surfactant (1a2) and water soluble inorganic salt (1a3),

wherein the first monomers mixture (1a1) comprises

1) carboxylic acid functional monomers,

2) optional crosslinking monomers other than 1

3) vinyl monomers other than 1) and 2) and

4) optional chain transfer agents,

wherein surfactant (1a2) is a sulfur based anionic surfactant containing less than 60 wt% ethylene oxide and

wherein the water soluble inorganic salt (1a3) content at the start of polymerization (1b) is between 0.01 and 3 gr/kg water,

(1b) emulsion polymerizing the obtained emulsion 1A forming a hydroplasticisable first stage polymer particle dispersion (1B) said first stage polymer having a Tg calculated from the Fox equation from 10 to 125°C,

(2) a second polymerization step comprising

(2a) adding to dispersion 1B a second monomer mixture (2a1) comprising

1) monomers chosen from the same group as in the first monomer mixture (1a1)

2) optional monomers (2a2) comprising 2 or more ethylenically unsaturated groups for pre-crosslinking, preferably in an amount less than 2 wt%,

wherein carboxylic acid functional monomers in the second monomer mixture is present in an amount such that the acid value of the resulting second polymer is less than 23 mg KOH/g and

wherein the amount of monomer mixture (2a1) is between 10 and 90 wt% of the total weight of monomer mixtures (1a1) plus (2a1)

(2b) polymerizing second monomer mixture (2a1) to form a second stage polymer in the first particle dispersion (1B) to form a multiphase particle dispersion (2B)

(3) hydroplasticising the multiphase particle dispersion (2B) by addition of base, preferably a volatile base, to a pH between 6.5 and 10, preferably 9,

(4) optionally adding a separate crosslinking agent for reaction with crosslinking monomers in monomer mixtures (1a1) or (2a1) or with unsaturated groups (2a2),

wherein hydroplasticisable dispersion 2B is formulated to a coating composition by addition of coating additives before or during the hydroplasticising step (3).

[0001e] In an embodiment, there is provided the use of the multiphase vinyl polymer particle dispersion as defined herein for the manufacture of a coating composition having a pH between 4 and 8 for coating wood.

DETAILED DESCRIPTION OF THE INVENTION

[0013] In the first polymerization step the monomer mixture (1a1), the specified sulfur based anionic surfactant (1a2) and preferably also an initiator are mixed in water to prepare an emulsion (1A) wherein the water soluble inorganic salt (1a3) is present in a specified low amount (1a1). In principle the components in the emulsion 1A can be mixed in any several different orders as known in the art before polymerization step 1b. The monomers in the monomer mixture can be provided premixed or separately, continuous or in one or more portions, before during or after charging water, surfactant, initiator and before, during or after heating to the reaction temperature.

[0014] In a preferred embodiment however, an emulsion polymerization reactor is charged with water and a sulfur based anionic surfactant. The pre-charge of water and surfactant is heated to the reaction temperature. Emulsion polymerization reactions can be carried out over a wide temperature range; for example between 50 and 120°C, preferably between 60 and 100 °C, but in order to have a sufficiently fast conversion of monomer to polymer a temperature between 70 and 95 °C is preferably selected when the reaction is carried out under atmospheric pressure. A free radical initiator is normally added to the

wherein the amount of monomer mixture (2a1) is between 10 and 90 wt% of the total weight of monomer mixtures (1a1) plus (2a1)

(2b) polymerizing second monomer mixture (2a1) to form a second stage polymer in the first particle dispersion (1B) to form a multiphase particle dispersion (2B)

(3) optionally hydroplasticising the multiphase particle dispersion (2B) by addition of base, preferably a volatile base, to a pH between 6.5 and 10, preferably 9.

(4) optionally adding a separate crosslinking agent for reaction with crosslinking monomers in monomer mixtures (1a1) or (2a1) or with unsaturated groups (2a2).

2. The process according to claim 1, wherein in the polymerization step (2b) the multiphase particles in the multiphase particle dispersion (2B) have an average particle size of less than 80 nm (Z average mean as measured by dynamic light scattering).

3. The process according to claim 1 or 2, wherein the multiphase particle dispersion (2B) has a transparency value of at least 35 at a solids content of at least 35 wt%.

4. The process according to claims 1 to 3, wherein the first monomer mixture (1a1) comprises

1) 1-45 wt% carboxylic acid functional monomers (wt% relative to the total weight of monomers in the first monomer mixture)

2) 0-20 wt% optional crosslinking monomers other than 1,

3) 98.5-50 wt% vinyl monomers other than 1) and 2),

4) optional chain transfer agents.

5. The process according to claims 1 to 4, wherein the amount of surfactant (1a2) is less than 2 wt% relative to the total amount of the first monomer mixture (1a1).

6. The process according to claims 1 to 5, wherein the surfactant (1a2) is chosen from the group of salts of alkylethoxylate sulfates and sulfonates, alkylphenolethoxylate sulfates and sulfonates, alkylsulfates and sulfonates, alkylaryl sulfonates, sulfosuccinates, sulfur-based surfactants containing less than 50 wt% ethylene oxide, sulfur-based surfactants having an ethylenically unsaturated bond that can participate in a free radical polymerization and mixtures thereof.