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(54) **Title**: USE OF A POLYMER COMPOSITION

(57) **Abstract**: There is described use of a biorenewable copolymers in one or more of: in a topical and/or personal care composition, as a binder for toner, as an encapsulating agent for a colorant, as a hybrid colorant, as additive for sheet moulding compounds, as a plastic pigment, as a filler for composite materials such as concrete, as a filler for coatings and/or waxes; and/or as a spacer in a display; where the biorenewable copolymer comprises (a) at least 8. 5 wt-% preferably >=20 wt-% of a higher itaconate diester (preferably dibutyl itaconate -DBI); (b) less than 23 wt-% acid monomer but also sufficient to have an acid value less than 150 mg KOH/g of polymer, (c) optionally with less than 50 wt-% of other itaconate monomers, and (d) optionally less than 77 wt-%of other monomers not (a) to (c). The DBI may be biorenewable. One embodiment is an aqueous dispersion of vinyl sequential polymer of two phases: A) 40 to 90 wt-% of a vinyl polymer A with Tg from -50 to 30°C; and B) 10 to 60 wt-% of a vinyl polymer B with Tg from 50 to 130°C; where DBI is used to prepare A and/or B and polymer A has from 0.1 to 10 wt-% of at least one acid-functional olefinically unsaturated monomer.

USE OF A POLYMER COMPOSITION

The present invention relates to polymers and polymeric materials obtained and/or obtainable from certain 2-methylidenebutanedioate diester monomers (also referred to herein as higher itaconate diesters) to a process for making such a polymers and their use to prepare for example coatings, inks and/or adhesives. It is preferred that polymers of the invention, and/or the higher itaconate diesters, are obtained from bio-renewable sources.

Many conventional polymers often suffer from undue sensitivity to water. This is especially true for water based polymer emulsions which can suffer from an increased water sensitivity compared to their solvent borne counterparts. A common way of countering this is to incorporate very hydrophobic monomers, such as butyl acrylate (BA) or 2-ethylhexyl acrylate (EHA). However, as homopolymers from these monomers have an extremely low Tg, incorporation of large amounts of these monomers produces a composition which is very often too soft (low Tg), yet is not sufficient hydrophobic if the amount of these monomer is sufficiently low to produce a satisfactory Tg. This might in turn be mitigated by introduction of high Tg, hydrophobic monomer such as styrene and the like. However polymer compositions comprising stryenic monomers, suffer from reduced outdoor durability because of the inherent UV sensitivity of styrene.

We have now surprisingly found that the dilemma described above can be solved. Good water resistance and low water sensitivity combined with high hardness and high elongation at break may be achieved by introducing higher ester itaconates such as dibutyl itaconate (DBI) as the hydrophobic monomer. Even though these monomers are very hydrophobic, the applicant has unexpectedly found that polymers made from higher itaconate esters do not suffer the same reduction in hardness typically observed for copolymers made from high concentrations of the typical hydrophobic monomers such as butyl acryate (BA) and/or 2-ethyl hexyl acrylate (EHA).

Itaconate ester monomers have been described for very many years. However they have not been widely used to make commercial vinyl polymers because they are expensive and difficult to process. Prior art documents describe the use of itaconate esters only in general terms and typically describe or exemplify lower itaconate diesters such as dimethyl itaconate (DMI). The few documents which describe higher itaconate esters are described below.

US4206292 (Kureha Kagaku Kogyo Kabushiki Kaisha) describes a vinyl chloride resin coating with a smooth surface. The coating comprises: (1) 100 parts of vinyl chloride polymer; and (2) 0.1 to 30 parts of a polymer processing aid comprising: (A) 10 to 100 parts of a copolymer comprising 20 to 99% of an alkyl methacrylate, 1 to 70% of a dialkyl itaconate, and 0 to 60% of a copolymerizable monomer; and (B) 0 to 90 parts of a copolymer comprising 80 to 100% of an alkyl methacrylate, and 0 to 20% of a copolymerizable monomer. The vinyl chloride resins are not prepared from bio-based or other environmentally benign sources. The maximum amount of DBI that is used in the examples is 30% by weight.

US4547428 (Monsanto) describes a terpolymer comprising repeating units derived from an olefin, a diester of an addition polymerizable unsaturated dicarboxylic acid, and a solubilizing monomer which promotes compatibility between the terpolymer and a vinyl halide polymer. A granular form of the processing aid and a method for its preparation are also disclosed. These polymers are not suitable for coating applications and the highest concentration of DBI in the examples is 17% by weight.

US4588776 (Monsanto) describes a polymer composition comprising a blend of a vinyl halide polymer and a particulate terpolymer having a molecular weight of at least 100,000 and a glass transition temperature of at least 50°C. The terpolymer comprises repeating units derived from an olefin, a diester of an addition polymerizable unsaturated dicarboxylic acid, and a solubilizing monomer which promotes compatibility of the terpolymer with the vinyl halide polymer. These polymers are used to prepare shaped plastic articles and not for coating applications. The maximum concentration of DBI used in the examples is 17% by weight.

US6951909 (3M) describes a polymerizable system comprises an organoborane, at least one polymerizable monomer, and a work-life extending agent. These compositions are not suitable for coating applications and the maximum concentration of DBI used in the examples is 17% by weight.

WO11/073417 (DSM) discloses an aqueous emulsion comprising at least a vinyl polymer, said vinyl polymer comprising: a) 45 to 99 wt-% of itaconate ester monomers having formula (I), wherein R and R' are independently an alkyl or an aryl group; b) 0.1 to 15 wt-% of ionic or potentially ionic unsaturated monomers; c) 0 to 54 wt-% of unsaturated monomers, different from a) and b); and 0.9 to 54.9 wt-% by weight of total monomers of a chaser monomer composition added subsequently and polymerised after the polymerisation of monomers a), b) and c); wherein a) + b) + c) and the chaser monomer composition add up to 100 wt-%; and wherein the aqueous emulsion contains less than 0.5 wt-% free itaconate ester monomers of formula I based on the total weight of the aqueous emulsion. Although it is a stated object of the invention to provide a vinyl polymer with a high total concentration of itaconate ester monomers (see page 2, lines 14 to 17) in practise the larger proportion of such itaconate esters are lower itaconate esters (i.e. esters of small alkyl groups such as DMI). This document does not teach that it would be desirable to use a high concentration of higher itaconate esters (i.e. esters of large alkyl groups such as DBI). Indeed '417 states that itaonate esters are difficult to process (see page 2, lines 23 to 25) which combined with the teaching of the examples demotivates a reader to incorporated large amounts of hydrophobic higher itaconate esters like DBI in a copolymer.

The only examples in '417 that describe use of a DBI monomer are Examples 2, 4, 5 and 6. The amounts of DBI and other monomers used to prepare these Examples is given in Table A below. It can be seen that DBI is used as co-monomer only at a low concentrations in the final copolymer prepared in these Examples (at a maximum of 22.7 wt-%) which are each also prepared with significant amounts of another hydrophobic monomer butyl acrylate (BA). A styrene chaser monomer is always present in the final product (at least 1,5 wt-%). These examples teach away from using DBI or other higher itaconate esters to replace common hydrophobic monomers such as BA, EHA and/or styrene. No significant improvement is seen in film properties such as hardness and water sensitivity of the copolymers prepared in this document.

GB1009486 (Borden) describes a latex of composite polymeric particles where the core and shell may comprise a copolymer of a vinylidene chloride and an ester of an alpha unsaturated aliphatic acid (the amount of ester in the shell being greater than the core). One example (Example 3) describes use of dibutyl itaconate (DBI) as the ester in an total amount of 17% by weight of total monomers (5% in the outer shell and 12% in an inner non core layer). These composite multi-layer polymer particles address a problem of providing a water vapour barrier coating for paper and the like and they use much lower amounts of DBI than the present invention.

Table A (prior art DBI examples from WO11/073417)

Example of ‘417	Composition	Monomers / wt-% (1 d.p.)									
		AA	BA	MMA	Plex 652	DAAM	MAA	DMI	DBI	S (chaser)	Total Itaconate
Ex 2	Initial feed	2.0	28.0	-	-	-	-	45.0	25.0	-	60.0
	Single phase copolymer	1.8	25.2	-	-	-	-	40.5	22.5	10.0	63.0
Ex 4	First feed	4.4	32.4	13.2	-	-	-	20.0	30.0	-	50.0
	Second feed	5.0	11.0	34.0	-	-	-	45.0	5.0	-	50.0
	Sequential copolymer	4.1	25.5	15.8	-	-	-	22.7	22.7	9.1	45.4
Ex 5	First feed	4.2	30.0	9.5	8.4	-	-	19.1	28.7	-	47.8
	Second feed	4.7	9.3	28.8	9.5	-	-	42.9	4.7	-	47.6
	Sequential copolymer	3.9	23.6	12.2	7.9	-	-	21.8	21.8	8.7	43.6
Ex 6	Olg initial feed	35.4	-	-	-	8.0	5.0	51.6	-	-	51.6
	Olg-plr initial feed	-	41.2	-	--	-	-	17.6	41.2	-	58.8
	Polymer - oligomer	26.8	10.7 (inc 2.2 BA chaser)	-	-	6.1	3.8	42.7	8.5	1.5	51.2

In Examples 2, 4 and 5 of WO11/073417-the chaser monomer was 100 wt-% styrene, in Example 6 the chaser monomer composition was a mixture of styrene (40 wt-%) and BA (60 wt %).

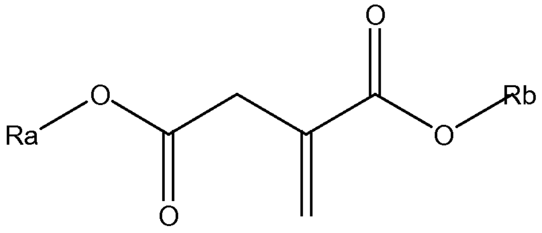
US3766112 describes a high gloss latex for floor polish comprising a chlorinated paraffin wax with a polyvinyl pyrrolidone protective colloid. Four monomer components used to prepare the colloid: styrene (70 to 85%), 2-ethylhexyl acrylate (EHA) (5 to 15%) (meth)acrylic acid (3 to 10%) and a fourth monomer (1 to 5 %) all percentages by weight of total monomers of the polyvinyl pyrrolidone. One of the seven monomers suggested as the fourth monomer is DBI. These polymers address the problem of providing high gloss floor coatings and DBI is used in much lower amounts than in the present invention.

US2011-144265 (Durant Yvon) describes polymer particles prepared by polymerising esters of itaconic acid in the presence of seed particles to control particle size.

WO2002-068479 (3M) describes polymerisation of (meth)acrylic monomers using a two part initator system of organoborane amine complex and an activator. One of the many different examples (Example 6) is prepared from a low amount of DBI (20% by weight) and this example does not use any other itaconate diester monomer.

WO 2007-026949 (Nippon Cat.) describes emulsion resin compositions that have a minimum film forming temperature (MFT) of ≤ 0°C and are free of volatile organic compounds (VOC). These compositions are obtained by mixing a polymer with a high glass transition temperature (high Tg) with a polymer with low Tg. These polymers may be water dispersible and a wide variety of carboxy acid fucnctional acid monomers are suggested to impart such water solubility including itaconic acid, mono-methyl itaconate ester and mono butyl itaconate ester (see page 12 lines 12 to 14). No other itaconic acid derived monomers are described and a reader of this document would have no reason to incorporate (non carboxy-acid functional) itaconate diester monomers.

The esters (including both mono and di-esters) of 2-methylidenebutanedioate (also referred to herein generically as itaconate esters) may be represented by Formula A:



(A)

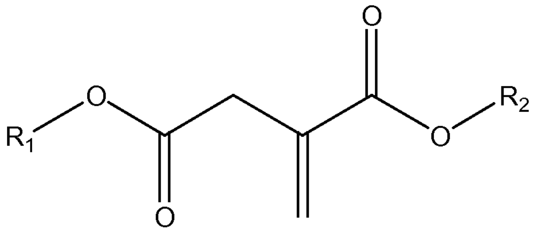
where Ra and Rb can independently be H or any optionally substituted hydrocarbo moiety (such as any aliphatic, cycloaliphatic or aromatic moieties) provided that Ra and Rb are other than H (which is not an ester but itaconic acid).

It has been found that certain hydrophobic itaconate diesters (e.g. di esters of large alkyl groups) are difficult to use in conventional polymerisation processes (especially in aqueous emulsion polymerisation) and are also expensive. Therefore there has been a reluctance to use such hydrophobic higher itaconate esters at high concentrations in such processes.

It is an object of the present invention to solve some or all of the problems identified herein for example by providing polymeric materials made from larger amounts of higher itaconate esters (such as DBI) optionally together with other olefinically unsaturated monomers (also optionally from a biorenewable source). The resultant polymers may have various additional advantages as well as those already described herein such as good film forming at room temperature with the films having high flexibility (elasticity) and good resistance to blocking.

Therefore broadly in accordance with the present invention there is provided a copolymer composition comprising (preferably consisting essentially of):

(a) greater than 8.5 wt-%, usefully ≥ 15 wt-%, preferably at least 20 wt-%, more preferably at least 24 wt-%, more preferably at least 30 wt-% for example at least 45 wt-% of at least one monomer represented by Formula 1

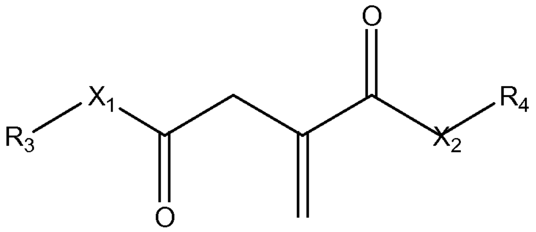


Formula 1

where both R_1 and R_2 independently represent an optionally substituted hydrocarbo moiety having from 4 to 10 carbon atoms.

(b) optionally at least one hydrophilic monomer preferably in an amount less than 23 wt-%, more preferably 0.5 to 15 wt-%, and also in an amount sufficient that the resultant polymer has an acid value of from 0 to 150 mg KOH / g, preferably less than 150 mg KOH / g, more preferably from 3 to 100 mg KOH per g of polymer,

(c) optionally less than 50 wt-%, for example from 0.01 to 10 wt-% and/or one or more monomers represented by Formula 2



Formula 2

(Formula 2 including itaconate diester monomers being other than those represented by Formula 1)

where R_3 and R_4 independently represent H or an optionally substituted hydrocarbo moiety having from 1 to 20 carbon atoms

X_1 and X_2 independently represents O or NR_5 where R_5 denotes H or an optionally substituted hydrocarbo moiety having from 1 to 20 carbon atoms with the proviso that when X_1 and/or X_2 are O then the respective R_3 and/or R_4 attached to the oxy group independently represent an optionally substituted hydrocarbo having from 1 to 3 carbon atoms

(d) optionally less than 80 wt-%, usefully less than 77 wt-%, preferably less than 75 wt-%, more preferably < 70 wt-%, most preferably < 65%wt-% of monomers other than components (a), (b) or (c).

where the weight percentages (also denoted herein as "% by weight" and/or "wt-%") of amounts of (a), (b) (c) (d) are calculated as a proportion of the total (weight) amount of (a) + (b) + (c) + (d) which thus totals 100%.

Copolymers of the invention may also be limited by one or more of the following optional provisos:

(I) when component (a) consists of DBI in an amount of less than 30% by weight of the total monomers then the copolymer is substantially free of any chloro groups; and

(II) when component (a) consists of DBI in an amount of less than 23% by weight of the total monomers then the copolymer is prepared by other than an emulsion polymerisation method in which a chaser monomer is used; and

(III) when component (a) consists of DBI in an amount of less than 23% by weight of the total monomers then if component (d) is present, component (d) is other than styrene or a mixture consisting of butyl acrylate (60 wt-% of mixture) and styrene (40 wt-% of mixture)

(IV) the copolymer is substantially free of styrene (preferably styrene free), more preferably component (d) if present is other than styrene or a mixture consisting of butyl acrylate (60 wt-% of mixture) and styrene (40 wt-% of mixture), more preferably component (d) if present is other than styrene (S), butyl acrylate (BA), 2-ethyl hexyl;acrylate (EHA) or mixtures thereof.

(V) is prepared by other than an emulsion polymerisation method in which a chaser monomer is used; and

(VI) the copolymer is prepared by other than an emulsion polymerisation method in which a chaser monomer is used optionally this proviso applying only when component (a) consists of DBI preferably in an amount of from 8.5 to 15% by weight of the total monomers (a) + (b) + (c) + (d).

(VII) when component (a) consists of DBI then component (a) is present in an amount other than 8.5 wt-%, 21.8 wt-%, 22.5 wt-% or 22.7 wt % of the total monomer composition, preferably other than from 8 wt-% to 23 wt%,

(VIII) when component (a) consists of DBI then component (a) is present in an amount other than 4.7 wt-%, 5.0 wt-%, 8.5 wt-%, 21.8 wt-%, 22.5 wt-%, 22.7 wt %, 25.0 wt-%, 28.7 wt-%, 30,0 wt-% or 41,2 wt-% of the total monomer composition, preferably other than from 4 wt-% to 42 wt%,

(IX) the copolymer is obtained other than from a polymerisation of a dimethyl itaconate (DMI) and dibutyl itaconate (DBI) in the respective weight ratio of 15 to 85 in the presence of poly diethyl itaconate seed polymer; more preferably the copolymer is obtained other than from polymerisation of dialkyl itaconate(s) in the presence of a poly diethyl itaconate seed polymer; most preferably the copolymer is obtained other than from polymerisation in the presence of a poly dialkyl itaconate seed polymer;

(X) if polymerisation of the copolymer occurs in the presence of an initator system comprising organoborane amine complex and an activator then component (a) is present in an amount greater than 20 wt-%, preferably at least 24 wt-% of total monomers (a) + (b) + (c) + (d).

As used herein the term seed polymer is as defined in US2011-144265 (e.g. see paragraph [007]) i.e. a polymer seed particle is dispersed in an aqueous medium such that the seed particle absorbs further added (co)monomer and the seed particle is present at a concentration to allow for control of particle size of that (co)monomer.

Preferably the copolymer composition is an emulsion copolymer (usefully an emulsion polymer prepared where no chaser monomer has been used), more preferably an aqueous emulsion copolymer, most preferably an aqueous coating composition.

Conveniently the composition is substantially free of polyvinyl chloride polymer and/or chlorinated paraffin wax, more preferably is substantially free of any monomer comprising chloro groups, most preferably is substantially free of any species comprising Cl whether as a substituent, atom, di-molecule, ion or otherwise

Broadly there is provided in a yet further aspect of the present invention a process for preparing a copolymer comprising the step of polymerising polymer precursors in a polymerisation method the polymer precursors comprising component (a), component (b) and optionally component (c) and/or component (d) as described above.
to obtain a copolymer.

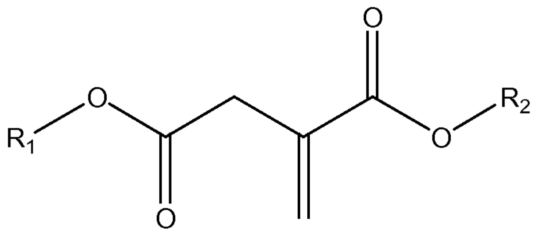
Preferably the polymerisation method is selected from an emulsion and/or suspension polymerisation.

Preferably the copolymer is an emulsion copolymer and/or a dispersion of polymeric beads.

Another aspect of the invention broadly provides for a copolymer obtained and/or obtainable by a process of the present invention.

Hydrophobic component (a) (higher itaconate esters)

The present invention is particularly concerned with polymers obtained and/or obtainable from a narrow class of itaconate diester monomers selected from the broad disclosure of general itaconate esters of Formula A. Thus the hydrophobic component (a) comprises itaconate diester(s) of Formula 1:



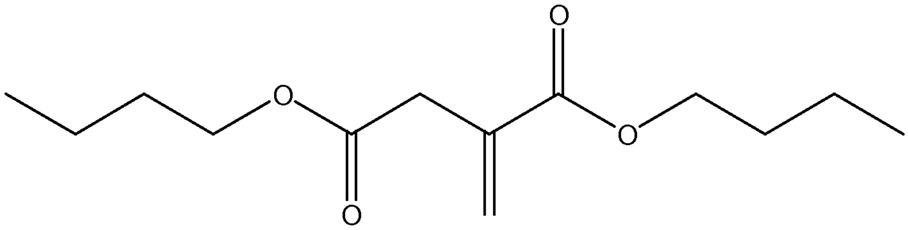
Formula 1

where both R_1 and R_2 independently represent an optionally substituted hydrocarbo moiety having from 4 to 10, preferably from 4 to 8, more preferably from 4 to 6, most preferably 4 carbon atoms.

The diesters of Formula 1 are also referred to herein as higher itaconate diesters.

Usefully R_1 and R_2 may independently represent optionally substituted $C_{4\text{-}10}$alkyl and/or $C_{4\text{-}10}$aryl, more usefully $C_{4\text{-}8}$alkyl and/or $C_{4\text{-}8}$aryl and most usefully $C_{4\text{-}6}$alkyl, even more usefully butyl (n-butyl being especially useful).

Whilst R_1 and R_2 may be different, more conveniently they represent identical moieties. Especially preferred examples of Formula 1 include those where R_1 and R_2 are identical, such di(benzyl)itaconate, di(phenyl)itaconate, di-n-butyl itaconate, di-i-butyl itaconate, and/or di-2-ethyl hexyl itaconate. Where R_1 and R_2 both represent n-butyl Formula 1 represents dibutyl 2-methylidenebutanedioate (also referred to herein as di(n-butyl)itaconate or DBI) which has the following structure:



DBI is the most preferred monomer for use as component (a) in the present invention.

The itaconate functional component (a) is present in the compositions and/or copolymers of the invention in an amount of greater than 8.5% wt-%, usefully ≥ 15 wt-%, preferably at least 20 wt-%, usefully at least 24 wt-%, more usefully at least 30 wt-%, even more usefully at least 35 wt-% and most usefully at least 40 wt-%, for example at least 50% based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Conveniently the itaconate functional component (a) may be present in the compositions and/or copolymers of the invention in an amount of less than 80 wt-%, more conveniently less than 70 wt-%, even more conveniently less than 65 wt-%, most conveniently less than 58 wt-%, and for example less than 55 wt-%; based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Preferably the itaconate functional component (a) may be present in the compositions and/or copolymers of the invention in an amount of from 20 to 80 wt-%, more preferably from 24 to 70 wt-%, even more preferably from 30 to 65 wt-%, most preferably from 35 to 65 wt-%, for example from 40 to 55 wt-% based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Hydrophilic component (b) (acid functional monomers)

Suitable hydrophilic monomers of component (b) are those that are co-polymerisible with the hydrophobic monomer(s) of component (a) and are water soluble. Conveniently the at least one hydrophilic monomer of component (b) may comprise at least one activated unsaturated moiety as defined herein.

Usefully the hydrophilic monomer of component (b) is an acid functional ethylenically unsaturated monomer for example an acid functional acrylic monomer.

It will be understood that when referring to acid functional and/or acidic components herein this may relate to acidic moieties and/or potential acidic moieties which under the conditions of use may form acidic groups (e.g. anhydrides). An acid bearing monomer could be polymerised as the free acid or as a salt, e.g. the ammonium and/or alkali metal salt thereof. References herein to acids should therefore also be understood to include suitable salts and/or derivates thereof (such as anhydrides and/or acid chlorides thereof).

Preferred hydrophilic monomers comprise, advantageously consist essentially of, at least one ethylenically unsaturated carboxylic acid although other acid groups such as optionally substituted organo phosphoric and/or sulphonic acids may also be used.

Examples include phosphated alkyl (meth)acrylates, sulphonic acids (and derivatives thereof) of arylalkylenes, sulphonic acids (and derivatives thereof) of alkyl (meth)acrylates and/or other organo substituted sulphonic acids (such as acrylamidoalkyl sulfonic acids).

Preferred arylalkylene sulphonic acids are those where the arylalkylene moiety comprises optionally hydrocarbo substituted styrene, conveniently optionally C_{1-10}hydrocarbyl substituted styrene more conveniently optionally C_{1-4}alkyl substituted styrene. Useful acids are sulphonic acid substituted derivatives of stryenic compounds selected from the group consisting of styrene, α-methyl styrene, vinyl toluene, t-butyl styrene, di-methyl styrene and/or mixtures thereof. Especially preferred is styrene p-sulphonic acid and its corresponding acid chloride styrene p-sulphonyl chloride.

Preferred phosphated organo acids comprise phosphated (meth) acrylates optionally substituted for example with one or more hydroxyl groups, for example phosphated hydroxy(meth)acrylates and C_{1-4}alkyl esters thereof.

Other preferred hydrophilic monomers of component (b) comprises partial acids of multivalent esters, more preferably. half esters of diesters, most preferably mono acid half itaconate esters (i.e. those esters of Formula A where either R_a or R_b is H). Itaconic acid is also another example of a (di)acid functional monomer which is also suitable as component (b).

More preferred acids have one ethylenic group and one or two carboxy groups. Most preferably the acid(s) (and/or suitable acid derivative(s) thereof) are selected from the group consisting of: acrylic acid (and copolymerisable oligomers thereof), beta carboxy ethyl acrylate, citraconic acid, mesaconic acid, crotonic acid, fumaric acid, itaconic acid, maleic acid, methacrylic acid, methylene malonic acid, anhydrides thereof, salts thereof, acid chlorides thereof, combinations thereof in the same species and/or mixtures thereof.

Especially preferred monomers that may comprise component (b) are selected from:

acrylic acid, methacrylic acid, beta carboxy ethyl acrylate, methylene malonic acid, maleic anhydride, itaconic acid, itaconic anhydride, phosphated hydroxyl ethyl methacrylate (phosphated HEMA), phosphated hydroxyl ethyl acrylate (phosphated HEA), phosphated hydroxyl propyl methacrylate (phosphated HPMA), phosphated hydroxyl propyl acrylate (phosphated HPA), sulphonated styrene (and its chloride), 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and ethylmethacrylate-2-sulphonic acid.

Particularly preferred acid monomers are acrylic acid, methacrylic acid, beta carboxy ethyl acrylate, itaconic acid, and/or itaconic anhydride.

For emulsion polymerization acrylic acid, methacrylic acid, beta carboxy ethyl acrylate, and/or itaconic acid may be convenient. For SAD copolymerization, acrylic acid, methacrylic acid, and/or itaconic anhydride are preferred.

The hydrophillic monomer component (b) may optionally be absent from the compositions and/or copolymers of the invention but if present is present in an amount of more than a trace amount usefully greater than or equal to 0.1 wt-%, conveniently greater than or equal to 0.5 wt-%, for example greater than 0.8 wt-% based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Conveniently component (b) if present is present in the compositions and/or copolymers of the invention in an amount of less than 23 wt-%, more conveniently less than or equal to 20 wt-%, even more conveniently less than or equal to 10 wt-%, most conveniently ≤ 5 wt-%, such as ≤ 3 wt-%; for example ≤ 1 wt % based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Preferably, component (b) may be used in a total amount from 0 to 10 wt-%, more preferably from about 0.1 to about 5 wt-%, even more preferably from about 0.1 to about 3 wt-%, most preferably from about 0.5 to about 1% by weight based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

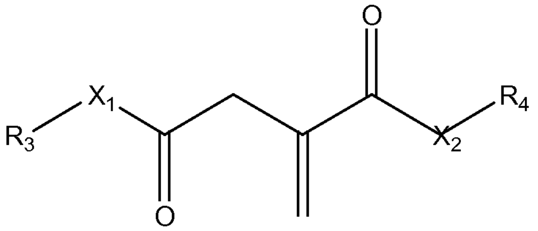
Conveniently component (b) may be used in a total amount sufficient that the resultant polymer has an acid value (AV) of between 3 and 100 mg KOH per g of solid polymer, preferably from 8 to 80 mg KOH per g, more preferably from 15 to 65 mg KOH per g, and most preferably from 15 to 45 mg KOH per g.

Usefully component (b) satisfies both the acid value (AV) and weight limits herein, but it will be appreciated that depending on the monomer used the AV specified herein may be achieved using weight percentages outside those preferred wt-% values given herein. Where there is an apparent inconsistency herein between any weight% of monomer or other component and the acid values specified it will be appreciated that satisfying the AV is generally the more desirable objective. If necessary the values for weight% of the relevant ingredients can be modified appropriately in a manner well known to a skilled person.

Component (c) (lower itaconate esters and itaconate amides)

Component (c) comprises one or more other diester itaconate monomers other than those of Formula 1, preferably a monomer of Formula A where neither Ra nor Rb are H or an optionally substituted C_{4-10}hydrocarbo. More preferably component (c) comprises a lower itaconate diester. As used herein the term lower itaconate diester denotes diesters of Formula A where Ra and Rb are independently optionally substituted C_{1-3}hydrocarbo groups, such as C_{1-3}alkyl, an example of which is dimethyl itaconate (DMI).

Usefully component (c) may comprise lower itaconate diesters (i.e. diesters other than those of Formula 1), and/or higher or lower itaconate amides and thus component (c) may be represented by Formula 2



Formula 2

where R_3 and R_4 independently represent H or an optionally substituted hydrocarbo moiety having from 1 to 20 carbon atoms (e.g. from 1 to 6 carbon atoms); preferably C_{1-20}alkyl, preferably C_{1-6}alkyl, more preferably C_{1-4}alkyl, most preferably C_{1-3}alkyl; X_1 and X_2 independently represents O or NR_5 where R_5 denotes H or an optionally substituted hydrocarbo moiety having from 1 to 20 carbon atoms (e.g. from 1 to 6 carbon atoms); preferably C_{1-20}alkyl, more preferably C_{1-6}alkyl; even more preferably C_{1-4}alkyl; for example C_{1-3}alkyl;
with the proviso that when X_1 and/or X_2 are O then the respective R_3 and/or R_4 attached to the oxy group independently represent an optionally substituted hydrocarbo having from 1 to 3 carbon atoms, preferably C_{1-3}alkyl.

Components (a), (b), (c) and (d) are mutually exclusive. Thus compounds of Formula 2 are different from those of Formula 1 and the mono acid half itaconate esters are also excluded from Formulae 1 and 2, optionally comprising part of hydrophilic component (b).

Thus in one preferred embodiment of the invention components(a) and (b) (and optionally (c) where present) are each derived from itaconates and/or acids and/or derivatives thereof, more preferably from a biorenewable source. Thus for example component (a) may be a di(C_{4-6}dialkyl)itaconate, (e.g. DBI), component (b) may be itaconic anhydride itaconic acid, and/or C_{1-4}alkyl monoester of itaconic acid and component (c) where present may be a di(C_{1-3}dialkyl)itaconate (e.g. DMI). In such an embodiment optionally there is no component (d) so the copolymer may advantageously be obtained from monomers from the same itaconate source.

Whilst R_3 and R_4 may be different, more conveniently they represent identical moieties.

Whilst X_1 and X_2 may be different, more conveniently they represent identical moieties.

Preferably component (c) may be used in a total amount of less than 35%, more preferably from 0 to 25% by weight.

The component (c) if present may optionally be present in an amount usefully greater than or equal to 0.1 wt-%, conveniently greater than or equal to 0.5 wt-%, for example greater than 1.0 wt-% based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Conveniently component (c) is present in the compositions and/or copolymers of the invention in an amount of less than 40 wt-%, more conveniently less than or equal to 35 wt-%, even more conveniently less than or equal to 25 wt-%, most conveniently ≤ 20 wt-%, for example ≤ 15 wt % based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Component (c) may be used in a total amount from 0 to 10 wt-%, preferably from 0.01 to 10 wt-%, more preferably from 0.1 to 40 wt-%, even more preferably from 0.5 to 35 wt-%, most preferably from 1.0 to 30 wt-%, for example from 1.0 to 25 wt-% by weight based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Component (d) (other copolymerisable monomers)

Preferably component (d) comprises monomers not part of components (a), (b) or (c), more preferably that are copolymerisable with them in any suitable technique such as any of those described herein (for example in a SAD and/or an emulsion polymerisation).

Component (d) may comprise a suitable activated unsaturated moiety (such as ethylenic unsaturation) where the structure(s) of component (d) do not overlap with any of components (a), (b) or (c).

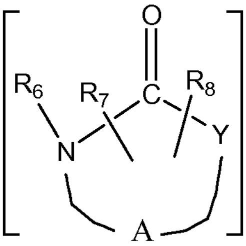
Preferably component (d) is used in an amount of less than 50% and more preferably less than 40% by weight.

Component (d) may comprise monomers that can undergo crosslinking, that can improve adhesion of the coating to various substrates, that can enhance the colloidal stability of the polymer emulsion, or that can be used to affect Tg, or polymer polarity.

Conveniently component (d) may comprise (meth)acrylate monomers having alkyl moieties comprising between 1 and 20 carbon atoms, styrene, alpha-methyl styrene, (meth)acrylonitrile, (meth)acryl amide or alkylated (meth)acryl amides, diacetone acryl amide, acetoacetoxyethyl methacrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, silane functional monomers, such as 3-methacryloxypropyl trimethoxysilane (Geniosil GF31, ex Wacker), ureido functional monomers, such as Plex 6852-O (ex. Evonik), *i*-bornyl (meth)acrylate, polyethylene (meth)acrylate, polypropylene (meth)acrylate.

Component (d) may also comprise crosslinking monomers that can induce crosslinking of the copolymer composition. Crosslinking can occur at ambient temperatures (using for instance diacetone acryl amide combined with adipic dihydrazide), at elevated temperatures (stoving conditions in which for instance copolymerized hydroxyethyl (meth)acrylate reacts with hexamethoxy methyl melamines), as 2C composition (copolymerized hydroxyethyl (meth)acrylate reacting with polyisocyanates, such as Bayhydur 3100), or as UV coating (when polymers or oligomers having multiple unsaturated groups are admixed. Typical examples include di- or tri-functional multifunctional acrylates such as trimethylol propane triacrylate or ethoxylated or propoxylated versions thereof).

Optionally component (d) may also comprise least one polymer precursor(s) of Formula 3



Formula 3,

where Y denotes an electronegative group,

R_6 is H, OH or an optionally hydroxy substituted C_{1-10}hydrcarbo

R_7 is H or a C_{1-10}hydrocarbo;

R_8 is a C_{1-10}hydrocarbo group substituted by at least one activated unsaturated moiety; and; either:

A represents a divalent organo moiety attached to both the –HN- and –Y- moieties so the –A-, -NH-, -C(=O)- and –Y- moieties together represent a ring of 4 to 8 ring atoms, and R_7 and R_8 are attached to any suitable point on the ring; or

A is not present (and Formula 3 represents a linear and/or branched moiety that does not comprise a heterocyclic ring) in which case R_7 and R_8 are attached to R_6; and

m is an integer from 1 to 4.

The ring moiet(ies) of Formula 3 are each attached to R_8 and in Formula 3 when m is 2, 3 or 4 then R_8 is multi-valent (depending on the value of m). If m is not 1 R_7 and –Y- may respectively denote the same or different moieties in each ring, preferably the same respective moieties in each ring. R_7 and R_8 may be attached at any suitable position on the ring.

Preferred monomers of Formula 3 comprise, conveniently consist essentially of, those where: A represents a optional substituted divalent C_{1-5}hydrocarbylene; and

-Y- is divalent –NR_9- (where R_9 is H, OH, optionally hydroxy substituted C_{1-10}hydrocarbo or R_8) or divalent O,

More preferred monomers of Formula 3 comprise those where: m is 1 or 2

-Y- is -NR_8- (i.e. where Formula 2 is attached to R_8 via a ring nitrogen), A represents a divalent C_{1-3}hydrocarbylene; R_6 is H, R_7 is a C_{1-10}hydrocarbo; and

R_8 comprises a (meth)acryloxyhydrocarbo group or derivative thereof (e.g. maleic anhydride).

Monomers represented by Formula 3 include some monomers informally referred to as ureido monomers. Further suitable ureido monomers of Formula 3 are described in "Novel wet adhesion monomers for use in latex paints" Singh et al, Progress in Organic Coatings, 34 (1998), 214-219, (see especially sections 2.2 & 2.3) and EP 0629672 (National Starch) both of which are hereby incorporated by reference. Conveniently the monomers of Formula 3 may be used as a substantially pure compound (or mixture of compounds) or may be dissolved in a suitable solvent such as a suitable (meth)acrylate or acrylic derivative for example methyl methacrylate..

Other and/or additional component (d) may be used in those cases where higher molecular weights are desired, such as suitable multi functional (meth)acrylates or divinyl aromatics. Typical examples include di-, tri-, or tetra-functional (meth)acrylates, especially difunctional (meth)acrylates and divinyl benzene. Typical concentrations are less than 10%, more preferred less than 5%, even more preferred between 0.05 and 4%, most preferred between 0.1 and 2.5%, and even most preferred between 0.15 and 1.5% by weight based on total monomers.

The component (d) may optionally be present in an amount usefully greater than or equal to 0.1 wt-%, conveniently greater than or equal to 0.5 wt-%, for example greater than 1.0 wt-% based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Conveniently component (d) is present in the compositions and/or copolymers of the invention in an amount of less than 77 wt-%, more conveniently less than or equal to 50 wt-%, even more conveniently less than or equal to 40 wt-%, most conveniently ≤ 30 wt-%, for example ≤ 25 wt % based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Preferably, component (d) may be used in a total amount from 0 to 77 wt-%, more preferably from about 0.1 % to about 50 wt-%, even more preferably from about 0.5% to about 40 wt-%, most preferably from about 1.0% to about 30% by weight based on the total weight of monomers (a), (b), (c) and (d) used to prepare the copolymer being 100%.

Other aspects of the invention

One aspect of the invention relates to an aqueous sequential vinyl polymer dispersion comprising 30% by weight (preferably at least 40%) of polymer obtained or obtainable from one or more higher itaconate diester(s).

Another aspect of the invention relates an aqueous vinyl polymer coating compositions comprising blends, copolymers and/or mixtures thereof of an oligomeric component and a polymeric component where the polymeric component comprises 30% by weight (preferably at least 40%) of material obtained or obtainable from one or more higher itaconate diester(s).

A yet other aspect of the invention relates vinyl polymer beads comprising 30% by weight (preferably at least 40%) of polymer obtained or obtainable from one or more higher itaconate diester(s).

Other examples of suitable monomers that may comprises all or part of components (a), (b), (c), or (d) may be described in the various further aspects of the invention later in this application. It will be understood that where suitable such monomers where not already mentioned above may also be used as components in the above aspect of the invention.

Polymerisation processes

Copolymers of the invention_may be formed using a number of processes. These include emulsion polymerisation, suspension polymerisation, bulk polymerisation and solution polymerisation. Such processes are extremely well known and need not be described in great detail.

In one embodiment emulsion polymerisation is used to form copolymers of the invention.

A conventional emulsion process involves dispersing the monomers in an aqueous medium and conducting polymerisation using a free-radical initiator (normally water soluble) and appropriate heating (e.g. 30 to 120 C^{o}) and agitation.

The aqueous emulsion polymerisation can be effected with conventional emulsifying agents (surfactants) being used such as anionic and/or non-ionic emulsifiers. The amount used is preferably low, preferably 0.3 to 2% by weight, more usually 0.3 to 1% by weight based on the weight of total monomers charged.

The aqueous emulsion polymerisation can employ conventional free radical initiators such as peroxides, persulphates and redox systems as are well known in the art. The amount of initiator used is generally 0.05 to 3% based on the weight of total monomers charged.

The aqueous emulsion polymerisation process may be carried out using an "all-in-one" batch process (i.e. a process in which all the components to be employed are present in the polymerisation medium at the start of polymerisation) or a semi-batch process in which one or more of the components employed (usually at least one of the monomers), is wholly or partially fed to the polymerisation medium during the polymerisation. Although not preferred, fully continuous processes could also be used in principle. Preferably a semi-batch process is employed.

The polymerisation technique employed may be such that a low molecular weight polymer is formed, e.g. by employing a chain transfer agent such as one selected from mercaptans (thiols), certain halohydrocarbons and alpha-methyl styrene; or catalytic chain transfer polymerisation using for example cobalt chelate complexes as is quite conventional. Alternatively a controlled radical polymerisation process can be used, for instance by making use of an appropriate nitroxide or a thiocarbonylthio compounds such as dithioesters, dithiocarbamates, trithiocarbonates, and xanthates in order to mediate the polymerization via for example a nitrox mediated polymerisation (NMP), a reversible addition fragmentation chain-transfer process (RAFT) or atom transfer radical polymerization (ATRP).

When the copolymer of the invention is an emulsion polymer it may be mixed with a variety of other polymer emulsions such as those that do not comprise DBI (or higher itaconate esters). Examples of such second polymer emulsions can be polyurethane emulsions, polyurethane-poly(meth)acrylate emulsions, alkyd emulsions, polyester emulsions and/or polyvinyl emulsions. This latter group of copolymer emulsions may comprise oligomer-polymer emulsions, gradient morphology emulsions, sequentially polymerized emulsions, or single phase copolymer emulsions.

The emulsions according to the description above can be produced via emulsion polymerization or via a process called solvent assisted dispersion (SAD) polymerization.

When the copolymer emulsion is produced via emulsion polymerization this can be according to a single feed process, a sequentially fed multi-phase copolymerization process, an oligomer supported emulsion polymerization process or a power feed process, resulting in a gradient particle morphology.

In the case of solvent assisted dispersion polymerization process, or SAD polymerization, the polymerization is performed in organic solvents. Next, base and/or surfactant are added and the polymer solution is emulsified. Preferably, the solvent is removed via evaporation at the end of the complete process.

SAD polymer emulsions can be produced via as single feed solution polymerization or by a sequentially fed multi-phase polymerization. It is also envisaged that an SAD polymer emulsion, prior or after the optional removal of the solvent, is used as a seed for an emulsion polymerization stage. In this case, the polymer emulsion prepared according to the SAD process is used as seed in a batch or semi-batch polymerization process.

The preferred polymerization process is emulsion polymerization.

Preferably, the weight average molecular weight (M_w) (as determined with GPC as described herein) of the DBI containing copolymers is more than 2000 g/mol, more preferably more than 10,000 g/mol, even more preferably more than 25,000 g/mol, most preferably more than 40,000 g/mol, and even most preferably more than 100,000 g/mol.

In the case of oligomer-polymer emulsions prepared via emulsion polymerization lower molecular weights may be desired. In those cases chain transfer agents may be employed. Typical chain transfer agents can be mercaptans, such as lauryl mercaptan, *i*-octyl thioglycolate, or 3-mercapto propionic acid, or halogenides, such as bromomethane, bromoethane. Typical chain transfer concentrations in these cases are enough to reduce the weight average molecular weight of the oligomer phase to between 500 and 100,000 g/mol, more preferred between 1,000 and 60,000 g/mol, even more preferred between 2,500 and 50,000 g/mol, and most preferred between 5,000 and 25,000. Typical chain transfer agent concentrations are below 5%, more preferably below 2.5%, and most preferably between 0.5 and 2.5% by weight of total monomer. In the case that the oligomer is combined with a high molecular weight polymer, the preferred molecular weights for the high molecular weight fraction will be as described earlier.

In those cases where the copolymer emulsion comprises multiple phases or is made up from multiple monomer feeds (sequential, oligomer-polymer or power feed) one of the copolymer phases preferably comprises between 10 and 80%, more preferably between 15 and 50%, and most preferably between 20 and 40% by weight of the total monomers used to prepare the sequential, power feed, and/or oligomer-polymer composition. This particular copolymer phase has a Tg, as calculated using the Fox equation, of higher than 40 °C, more preferably higher than 60 °C, and most preferably higher than 80 °C. The other copolymer phase(s) may then comprise between 20 and 90% of the total monomers more preferably between 50 and 85%, and most preferably between 60 and 80% by weight of the total monomers used to prepare the sequential, power feed, and/or oligomer-polymer composition. These particular copolymer phase(s) have a Tg, as calculated using the Fox equation, of less than 40 °C, more preferably of less than 20 °C, and most preferably of less than 0 °C.

The difference in Tg in such emulsions between that of the high Tg phase(s) and that of the low Tg phase(s) is preferably at least 20 °C, more preferably at least 30 °C, and most preferably at least 40 °C.

In a special case it is envisaged that the itaconic anhydride which is copolymerized in an SAD copolymerization process can be post modified using chemicals having anhydride reactive groups. The objective in these cases is to introduce special functionalities, such as crosslinking or adhesion promoting groups, while maintaining an acid group that can be used for colloidal stabilization.

Modification of the anhydride groups can occur with any nucleophilic functionality. Preferred functionalities include hydroxyl groups, hydrazide groups, hydrazine groups, semi-carbazide groups and amine groups. In all cases, modification will result in the introduction of the moiety attached to the hydroxyl, hydrazide, hydrazine, semi-carbazide or amine group and, simultaneously, of an acid group. The acid group can subsequently be used for emulsifying the copolymer.

The modification can be done with monofunctional hydroxyl groups, hydrazide, or hydrazine, or primary, or secondary amines, but also with di-functional or higher functional hydroxyl, hydrazine, hydrazide, semi-carbazide, or primary or secondary amines. Potential hydroxyl functionalities can include C1-C20 aliphatic, aromatic, or cycloaliphatic mono-, di-, or high functional alcohols. The aliphatic, aromatic, or cycloaliphatic groups can include other functionalities that can, for instance, be used for improved adhesion, crosslinking or other purposes. Typical examples of such functionalities can include phosphate, phosphonate, sulphate, sulphonate, ketone, silane, (cyclic) ureido, (cyclic) carbonate, hydrazide, hydrazine, semi-carbazide, urethane, urea, carbamate, and melamine

The preferred (poly)amines, (poly)hydrazines, or (poly)hydrazides can be characterized by the same description.

In the case where the copolymer composition is prepared via emulsion polymerization, the pH of the emulsion can preferably be increased using organic or inorganic bases. Typical examples include ammonia, primary and secondary organic amines, lithium hydroxide, sodium hydroxide or potassium hydroxide, sodium carbonate or sodium bicarbonate. Typically, the pH is increased only at the end of the manufacturing process, although it can be envisaged that either at the start of the polymerization the pH of the aqueous phase is already increased (buffered) or that the pH of a polymerizing mixture is increased for instance between sequential monomer feeds. In the case of copolymers prepared via emulsion polymerization the pH is preferably increased at the end of the manufacturing process, preferably using ammonia or lithium hydroxide.

Typically, the pH is raised to values above 5, more preferred above 6, and most preferred to values of between 6 and 9.

When the copolymer emulsion is prepared via the SAD polymerization process, emulsification can be done by addition of surfactants, but is preferably done by first neutralizing the polymer acid groups. This can be done by addition of base to the solution polymerized polymer followed by the addition of water or by addition of base to an aqueous phase followed by the addition of the polymer solution. In both cases, suitable bases are the same as above. Preferred bases are ammonia, lithium hydroxide or dimethyl ethanol amine, diethanol methyl amine, diethanol ethyl amine, diethyl ethanol amine and the like. Typically, the molar ratio of base to acid groups is between 0.5 and 1.3, more preferred between 0.6 and 1.2, most preferred between 0.6 and 1.

The concentration of volatile organic compounds (VOC) in the aqueous copolymer emulsions is preferably low. In a preferred case, the VOC level is below 20 wt-%, more preferred below 10 wt-%, even more preferred below 5 wt-%, most preferred below 1 wt-%, and even most preferred below 0.5 wt-%. Intentionally, the VOC level of the copolymer emulsions, prior to formulating them into paints, is close to 0 wt-%, typically below 0.1 wt-%.

When the copolymer composition is prepared via SAD polymerization, solvents are required for the solution polymerization process. Typical solvents include organic solvents that are well known to those experienced in the field, such as acetone, methyl ethylketone, ethanol, methanol, *i*-propanol, *i*-octyl alcohol, xylene, glycol ethers, glycol esters. Preferably solvents are used that – following polymerization at elevated pressure – can be removed from the emulsion by evaporation. Preferred solvents in this respect are acetone and methyl ethylketone.

Initiators are required to start the radical polymerization. These, too, are well known to those experienced in the field. The aqueous emulsion polymerisation can employ conventional free radical initiators such as peroxides, persulphates and redox systems. Useful examples include inorganic peroxides, such as ammonium persulphate, sodium persulphate, potassium persulphate, AZO initiator, such as azobisisobutyronitrile (AIBN), 2,2'-azodi(2-methylbutyronitrile) (AMBN), and organic peroxide and hydroperoxides., (Hydro)peroxide can readily be used in combination with suitable reducing agents.Preferably, initiators are used in an amount of between 0.05 and 6%, more preferably between 0.5 and 4%, most preferably from 0.5 to 3% by weight of the total monomers.

Surfactants are used in emulsion polymerization as known to those skilled in the art. Typical surfactants have been extensively described in all kinds of patent applications. The choice and concentration of surfactants are not deemed to be critical for this invention. The aqueous emulsion polymerisation can be effected with conventional emulsifying agents (surfactants) being used such as anionic and/or non-ionic emulsifiers. The amount used is preferably low, preferably 0.3 to 2% by weight, more usually 0.3 to 1% by weight based on the weight of total monomers charged to make the polymer.

In the case of SAD copolymer emulsions, emulsification can be aided by selecting the right anionic, nonionic and mixed anionic/nonionic surfactant(s). Typically, surfactant is used in an amount of less than 5% more preferably less than 3%, and most preferably between 0.2 and 2.5% by weight of the total monomers.

Preferably (and subject to the provisos herein) in one embodiment of the invention the process of making a copolymer emulsion of the invention comprises using a chaser monomer composition as described in WO2011073417. In another embodiment a chaser monomer may optionally not be used.

In a preferred case the residual monomer content of the copolymer emulsion is below 2000 mg/L, more preferred below 1500 mg/L, most preferred below 1000 mg/L, and especially preferred below 550 mg/L.

The aqueous coating composition yields coatings with typical König hardness values of at least 30 s, more preferred at least 40 s, even more preferred at least 50 s, and most preferred at least 60 s.

In another embodiment the polymer of the invention may be made using a bulk polymerisation process. Bulk polymerisation of olefinically unsaturated monomers is described in detail in EP 0156170, WO82/02387, and US4414370 the contents of which are hereby incorporated by reference.

In general in a bulk polymerisation process a mixture of two or more monomers are charged continuously into a reactor zone containing molten vinyl polymer having the same ratio of vinyl monomers as the monomer mixture. The molten mixture is maintained at a preset temperature to provide a vinyl polymer of the desired molecular weight. The product is pumped out of the reaction zone at the same rates as the monomers are charged to the reaction zone to provide a fixed level of vinyl monomer and vinyl polymer in the system. The particular flow rate selected will depend upon the reaction temperature, vinyl monomers, desired molecular weight and desired polydispersity.

For polymers of the invention especially those to be used in coating compositions, providing amino functional groups thereon may also be useful as such groups provide enhanced adhesion to certain substrates, such as wood and alkyd resins. Amino groups may be incorporated into a polymer by using a carboxyl functional precursor for example prepared by employing ethylenically unsaturated acid functional monomer(s) such as acrylic acid or methacrylic acid. At least some of the carboxy-functional groups may be converted to amino groups (as part of amino ester groups) by reaction with alkylene imines such as ethylene imine, propylene imine or butylene imine. Such a reaction is well established in the art, being known as an imination reaction and the details of this are for example taught in US 7049352 the contents of which are hereby incorporated herein by reference. Therefore a further aspect of the invention comprises iminated versions of the all the copolymers of the present invention as described herein.

If it is desired to crosslink polymers (for example in a polymer dispersion), the relevant polymers can carry functional groups such as hydroxyl groups and the dispersion subsequently formulated with a crosslinking agent such as a polyisocyanate, melamine, or glycoluril; or the functional groups on one or both polymers could include keto or aldehyde carbonyl groups and the subsequently formulated crosslinker in step c) could be a polyamine or polyhydrazide such as adipic acid dihydrazide, oxalic acid dihydrazide, phthalic acid dihydrazide, terephthalic acid dihydrazide, isophorone diamine and 4,7-dioxadecane-1,10 diamine. It will be noted that such crosslinking agents will effect crosslinking by virtue of forming covalent bonds.

Another aspect of the invention is described as follows including the specific additional and/or sub-problems it is designed to address and additional prior art.

Traditional coatings may be unsatisfactory because the polymer films possess little flexibility and the coatings on substrates, such as wood, which are not dimensionally stable; tear and chip off. A disadvantage of hard polymer dispersions is that they can only be processed with the addition of large amounts of film formation assistants that are disadvantageous to initial block resistance.

The initial block resistance is the tendency of the freshly applied coatings which have dried for only a short time to block. This tendency to block makes it virtually impossible, for example, for coated substrates to be stacked rapidly, and is due to the large amounts of film formation assistants which are still present in the binder film and are released only gradually by the conventional polymers at room temperature. When drying is carried out at room temperature, the final block resistance is frequently reached only after several days.

EP 387664 discloses an aqueous synthetic resin dispersion having a minimum film forming temperature below 50 °C containing an emulsion polymer with a core/shell structure consisting of A) 65-90 percent by weight of a weakly crosslinked core polymer having a glass transition temperature below 0 °C and an extension at break of at least 150 percent and B) 10-35 percent by weight of an essentially non-crosslinked shell polymer having a glass transition temperature below 60 °C, the glass transition temperature of said core polymer being at least 10 °C below that of said shell polymer.

US 5,021,469 discloses a binder, for water based gloss paints contains, dispersed in a aqueous phase, particles of a multiphase emulsion polymer made up of (a) core material having a glass transition temperature exceeding 40 °C. and (b) a shell material having a glass transition temperature of less than 70 °C.

US 4,654,397 discloses a process for the preparation of aqueous polymer dispersions which have a low film-forming temperature but still give films having a high block resistance, and the use of these polymer dispersions as binders for coating materials.

None of the above-discussed disclosures teaches a dispersion having the selected combination of features and integers as defined below to produce the advantageous combination of properties as discussed above.

This aspect of the invention has as its preferred object to provide a physically-drying binder in the form of an aqueous synthetic resin dispersion which physically dries at low temperatures to give highly elastic films which are more or less non-tacky from the beginning.

The emulsion polymers according to this aspect of the invention address some or all of the problems described herein.

The designation of the polymer phase involved as a first phase or core material and second phase or shell material does not mean that the invention should be bound by any particular morphology of the latex particles. The term polymer phase is to be understood as meaning a portion of the emulsion polymer which is prepared during a temporally-limited segment of the emulsion polymerization and the dispersion of which differs from that of the foregoing or following phase. This is also known as a multi-stage polymerization.

The two-phase structure of the dispersions of the invention influences the properties of the film formed when the dispersion dries after coating a substrate.

This aspect of the invention provides an aqueous vinyl polymer dispersion with an advantageous combination of MFFT and anti-blocking properties which can be prepared at least in part from bio-renewable monomers (such as biorenewable DBI).

According to this aspect of the present invention there is provided an aqueous polymer dispersion having a minimum film forming temperature below 50 °C, more preferably below 30 °C comprising a vinyl polymer derived from olefinically unsaturated monomers, with at least two phases comprising:

A) 40 to 90 wt-%, more preferably 50 to 85 wt-% and especially 60 to 80 wt-% of a vinyl polymer A having a glass transition temperature in the range of from – (minus)50 to 30°C; and

B) 10 to 60 wt-%, more preferably 15 to 50 wt-% and especially 20 to 40 wt-% of a vinyl polymer B having a glass transition temperature the range of from 50 to 130°C; where

(i) at least one of the monomers used to prepare vinyl polymer A and/or vinyl polymer B is represented by Formula 1 as described herein (usefully a higher itaconate ester such as DBI) preferably in an amount from 20 to 80 wt-%, more preferably from 20 to 65 wt-%, most preferably 30 to 55 wt-% of the total monomers

(ii) optionally 10% by weight (preferably at least 20 wt-%) of the total amount of monomer used to form vinyl polymer A and vinyl polymer B is derived from at least one bio-renewable olefinically unsaturated monomer;

where the weight percentage of monomers in A and B are calculated in (i) and (ii) based on the total amount of olefinically unsaturated monomers used to prepare polymer A and polymer B being 100%;

(iii) vinyl polymer A comprises 0.1 to 10 wt-% of at least one acid-functional olefinically unsaturated monomer where the weight percentage of acid functional monomer is calculated based on the total amount of olefinically unsaturated monomer used to prepare polymer A being 100%.

In this aspect of the invention features (i) and (iii) correspond respectively to components (a) and (b) of the present invention and the other monomers used to prepare polymers A and B corresponding to optional components (c) and/or (d) as appropriate.

Other preferred features of this aspect of the present invention are given below and/or in the claims.

The acid-functional olefinically unsaturated monomer may be selected from the group consisting of acrylic acid, methacrylic acid, itaconic anhydride, maleic anhydride methylene malonic acid, itaconic acid, crotonic acid and fumaric acid.

Vinyl polymer A may comprise 0.1 to 20 wt-% of at least one crosslinking olefinically unsaturated monomer, preferably 0.4 to 6 wt-% of at least one olefinically unsaturated monomer with a wet-adhesion promoting functionality.

The crosslinking monomer(s) and wet adhesion promoting monomer(s) can be used together in the same polymer composition. It is, however, often desired to use either crosslinking monomer(s) or wet adhesion promoting monomer(s) in any phase. This means that vinyl polymer A can comprise crosslinking monomer(s) or wet adhesion promoting monomer(s), while vinyl polymer contains wet adhesion promoting monomer(s) or crosslinking monomer(s). In addition to this it is also possible to use wet adhesion promoting monomer(s) in either vinyl polymer A and/or vinyl polymer B or in both and no crosslinking monomer(s) or to use crosslinking monomer(s) in vinyl polymer A and/or vinyl polymer B and no wet adhesion promoting monomer(s).

Olefinically unsaturated monomer with a wet-adhesion promoting functionality contain wet-adhesion promoting functional groups such as acetoacetoxy groups and optionally substituted amine or urea groups, for example cyclic ureido groups, imidazole groups, pyridine groups, hydrazine or semicarbazide groups.

The bio-renewable olefinically unsaturated monomers may comprise bio-renewable (meth)acrylic acid and or bio-renewable alkyl (meth)methacrylate.

The bio-renewable olefinically unsaturated monomers may also comprise bio-renewable: α-methylene butyrolactone, α-methylene valerolactone, α-methylene γ-R^1 butyrolactone (R^1 can be an optionally substituted alkyl or optionally substituted aryl); itaconates such as dialkyl itaconates and monoalkyl itaconates, itaconic acid, itaconic anhydride, crotonic acid and alkyl esters thereof, citraconic acid and alkyl esters thereof, methylene malonic acid and its mono and dialkyl esters, citraconic anhydride, mesaconic acid and alkyl esters thereof.

The bio-renewable monomers may also comprise bio-renewable: N-R^2, α-methylene butyrolactam (R^2 can be an optionally substituted alkyl or optionally substituted aryl); N-R^2, α-methylene γ-R^1 butyrolactam; N-alkyl itaconimids; itaconmonoamids; itacondiamids; dialkyl itaconamides, mono alkyl itaconamides; furfuryl (meth)acrylate; and fatty acid functional (meth)acrylates.

Vinyl polymer A and vinyl polymer B may comprise at least about 1.5 dpm/gC of carbon-14.

In a further aspect of the present invention provides a process for preparing the aqueous polymer dispersion (or polymer A and polymer B as described above)

which process comprises steps:

a) a first polymerization step, to form a first phase vinyl polymer;
b) a second polymerization step in the presence of the resulting first phase vinyl polymer from step a) to form a second phase vinyl polymer.

Vinyl polymer A may be the first phase in which case vinyl polymer B is the second phase. Alternatively vinyl polymer B may be the first phase in which case vinyl polymer A is the second phase. Preferably vinyl polymer A is the first phase.

Preferably the second phase vinyl polymer is prepared in the presence of the first phase vinyl polymer.

Optionally the process includes c) a neutralisation step before /after or during step c) to solubilise the first polymer phase.

Optionally the process includes d) the addition of a crosslinking agent after the polymerization step a) and/or step b), said crosslinking agent being reactable with any crosslinking functional groups of vinyl polymer A and /or vinyl polymer B on subsequent drying of the coating dispersion to effect covalent bond crosslinking.

Optionally the process includes a post treatment imination step e) with alkylene imines like for instance propylene imine) which can greatly improve wet adhesion.

A film, polish, varnish, lacquer, paint, ink and/or adhesive may comprise the aqueous polymer dispersion comprising polymer A and polymer B described above and these aqueous polymer dispersions may also be used protective coatings on wood, plastic, paper and/or metal substrates.

An embodiment of the invention provides an aqueous polymer dispersion where vinyl polymers A and B comprise individually at least 30 wt-%, more preferably at least 40 wt-%, most preferably at least 60 wt-%, and especially preferably at least 70 wt-% of compounds of Formula 1 such as higher itaconate diesters for example DBI. Although the concentration of itaconate monomers in polymers A and B can be similar, it is preferred that the concentrations are different. In each of the preferred cases described above, it is envisaged that the concentration of itaconate monomers in the other phase can always be below 20 wt-% or even be 0 wt-%.

Preferably the concentration of itaconate esters according to the invention in the low Tg phase is at least 10 wt-% higher than that in the high Tg phase, more preferably at least 20 wt-%.

In yet another preferred embodiment of the invention there is provided an aqueous polymer emulsion according to the invention where the monomer feed making up polymer A or the feed making up polymer B comprise up to 20 wt-% of organic solvent, more preferably less than 10 wt-%, even more preferably less than 5 wt-%, and most preferably between 0.1 and 2.5 wt-%.

Improved properties of the copolymers of the this aspect of the invention may include heat resistance, colloidal stability, pigment compatibility, surface activity, blocking resistance and reduced MFFT depending on the monomers used.

The monomer system used for the preparation of vinyl polymer A and vinyl polymer B is any suitable combination of olefinically unsaturated monomers which is amenable to copolymerisation (including bio-renewable monomers described herein which may of course also be acid-functional, crosslinkable etc at described below).

Preferably vinyl polymer A comprises 0.5 to 9 wt-%, more preferably 1 to 8 wt-% and especially 1.5 to 5 wt-% of at least one acid-functional olefinically unsaturated monomer.

Preferably vinyl polymer B comprises less than 5 w% of any acid functional monomers and preferably less than 2 w%, and in some preferred embodiments none at all.

Other, non-acid functional, non-crosslinking monomers which may be copolymerized with the acid monomers include acrylate and methacrylate esters and styrenes; also dienes such as 1,3-butadiene and isoprene, vinyl esters such as vinyl acetate, and vinyl alkanoates. Methacrylates include normal or branched alkyl esters of C1 to C12 alcohols and methacrylic acid, such as methyl methacrylate, ethyl methacrylate, and n-butyl methacrylate, and (usually C5 to C12) cycloalkyl methacrylates acid such as isobornyl methacrylate and cyclohexyl methacrylate. Acrylates include normal and branched alkyl esters of C1 to C12 alcohols and acrylic acid, such as methyl acrylate, ethyl acrylate, n-butyl acrylate, and 2-ethylhexyl acrylate, and (usually C5-C12) cycloalkyl acrylates such as isobornyl acrylate and cyclohexylacrylate. Also included are (meth)acrylamide, and mono- or di-alkyl amides of (meth)acrylic acid. Styrenes include styrene itself and the various substituted styrenes, such as .alpha.-methyl styrene and t-butyl styrene. Nitriles such as acrylonitrile and methacrylonitrile may also be polymerised, as well as olefinically unsaturated halides such as vinyl chloride, vinylidene chloride and vinyl fluoride.

Functional monomers which impart crosslinkability (crosslinking monomers for short) include epoxy (usually glycidyl) and hydroxyalkyl (usually C1-C12, e.g. hydroxyethyl)methacrylates and acrylates, as well as keto or aldehyde functional monomers such as acrolein, methacrolein and vinyl methyl ketone, the acetoacetoxy esters of hydroxyalkyl (usually C1-C12) acrylates and methacrylates such as acetoacetoxyethyl methacrylate and acrylate, and also keto-containing amides such as diacetone acrylamide. The purpose of using such functional monomer is to provide subsequent crosslinkability in the resulting polymer system as discussed. In principle the functional monomer used for imparting crosslinkability could be acid-bearing monomer, but this is not usual.

Preferably vinyl polymer A comprises 0.1 to 3 wt-% of at least one crosslinking monomer containing at least two olefinically unsaturated groups.

Preferably vinyl polymer A comprises 0.1 to 20 w%, preferably 1 to 15 w%, and particularly 1 to 10 w% of crosslinking monomers.

Adhesion promoting monomers include amino, urea, or N-heterocyclic groups. As known to those skilled in the art this property can also be achieved by imination i.e. reaction of the acid groups with propylene imine.

Preferably vinyl polymer A comprises 0.4 to 6 wt-% of at least one olefinically unsaturated monomer with a wet-adhesion promoting functionality, more preferably between 0.5 and 4 wt-%.

Vinyl polymer A preferably has a weight average molecular weight (M_w) as determined with GPC of from 20,000 to 6,000,000 g/mol, preferably more than 80,000 g/mol and most preferably more than 100,000 g/mol. More preferably the upper limit does not exceed 4,000,000 g/mol.

Vinyl polymer B preferably has a weight average molecular weight (M_w) as determined with GPC of from 20,000 to 6,000,000 g/mol, preferably more than 80,000 g/mol and most preferably more than 100,000 g/mol. More preferably the upper limit does not exceed 4,000,000 g/mol.

Preferably vinyl polymer A has a glass transition temperature in the range of from –(minus)20 to 20°C.

Preferably vinyl polymer B has a glass transition temperature in the range of from 65 to 110°C.

Preferably the polymer dispersion contains latex particles having a diameter from 30 to 900 nanometres (nm), particularly 60 to 300 nm. The particle size distribution can be unimodal, bimodal, or polymodal. Dispersions having bi- or poly-modal particle size distributions can be made according to the method described in DE3147 008 or US4456726.

In a preferred embodiment there is provided an aqueous polymer dispersion having a minimum film forming temperature of below 30 °C comprising a vinyl polymer derived from olefinically unsaturated monomers, with at least two phases comprising:

A) 60 to 80 wt-% of a vinyl polymer A having a glass transition temperature in the range of from -20 to 20°C; and

B) 20 to 40 wt-% of a vinyl polymer B having a glass transition temperature the range of from 65 to 110°C ;

wherein vinyl polymer A comprises 2 to 5 wt-% of at least one acid-functional olefinically unsaturated monomer, and
wherein at least 50 wt-% of the monomer composition used to form vinyl polymer A and vinyl polymer B comprises itaconate diesters of Formula 1, preferably from a biorenewable source.

If vinyl polymer A is made in the second phase then preferably vinyl polymer A has at least 80 %, more preferably at least 100 % and most preferably 110 % of the acid value of vinyl polymer B being made in the first phase and this helps to affect the morphology of the particles to get good film formation.

According to an embodiment of the invention there is also provided a process to obtain an aqueous polymer dispersion as defined herein which process comprises steps:

a) a first polymerization step, to form a first phase vinyl polymer;
b) a second polymerization step in the presence of the resulting first phase vinyl polymer from step a) to form a second phase vinyl polymer.

The first phase vinyl polymer may be formed using emulsion polymerisation. Such processes are extremely well known, are described elsewhere in this specification and need not be described further great detail.

If desired the pH of the polymer emulsion can be adjusted to higher values using suitable bases. Examples of which include organic amines such as trialkylamines (e.g. triethylamine, tributylamine), morpholine and alkanolamines, and inorganic bases such as ammonia, NaOH, KOH, and LiOH.

In an embodiment of the invention it is also possible to use a gradient polymerisation process as described in for example EP1434803 to make at least part of the first and second phase. The second phase monomer feed preferably starts after 20 to 80% completion of the first phase monomer feed.

In a preferred embodiment when > 30 wt-% of monomers of Formula 1 (such as DBI) are used the monomers are preferably fed into the reactor during polymerisation, with a preferred feed time > 60 minutes, more preferably > 120 minutes and most preferred > 150 minutes.

Preferably, the concentration of unreacted monomer according to Formula 1 during the polymerisation is less than 5 wt-% on total weight of the emulsion, more preferably less than 3 wt-%, most preferably less than 1 wt-%, and typically less than 0.5 wt-% on total weight of the emulsion. The concentration of unreacted monomer(s) other than according to Formula 1 during the polymerisation is less than 5 wt-%, more preferred less than 2.5 wt-%, most preferably less than 1 wt-%, and typically less than 0.3 wt-% on total weight of the emulsion.

Preferably the dispersions of the invention have VOC levels of less than 100 g/L and more preferably less than 80 g/L, most preferably less than 50 g/L and especially less than 20 g/L of volatile organic components (VOC) such as coalescing solvents.

If crosslinking monomers are present then preferably the amount of crosslinking agent that is employed is such that the ratio of the number of crosslinker groups present in the first phase vinyl polymer and (if employed) in the second phase vinyl polymer to the number of reactive groups (for crosslinking purposes) in the crosslinking agent is within the range of from 10/1 to 1/3, preferably 2/1 to 1/1.5.

A crosslinker reactive with a copolymerised crosslinking monomer, if present, is usually combined with the aqueous dispersion by adding it thereto after the preparation of the second phase vinyl polymer (and sometimes just before use of the dispersion), although it may in principle also be combined by performing the polymerisation of the second phase vinyl polymer in the presence of the crosslinking agent. A combination of both incorporation expedients may also in principle be used.

It will be appreciated that vinyl polymer A and optionally vinyl polymer B possess functional groups for imparting latent crosslinkability to the dispersion (i.e. so that crosslinking takes place e.g. after the formation of a coating therefrom) when combined with the crosslinking agent. For example, one or both polymers could carry functional groups such as hydroxyl groups and the dispersion subsequently formulated with a crosslinking agent such as a polyisocyanate, melamine, or glycoluril; or the functional groups on one or both polymers could include keto or aldehyde carbonyl groups and the subsequently formulated crosslinker in step c) could be a polyamine or polyhydrazide such as adipic acid dihydrazide, oxalic acid dihydrazide, phthalic acid dihydrazide, terephthalic acid dihydrazide, isophorone diamine and 4,7-dioxadecane-1,10 diamine. It will be noted that such crosslinking agents will effect crosslinking by virtue of forming covalent bonds.

According to an embodiment of the invention there is provided a process for the production of the aqueous polymer coating dispersion, which process comprises steps: a’) a first polymerization step, to form a first phase vinyl polymer; b’)a second polymerization step in the presence of the resulting first phase vinyl polymer from step a’) to form a second phase vinyl polymer. Optionally the process includes c’) a neutralisation step before /after or during step b’).Optionally the process includes a post treatment imination step d') with alkylene imines like for instance propylene imine) which can greatly improve wet adhesion. Optionally the process includes e') the addition of a crosslinking agent after the polymerization step a') and/or step b'), and preferably after the optional imination step d'), said crosslinking agent being reactable with any crosslinking functional groups of vinyl polymer A and /or vinyl polymer B on subsequent drying of the coating dispersion to effect covalent bond crosslinking (as described herein).

A still another aspect of the invention is described as follows including the specific additional and/or sub-problems it is designed to address and additional prior art.

There is an ever increasing demand to replace or supplement solvent-based polymer coating compositions with aqueous-based counterparts due to the environmental toxicity and flammability problems posed by the use of volatile organic solvents. However, even where aqueous-based polymer compositions have been devised, their production has usually entailed the intermediate use of organic solvents, requiring subsequent removal, or the incorporation of a certain amount of a solvent in the final composition which acts to ensure proper film-formation on coating (known as a coalescing solvent). There is therefore also now increasing pressure to significantly reduce or eliminate the volatile organic content (VOC) in aqueous-based polymer composition syntheses and also provide biorenewable monomers.

In addition, even if one can achieve a solvent-free aqueous polymer coating composition, it has been found difficult to achieve one with a balance of good properties conventionally required in most coating compositions, particularly acceptably high hardness and low minimum film forming temperature (MFFT) of the resulting coating. The coating should also have good water and solvent resistance.

EP0758364 discloses a process for making organic solvent-free aqueous cross-linkable polymer composition comprising an acid-functional polymer A with Tg 10 to 125 °C and having cross-linker functional groups and a polymer B having Tg at least 25 °C below that of polymer A in combination with a crosslinking agent having an advantageous balance of MFFT and Koenig hardness.

EP0758347 discloses a process for making organic solvent-free aqueous cross-linkable polymer composition comprising an acid-functional polymer A with Tg less than 50 °C and having cross-linker functional groups and a polymer B having Tg at least 25 °C above that of the polymer A in combination with a crosslinking agent having an advantageous balance of MFFT and Koenig hardness.

None of the above-discussed disclosures teaches a vinyl polymer coating composition having the selected combination of features and integers as defined in the invention below and an advantageous combination of properties as discussed above, using monomers such as DBI (optionally from a biorenewable source) to make the vinyl polymer.

In this aspect of the invention we provide an aqueous vinyl polymer coating composition with an advantageous combination of MFFT and hardness and which furthermore is prepared at least in part from a monomer of Formula 1 (such as di(n-butyl) itaconate (DBI)), preferably derived from a bio-renewable source.

According to this aspect of the present invention there is provided an aqueous vinyl polymer coating composition comprising at least:

α[alpha]) a vinyl polymer C, comprising:

- i) 1 to 45 wt-% of acid-functional olefinically unsaturated monomers;
- ii) 0 to 20 wt-% of crosslinking-functional olefinically unsaturated monomers; and
- iii) 99 to 50 wt-% of non-acid functional, non-crosslinking monomers selected from the group consisting of olefinically unsaturated monomers and aryl arylalkylene monomers;

where the weight percentages of each of (α[alpha])(i), (α[alpha]) (ii) and (α[alpha])(iii) are calculated based on the total of (α[alpha]) (i) + (α[alpha]) (ii) + (α[alpha])(iii) = 100%; and where

said polymer C having a molecular weight within the range of from 1,000 to 150,000 g/mol and an acid value > 5 mgKOH/g; and

(β[beta])) a vinyl polymer D, comprising:

- i) 0 to 10 wt-%, preferably less than 25 wt-%, of at least one acid-functional olefinically unsaturated monomer;
- ii) 0 to 25 wt-%, preferably less than 25 wt-%, of crosslinking-functional olefinically unsaturated monomers; and
- iii) 0 to 100-wt-% of non-acid functional, non-crosslinking monomers selected from the group consisting of olefinically unsaturated monomers and aryl arylalkylenemonomers other than a monomer of Formula 1

at least one of β[beta] (i) to (iii) being present; where

the weight percentages of each of (β[beta])(i), (β[beta])(ii) , (β[beta]) (iii) and (β[beta]) (iv) are calculated based on the total of (β[beta])(i) + (β[beta])(ii) + (β[beta])(iii) + (β[beta])(iv) = 100%; and where said polymer D has a molecular weight (M_w), as determined by GPC, of at least 80,000 g/mol and an acid value less than 65 mgKOH/g, preferably less than 50 mgKOH/g ; more preferably less than 30 mgKOH/g, most preferably less than 20 mgKOH/g, for example less than 10 mgKOH/g

wherein

I) the weight % of the monomers used to form polymer C (α[alpha]) (i), (α[alpha]) (ii), and (α[alpha])(iii) = polymer C monomers) and polymer D ((β[beta])(i), (β[beta])(ii), (β[beta])(iii) and (β[beta])(iv) = polymer D monomers) when calculated based on the total amount of (α[alpha]) (i) + (α[alpha]) (ii) + (α[alpha])(iii) + (β[beta])(i) + (β[beta])(ii) + (β[beta])(iii) + (β[beta])(iv) =100% have the weight percentages of:

for polymer C monomers from 5 to 75 %, preferably 5 to 70%; and

for polymer D monomers from 25% to 95%, preferably from 30% to 90%

II) from 20 to 75 wt-%, preferably from 24 to 60 wt-%, by weight of the total amount of monomers (α[alpha]) (i) + (α[alpha]) (ii) + (α[alpha])(iii) + (β[beta])(i) + (β[beta])(ii) + (β[beta])(iii) + (β[beta])(iv) used to form polymer C and polymer D comprises at least one monomer of Formula 1 (for example DBI);

III) optionally at least 10%, preferably at least 20%, by weight of the total amount of monomers (α[alpha]) (i) + (α[alpha]) (ii) + (α[alpha])(iii) + (β[beta])(i) + (β[beta])(ii) + (β[beta])(iii) + (β[beta])(iv) used to form polymer C and polymer D is derived from at least one bio-renewable olefinically unsaturated monomer;

IV) the acid value of polymer C is greater than the acid value of polymer D by at least 10 mgKOH;

V) polymer C and polymer D have a glass transition temperature difference of at least 20 °C;

VI) polymer C is prepared in the presence of polymer D;

VII) said coating composition on drying has a Koenig hardness of at least 20 sec; and

VII) said coating composition has a minimum film forming temperature of < 55 °C.

Preferably polymer C is an oligomer and polymer D is a non-oligomeric polymer.

In this aspect of the invention, feature (β[beta])(iv) corresponds to component (a) of the present invention; features (α[alpha]) (i) and (β[beta])(i) correspond to component (b) of the present invention, and the remaining features (α[alpha])(ii),(α[alpha])(iii), (β[beta])(ii) and (β[beta])(iii) correspond as appropriate to optional components (c) and/or (d) of the present invention.

Other preferred features of this aspect of the present invention are given below and/or in the claims.

The acid-functional monomer may be selected from the group consisting of acrylic acid, methacrylic acid, itaconic anhydride, maleic anhydride, methylene malonic acid, itaconic acid, crotonic acid and fumaric acid and monobutyl itaconate.

The bio-renewable monomers may comprise bio-renewable (meth)acrylic acid and or bio-renewable alkyl (meth)acrylate (as well as optionally monomers of Formula 1).

The bio-renewable monomers may also comprise bio-renewable: α-methylene butyrolactone, α-methylene valerolactone, α-methylene γ-R^1 butyrolactone (R^1 can be an optionally substituted alkyl or optionally substituted aryl); itaconates such as dialkyl itaconates and monoalkyl itaconates, itaconic acid, itaconic anhydride, crotonic acid and alkyl esters thereof, citraconic acid and alkyl esters thereof, methylene malonic acid and its mono and dialkyl esters, citraconic anhydride, mesaconic acid and alkyl esters thereof.

Other suitable bio-renewable monomers may comprise bio-renewable: N-R^2, α-methylene butyrolactam (R^2 can be an optionally substituted alkyl or optionally substituted aryl); N-R^2, α-methylene γ-R^1 butyrolactam; N-alkyl itaconimids; itaconmonoamids; itacondiamids; ialkyl itaconamides, mono alkyl itaconamides; furfuryl (meth)acrylate; and fatty acid functional (meth)acrylates.

Polymer C and/or polymer D may comprise at least about 1.5 dpm/gC of carbon-14.

The composition may additionally comprising a crosslinking agent, being reactable with any crosslinking functional groups of the polymer C and /or polymer D on subsequent drying of the coating composition to effect covalent bond crosslinking. The functional groups for providing crosslinking may be selected from the group consisting of epoxy, hydroxyl, ketone and aldehyde groups. The crosslinking agent may also be selected, depending on the crosslinking functionality in the polymer C and in the polymer D, from the group consisting of a polyisocyanate, melamine, glycoluril, a polyamine, and a polyhydrazide.

The composition may comprise less than 2 wt-% of added surfactant by weight of monomers used to make vinyl polymer C and vinyl polymer D.

The composition may comprise volatile organic compounds (VOC) in an amount of less than 100 g/L, preferably be substantially free of VOC.

A film, polish, varnish, lacquer, paint, ink and/or adhesive may comprise an aqueous coating composition of polymer C and polymer D and these compositions may also be used as a protective coating on a wood, plastic, paper and/or metal substrate.

In a preferred embodiment of the invention the monomers α[alpha]) iii) and β[beta])iii) comprise individually at least 10 wt-%, more preferably at least 20 wt-%, most preferably at least 30 wt-% and especially preferably at least 50 wt-%, based on the composition of monomers α[alpha]) iii) and β[beta])iii, of compounds of Formula 2 such as lower di- esters of itaconic acid (in addition to or replacing the higher itaconate diesters such as DBI). Although the concentration of itaconate monomers in α[alpha]) iii) and β[beta])iii, can be similar, it is preferred that the concentrations are different. In each of the preferred cases described above, it is preferred that the concentration of itaconate monomers in the other phase is 0 wt-%.

Preferably polymer C acts as a (co-)surfactant for the preparation of polymer D.

Preferably the concentration of olefinically unsaturated monomers used to form polymer C are 10 to 65 wt-%, more preferably 15 to 60 wt-% and especially 20 to 55 wt-% by weight of the monomers used to form polymer(s) C and polymer(s) D.

Preferably the concentration of olefinically unsaturated monomers used to form the polymer D are 90 to 35 wt-%, more preferably 85 to 40 wt-% and especially 80 to 45 wt-% by weight of the monomers used to form polymer(s) C and polymer(s) D.

The monomer system used for the preparation of polymer C and polymer D is any suitable combination of olefinically unsaturated monomers which is amenable to copolymerisation (including the bio-renewable monomers described herein which may of course also be acid-functional, crosslinkable etc as described herein).

Acid-functional olefinically unsaturated monomers (used in polymer C preferably in sufficient concentration to render the resulting polymer surface active) may be a monomer bearing an acid-forming group which yields, or is subsequently convertible to, an acid-functional group (such as an anhydride, e.g. methacrylic anhydride or maleic anhydride) or an acid. Examples of such acid functional monomers have already been given as component (b) previously and may also be used in this aspect of the invention.

Typically polymer C comprises 1 to 45 wt-% of acid functional monomers, preferably 3 to 30 wt-% and more preferably 3 to 20 wt-%.

Polymer C may comprise polyethylene glycol (meth)acrylates or their methyl ether analogues that can render polymer C surface active. When copolymerising these monomers, a lower acid concentration can be applied, for example polymer C may then comprise 1 to 10 wt-% of acid functional monomers.

Typically polymer D comprises less than 5 wt-% of any acid functional monomers and preferably less than 2 wt-%, and in some preferred embodiments none at all.

Polymer D may also comprise polyethylene glycol (meth)acrylates or their methyl ether analogues which may contribute to reducing the MFFT of the resulting composition.

Other, non-acid functional, non-crosslinking monomers which may be copolymerized with the acid monomers include acrylate and methacrylate esters and styrenes; also dienes such as 1,3-butadiene and isoprene, vinyl esters such as vinyl acetate, and vinyl alkanoates. Methacrylates include normal or branched alkyl esters of C1 to C12 alcohols and methacrylic acid, such as methyl methacrylate, ethyl methacrylate, and n-butyl methacrylate, and (usually C5 to C12) cycloalkyl methacrylates, such as isobornyl methacrylate and cyclohexyl methacrylate. Acrylates include normal and branched alkyl esters of C1 to C12 alcohols and acrylic acid, such as methyl acrylate, ethyl acrylate, n-butyl acrylate, and 2-ethylhexyl acrylate, and (usually C5-C12) cycloalkyl acrylates such as isobornyl acrylate and cyclohexylacrylate. Also included are (meth)acrylamide, and mono- or di-alkyl amides of (meth)acrylic acid. Styrenics include styrene itself and the various substituted styrenes, such as alpha-methyl styrene and t-butyl styrene. Nitriles such as acrylonitrile and methacrylonitrile may also be polymerised, as well as olefinically unsaturated halides such as vinyl chloride, vinylidene chloride; vinyl fluoride. and (meth)acrylamide.

Typically polymer C comprises 98.5 to 50 wt-% of non acid functional, non-crosslinking monomers, preferably 96 to 65 wt-%, and more preferably 96 to 75 wt-%.

Functional monomers which impart crosslinkability (crosslinking monomers for short) include epoxy (usually glycidyl) and hydroxyalkyl (usually C1-C12, e.g. hydroxyethyl)methacrylates and acrylates, as well as keto or aldehyde functional monomers such as acrolein, methacrolein and vinyl methyl ketone, the acetoacetoxy esters of hydroxyalkyl (usually C1-C12) acrylates and methacrylates such as acetoacetoxyethyl methacrylate and acrylate, and also keto-containing amides such as diacetone acrylamide. The purpose of using such functional monomer is to provide subsequent crosslinkability in the resulting polymer system as discussed. (In principle the functional monomer used for imparting crosslinkability could be acid-bearing monomer, but this is not usual and therefore for the purpose of this invention acid functional monomers are not considered as crosslinkable monomers although they may act as such.

Preferably, polymer C comprises 0.5 to 25 wt-%, more preferably 0.5 to 25 wt-%, most preferably 1 to 15 wt-%, and especially 1 to 10 wt-% of crosslinking monomers.

Preferably polymer C has a weight average molecular weight (M_w) as determined with GPC of from 1500 to 100,000 g/mol, more preferably 2000 to 50,000 g/mol and particularly 3,000 to 40,000 g/mol.

The weight average molecular weight (M_w) of polymer D as determined with GPC is preferably more than 100,000 g/mol, and most preferably more than 150,000 g/mol. The upper limit does not usually exceed 5,000,000 g/mol.

Preferably the weight average molecular weight (M_w) of polymer C is lower than the weight average molecular weight (M_w) of polymer D, and most preferably there is a molecular weight difference of at least 30,000 g/mol, especially at least 50,000 g/mol, and typically at least 100,000 g/mol.

Preferably the difference in Tg (expressed as degrees Celsius) between polymer C and polymer D is at least 40 degrees and more preferably at least 60 degrees.

In one embodiment of this aspect of the invention the Tg of polymer C is higher than that of polymer D. In this embodiment the preferred Tg of polymer C is from 50 to 125°C and particularly from 70 to 125°C. The Tg of polymer C should then be at least 20 degrees higher than, more preferably at least 40 degrees higher than the Tg of polymer D (both expressed as degrees Celsius). Preferably the Tg of polymer D in this embodiment is from –(minus)50 to 40°C and more preferably from –(minus)30 to 30°C and especially from –(minus)20 to 30°C.

In another embodiment of the invention the Tg of polymer C is lower than that of polymer D. In this embodiment the preferred Tg of polymer C is less than

50°C and more preferably is of from –(minus)15 to 49°C. Preferably the Tg of polymer D in this embodiment is from 50 to 125°C and particularly from 70 to 125°C.

Polymer C may be formed using a number of processes. These include emulsion polymerisation, suspension polymerisation, bulk polymerisation and solution polymerisation. Such processes are extremely well known are described elsewhere in this specification and need not be described further in great detail.

In another embodiment polymer C is made via a bulk polymerisation process. Bulk polymerisation of olefinically unsaturated monomers is described in detail in EP 0156170, WO 82/02387, and US 4414370.

In general in a bulk polymerisation process a mixture of two or more monomers are charged continuously into a reactor zone containing molten vinyl polymer having the same ratio of vinyl monomers as the monomer mixture. The molten mixture is maintained at a preset temperature to provide a vinyl polymer of the desired molecular weight. The product is pumped out of the reaction zone at the same rates as the monomers are charged to the reaction zone to provide a fixed level of vinyl monomer and vinyl polymer in the system. The particular flow rate selected will depend upon the reaction temperature, vinyl monomers, desired molecular weight and desired polydispersity.

The minimum reaction temperature will vary, depending on the particular monomers charged to the reactor. In order to obtain a polymer C for use in the invention with the desired molecular weight the reaction temperature is preferably maintained from about 135°C to about 310°C, more preferably from about 150°C to 275°C. A conventional free-radical-yielding initiator may be used and optionally a chain transfer agent may be added to control the molecular weight.

Alternatively polymer C may be prepared by means of a suspension or micro-suspension polymerisation process. In this process, monomer and water are introduced into the polymerisation reactor and a polymerisation initiator, along with other chemical additives, are added to initiate the polymerisation reaction. The contents of the reaction vessel are continually mixed to maintain the suspension and ensure a uniform particle size of the resulting polymer.

Polymer C may also be made by a solution dispersion polymerisation or solvent assisted dispersion polymerisation (SAD) process where the polymerisation process can be carried out in the presence of an organic solvent. Typical organic solvents which may be used include aromatic hydrocarbons such as benzene toluene, and the xylenes, ethers such as diethyl ether, tetrahydrofuran, alkoxylated ethylene glycol; alcohols such as methanol, ethanol, propanol, butanol and alcohols with at least six carbons, such as octanol. and their esters with carboxylic acids such as acetic, propionic and butyric acids, ketones such as acetone or methyl ethyl ketone, and liquid tertiary amines such as pyridine. Mixtures of solvents may also be used. Typical solvents would certainly include alkyl glycols, such as butyl glycol or dipropylene glycol dimethyl ether (Dowanol DMM) or dipropylene glycol methyl ether (Dowanol DPM). An example of an aromatic solvent that is regularly used is Solvesso 100. Preferably bio-renewable solvents (for example as available from Liberty Chemicals) are used.

Often the reaction temperature is around 140°C to 160°C and can also be a carried out at an elevated pressure so that lower boiling point solvents can be used. An advantage of lower boiling point solvents is that they can be more easily removed in order to make a low VOC aqueous composition.

Preferably the compositions of the invention have VOC levels of less than 100 g/L and more preferably less than 80 g/L, most preferably less than 50 g/L and especially less than 20 g/L of volatile organic components such as coalescing solvents.

Once polymer C is prepared then polymer D is prepared in the presence of polymer C and an aqueous composition is prepared by inter alia solubilising polymer C before during or after the preparation of polymer D. Polymer C can serve as an (co-)emulsifier for polymer D without which polymer D cannot be sufficiently dispersed in the aqueous composition of the invention. By (co-) emulsifier is meant that although polymer C acts as an emulsifier, additional emulsifiers may also be added.

Thus, polymer C contains a sufficient concentration of acid functionality or a high enough concentration of polyethylene glycol (meth)acrylates to render the polymer partially or more preferably fully soluble in aqueous media, if necessary by neutralization of acid groups of the polymer, as would e.g. be achieved by adjustment of the pH of the aqueous medium. (If the acid-functional polymer C is only partially soluble in the aqueous medium of the emulsion, it will exist therein partly dispersed and partly dissolved). Usually, the medium in which the polymer C finds itself will be acidic (pH <7) and the acid groups will be carboxyl groups so that dissolution and surface activity can be affected by raising the pH of the medium (usually the aqueous polymerisation medium in which the polymer C has been prepared) so as to neutralize the acid groups by the addition of a base, such as an organic or inorganic base, examples of which include organic amines such as trialkylamines (e.g.

triethylamine, tributylamine), morpholine and alkanolamines, and inorganic bases such as ammonia, NaOH, KOH, and LiOH. Of course, the aqueous medium containing the acid functional polymer A may already be alkaline (or sufficiently alkaline) such that the acid groups (such as carboxyl groups) become neutralized without the requirement for positively adding a base to raise pH, or the acid groups may be or include very strong acid groups such as sulphonic acid groups (pKa 1 to 2) so that neutralization may not be necessary to achieve dissolution. Further still, it is possible for acid monomers to be polymerised in salt form rather than as the free acid.

The solubilization of the polymer C is preferably effected before carrying out the polymerisation of step b') as preferably this produces a product having an improved balance of MFFT and Koenig hardness.

Polymer C is present during the polymerisation process to make polymer D. Polymer D may be formed using a number of processes. These include emulsion polymerisation, , bulk polymerisation and solution polymerisation.

A preferred feature of this aspect of the invention is that it is often possible to eliminate or much reduce the requirement for the addition of a surfactant to act as an emulsifier to make polymer D because polymer C itself can fulfil such a function (i.e. act as an emulsifying agent). Thus the aqueous composition of the invention preferably contains a very low level of such added emulsifier (not counting polymer C itself), with usually less than 0.5% (preferably less than 0.25%, and often zero) based on the total wt of monomers charged being used, and with the only surfactant present preferably being that remaining from polymer C polymerisation (not counting the polymer C itself). In fact the overall level of surfactant (not counting the polymer C itself) is preferably <1% more preferably <0.5%, particularly <0.35%, based on the total wt of monomers charged for polymer D.

The polymerisation to make polymer D could be carried out using a chain transfer agent, but (unlike in the preparation of polymer C) is usually effected without the use of such a material in order to ensure a higher molecular weight.

Polymer D may be considered as a hydrophobic polymer, this type of polymer being well understood by those skilled in the art. Generally speaking it may be considered herein as a water-insoluble polymer whose water-insolubility is maintained throughout the pH range. The hydrophobic nature of the polymer is achieved by virtue of the polymer containing a sufficient concentration of at least one hydrophobic monomer (i.e. in polymerised form) to render the polymer hydrophobic and water-insoluble throughout the pH range.

Polymer D may also comprises 0.5 to 25 wt-%, more preferably 0.5 to 20 wt-%, most preferably 1 to 12 wt-%, especially 1 to 8 wt-%, for example 1 to 5 wt-% of crosslinking multifunctional (meth)acrylate monomer(s). In general it will be appreciated that given the respective natures of polymers C and D for a given system the amount of multifunctional (meth)acrylate crosslinking monomer used in polymer C is more likely to be less than the amount used in polymer D.

It will be appreciated that polymer C and optionally polymer D possess functional groups for imparting latent crosslinkability to the composition (i.e. so that crosslinking takes place e.g. after the formation of a coating there from) when combined with the crosslinking agent (as described elsewhere herein).

If crosslinking monomers are present then preferably the amount of crosslinking agent that is employed is such that the ratio of the number of crosslinker groups present in the polymer C and (if employed) in the polymer D to the number of reactive groups (for crosslinking purposes) in the crosslinking agent is within the range of from 10/1 to 1/3, preferably 2/1 to 1/1.5.

Polymers of this aspect of the invention may also be iminated as described elsewhere herein.

The crosslinker is usually combined with the aqueous composition by adding it thereto after the preparation of polymer D (and sometimes just before use of the composition), although it may in principle also be combined by performing the polymerisation of polymer D in the presence of the crosslinking agent. A combination of both incorporation expedients may also in principle be used.

According to an embodiment of the invention there is provided an aqueous polymer coating composition comprising at least:

α(alpha)) a vinyl polymer C, comprising:

i) 4 to 25 wt-% of acid-functional olefinically unsaturated monomers;
ii) 0 to 15 wt-% of crosslinking unsaturated monomers; and
iii) 96 to 60 wt-% of non-acid functional, non-crosslinking olefinically unsaturated monomers; said polymer C being obtained by an emulsion polymerisation process and having a molecular weight within the range of from 3,000 to 65,000 g/mol, a Tg of at least 50 °C and an acid value > 20 mgKOH/g; and

β(beta)) a vinyl polymer D, made in the presence of neutralised polymer C and comprising:

i) 0 to 4 wt-%, more preferably 0 wt-% of acid-functional olefinically unsaturated monomers;

ii) 0 to 12 wt-%, more preferably 1 to 8 wt-% of crosslinking-functional olefinically unsaturated monomers; and

iii) 100 to 84 wt-% of non-acid functional, non-crosslinking olefinically unsaturated monomers;

wherein polymer D has a molecular weight of at least 80,000 g/mol and a Tg less than 50 °C ; and

where the wt-% of polymer C is 10 to 60, more preferred 20 to 50 wt-% based on the weight of polymer C and polymer D together; and

where polymer(s) C and polymer(s) D combined contain at least 30 wt-% of itaconate diester monomer according to Formula 1.

The wt-% of olefinically unsaturated monomers used to form polymer C are in the range of from 10 to 60, more preferably 20 to 50 wt-% based on the weight of olefinically unsaturated monomers used to form polymer C and polymer D together.

According to an embodiment of the invention there is provided a process for the production of the aqueous polymer coating composition, which process comprises steps:

1) a first polymerisation step, to form polymer C;
2) a second polymerisation step in the presence of the resulting polymer C from step 1) to form polymer D;
3) a neutralisation step before /after or during step 2) to solubilise polymer D;
4) the optional step of iminating (part of) the acid groups using alkylene imine
5) the optional addition of a crosslinking agent after the polymerisation step a) and/or step 2), said crosslinking agent being reactable with any crosslinking functional groups of the polymer C and /or polymer D on subsequent drying of the coating composition to effect covalent bond crosslinking.

In a preferred embodiment the acid functional monomer in polymer C is selected from acrylic acid; methacrylic acid, crotonic acid, itaconic anhydride and itaconic acid; the crosslinking functional monomer used in both polymer C and polymer D is diacetone acrylamide and the crosslinker is adipic acid dihydrazide.

According to another embodiment of the invention there is provided a process for the production of the aqueous polymer coating composition, which process comprises steps:

1) where vinyl polymer C is made by an emulsion polymerisation process,
2) a subsequent neutralisation step; and

3) where subsequently polymer D is made by polymerisation in the presence of polymer C;

wherein both vinyl polymer C and vinyl polymer D comprise at least one carbonyl functional olefinically unsaturated monomer;
wherein the acid value of vinyl polymer C is between 30 and 110 mgKOH/g and the acid value of vinyl polymer D is below 10 mgKOH/g, more preferred below 5 mgKOH/g;
and wherein the crosslinker is an aliphatic dihydrazide.

According to yet another embodiment of the invention there is provided a process for the production of the aqueous polymer coating composition, which process comprises steps:

1) where polymer C is made by a bulk polymerisation process and more preferably a continuous bulk polymerisation process,
2) where polymer C is dissipated in water and (partially) neutralised, preferably with an organic amine or NaOH, KOH or LiOH; and
3) where subsequently polymer D is made by polymerisation in an aqueous medium in the presence of the neutralised polymer C;

wherein the acid value of vinyl polymer C is between 40 and 300 mgKOH/g of solid polymer;
wherein polymer C has a Tg of at least 70 °C and more preferably at least 90 °C; and
wherein polymer C has a molecular weight in the range of from 2,000 to 25,000 g/mol.

According to yet a further embodiment of the invention there is provided a process for the production of the aqueous polymer coating composition, which process comprises steps:

1) where polymer C is made by solution polymerisation, preferably in a solvent selected from the group consisting of acetone, methyl ethylketone, ethanol, iso-propanol or mixtures thereof;
2) a subsequent neutralisation step comprising neutralising at least part of the acid groups with a base (preferably an organic amine), adding water and emulsifying polymer C
3) where subsequently polymer D is made by emulsion polymerisation in the presence of polymer C;
4) where the solvent is removed by evaporation;

wherein polymer C has a Tg of at least 50 °C,
wherein polymer D has a Tg of no more than 50 °C, and

wherein polymer c and polymer D have a glass transition temperature difference of at least 25 °C.

In yet another embodiment there is provided an aqueous copolymer composition according to this aspect of the invention wherein polymer D contains between 0.1 and 1.5 wt-% of a multi unsaturated monomer, preferably divinyl benzene.

It is preferred that most of the higher itaconate ester present in the composition is used to prepare polymer D rather than polymer C. Therefore in yet still another embodiment there is provided an aqueous copolymer composition according to this aspect of the invention wherein polymer D contains at least 50 wt-%, more preferably at least 75 wt-%, of all itaconate monomer according to Formula 1 present in the total copolymer composition, and polymer C contains no more than 50 wt-%, more preferably not more than 25 wt-% of all itaconate monomer according to Formula 1 present in the total copolymer composition.

Preferably the average particle size of the aqueous composition of the invention is between 70 and 140 nm.

The solids content of an aqueous composition of the invention is usually within the range of from about 20 to 65 wt-% on a total weight basis, more usually 30 to 55 wt-%. Solids content can, if desired, be adjusted by adding water or removing water (e.g. by distillation or ultrafiltration).

A still yet another aspect of the invention is described as follows including the specific additional and/or sub-problems it is designed to address.

The present invention relates to vinyl polymer beads comprising at least 20 wt-% (preferably at least 30 wt-%) of a monomer of Formula 1 (usefully DBI) preferably from a bio-renewable source and to such vinyl polymer beads as well as a process for making them and their use in coatings, inks and adhesives.

Vinyl polymers which are prepared with emulsion polymerisation technology allow a good control over critical polymer parameters like molecular weight, particle size in the nm (nanometre) range (typically 50-300 nm) and residual monomer content. However, few micron-sized particles are obtained during emulsion polymerisation. Due to the small particle size dried emulsion vinyl polymers have a much larger dusting tendency compared to dried vinyl polymer beads obtainable by suspension polymerization. On the other hand polymer emulsions used as such to avoid the dusting issue need to be preserved to prevent bacterial or fungal growth.

The problem of dustiness of dried emulsion polymers can be overcome by bead-type suspension polymerisation which is a well known method of polymerisation in which the polymer formed is obtained as micron sized spherical beads or pearls. Even though the water soluble by-products may be removed with the stationary water phase during the final de-watering and washing cycle the water insoluble by-products such as in particular the unreacted monomers stay within the polymer beads and lead to characteristic off odours, lowered glass transition temperatures (T_g) and toxicological issues, especially when the monomers are taken from vinyl acid / methyl vinyl acid and their esters.

An object of this aspect of the present invention is to solve some or all of the problems or disadvantages (such as identified herein) with the prior art.

By the term "polymer beads" in connection with the present invention is meant polymer particles that are simple to isolate e.g. by filtering or centrifuging. The polymer beads in connection with the present invention are micron-sized, for example. typically have an average diameter of at least 50 µm (micron), preferably at least 150 µm (micron). Generally, the beads have an average diameter between 50 and 1500 µm (micron), and more preferably between 150 to 600 µm (micron).

As used herein the term ‘micron sized' denotes an object that has at least one linear dimension having a mean size between about 0.1 µm (1 µm = one micron = 1 x 10^{-6}m) to about 2000 µm. A preferred mean size for the micron-sized materials described herein is less than about 1000 µm (micron), more preferably less than about 600 µm (micron) most preferably less than about 500 µm (micron), for example less that about 200 µm (micron). Micron-sized materials exist with the micron-size in three dimensions (micro-particles), two dimensions (micro-tubes having a micro-sized cross section, but indeterminate length) or one dimension (micro-layers having a micro-sized thickness, but indeterminate area). Usefully the present invention relates to materials that comprise micro-particles. The particle size values given herein may be measured by a Coulter LS230 Particle Size Analyser (laser diffraction) and are the volume mean. The particle sizes are quoted as a linear dimension which would be the diameter of an approximate spherical particle having the same volume as the volume mean measured.

Such vinyl polymer beads are widely applied in the field of coatings (e.g. road markings, marine coatings), adhesives, colorants, photographic applications, inks, powder coatings or plastics filler and even in personal care products if the residual monomer content is low enough. The beads may be used in a liquid medium which may be aqueous or solvent based. Preferably if a solvent is used, a bio-renewable solvent is used. Bio-renewable solvents include for example bio-alcohols, xylene, butyl acetate, ethyl acetate, ethyl lactate and the VertecBio^{TM} solvents available from Liberty Chemicals.

The preparation of vinyl polymer beads is well known and is described in for example EP739359 which discloses the use of a cobalt chelate for Mw control and in US 4463032 which discloses polymers in bead form which are conventionally produced by a bead (suspension) polymerisation method where with this method, the monomers (disperse phase) are dispersed in a non-solvent (continuous phase) by mechanical action (agitation) and polymerised in that form.

Thus, this aspect of the invention provides a process for preparing vinyl polymer beads having a molecular weight in the range of from 3,000 to 500,000 g/mol and a glass transition temperature in the range of from 30 °C to 175 °C and an acid value less than 150 mgKOH/g, preferably from 0 to 100 mgKOH/g; said process comprising aqueous suspension polymerisation of olefinically unsaturated monomers using a free-radical initiator, wherein at least 20 wt-% of the olefinically unsaturated monomers used comprises at least one monomer of Formula 1 (preferably di(n-butyl) itaconate (DBI), more preferably derived from a bio-renewable source.

The monomers of Formula 1 correspond to the component (a) of the process of present invention, and any acid functional monomers used to achieve the desired AV correspond to component (b) of the present invention; and the remaining monomers that may be used correspond as appropriate to optional components (c) and/or (d) of the process of the present invention.

Other preferred features of this aspect of the present invention are given below and/or in the claims.

A process for preparing vinyl polymer beads as described herein where the olefinically unsaturated monomers are biorenewable and also comprise at least one monomer are selected from the group consisting bio-renewable (meth)acrylic acid and or bio-renewable alkyl (meth)acrylate.

Preferred bio-renewable monomers are selected from the group consisting of bio-renewable: α-methylene butyrolactone, α-methylene valerolactone, α-methylene γ-R^1 butyrolactone (R^1 can be an optionally substituted alkyl or optionally substituted aryl); itaconates such as dialkyl itaconates and monoalkyl itaconates, itaconic acid, itaconic anhydride, crotonic acid and alkyl esters thereof, citraconic acid and alkyl esters thereof, maleic anhydride, methylene malonic acid and its mono and dialkyl esters, citraconic anhydride, mesaconic acid and alkyl esters thereof.

More preferred bio-renewable monomers are selected from the group consisting of bio-renewable: N-R^2, α-methylene butyrolactam (R^2 can be an optionally substituted alkyl or optionally substituted aryl); N-R^2, α-methylene γ-R^1 butyrolactam; N-alkyl itaconimids; itaconmonoamids; itacondiamids; ialkyl itaconamides, mono alkyl itaconamides; furfuryl (meth)acrylate; and fatty acid functional (meth)acrylates.

The above process may further comprise the isolation of the beads followed by a drying step at 40 to 100 C optionally carried out over a period of 3 to 40 hours.

Vinyl polymer beads obtained and/or obtainable by this process forms a further aspect of the invention.

The vinyl polymer beads of the invention and/or the copolymers that comprise them may additionally have one or more of the following preferred properties:
comprise at least about 1.5 dpm/gC of carbon-14.
have an acid value (AV) from 0 to 20 mgKOH/g, more preferably either in on embodiment from 45 to 65 mg KOH/g, or an alternative embodiment from 100 to 150 mg KOH/g.

A still yet other aspect of the invention provides a composition comprising the vinyl polymer beads of the invention and a carrier.

A another aspect of the invention provides a method of coating a surface of a substrate with a composition comprising vinyl beads comprising the steps of applying the composition to the surface and then drying the composition. Suitable substrate may be selected from the group consisting of tarmac, wood, plastic, metal and paper.

Compositions comprising the vinyl polymer beads of the invention may be used as a bio-renewable liquid medium in a coating composition.

The respective ratio of the weight of dispersed phase to the weight of the continuous phase may be from 10/90 to 50/50 and more preferably from 30/70 to 45/55..

In another embodiment, the invention relates to vinyl polymer beads obtainable by the process according to this aspect of the invention. In particular the vinyl polymer beads according to the invention have a residual monomer content of less than 2500 ppm and more preferably less than 1000 ppm.

The vinyl polymer beads according to the invention are prepared by suspension polymerisation (also known as granular, bead, or pearl polymerisation due to the shape of the resultant polymer particles) according to known methods in the art as illustrated in the examples.

Initiators for polymerizing the monomers to provide the vinyl polymer beads of the invention are those which are normally suitable for free-radical polymerisation of acrylate monomers and which are oil-soluble and have low solubility in water such as e.g. organic peroxides, organic peroxyesters and organic azo initiators. The initiator is generally used in an amount of about 0.1 to 2 wt-% based on the total monomer content.

Useful chain transfer agents include mercapto-acids and alkyl esters thereof, carbon tetrabromide, mixtures thereof and cobalt chelate. Dodecylmercaptane is preferred. The mercapto chain transfer agent generally is used in an amount of about 0.01 to 3.0 wt-% , preferably in an amount of 0.1 to 2 wt-% based on the total monomer content. Typical cobalt chelate levels used range from 1 to 200 ppm and more preferably from 10 to 100 ppm.

Optionally, a water soluble inhibitor can be added to inhibit polymerisation in the water phase in order to prevent the formation of too much polymer by emulsion and/or solution polymerisation in the water phase, which can result in bead agglomeration or emulsion type polymerization. Suitable inhibitors include those selected from thiosulfates, thiocyanates, water soluble hydroquinones and nitrites. When used, the water soluble inhibitor can generally be added in an amount of from about 0.01 to about 1 parts by weight based on 100 parts total monomer content.

Furthermore, a water soluble or water dispersible polymeric stabiliser is needed to stabilize the suspension and in order to obtain stable beads. The stabiliser is preferably a synthetic water soluble or water dispersible polymer such as e.g. polyvinylalcohol, gelatine, starch, methylcellulose, carboxymethylcellulose, hydroxyethylcellulose, poly(meth)vinyl acid and their sodium salts, and the like. The stabiliser is preferably used in an amount of about 0.001 to 10 wt-% , more preferably in an amount of about 0.01 to 1 wt-% based on the total monomer content.

Other additives can optionally be used such as e.g. mono-, di- and trivalent metal salts, borax, urea, glyoxal and urea formaldehyde resin. Biocides (both bactericides and fungicides) can also be added, in order to prevent microbial growth in the finished product and during its use in water based systems.

The monomers, free-radical initiator, and any optional materials can be mixed together in the prescribed ratio to form a premix. The stabiliser can be combined with water and then with the premix to form an oil in water suspension. The resulting suspension typically comprises from about 10 to about 50 weight percent monomer premix and from about 90 to about 50 weight percent water phase. Bead-type suspension polymerisation in accordance with the present invention is typically a thermally initiated polymerisation and is preferably carried out with agitation for about 2 to about 16 hours at a temperature between about 40° C and 90° C.

After isolation of the beads according to standard methods such as filtration or centrifugation the beads are preferably subjected to an extended drying, preferably at about 40 to 100°C depending on the actual Tg of the final polymer composition. The drying can be performed by commonly known means to a person skilled in the art such as e.g. using a fluidised bed dryer or a conventional oven. The drying time can be easily adjusted by a person skilled in the art and is usually carried out over a period of from about 3 to about 40 hours, more usually from 8 to 20 hours and in particular from 8 to 10 hours.

In a preferred embodiment the process further comprises the isolation of the vinyl polymer beads followed by the step of drying at a temperature of from 40 to 100°C and more preferably from 80 to 100°C.

In addition to the monomers of Formula 1 (such as higher itaconate esters e.g. DBI), other monomers that may be used to prepare copolymers of the invention comprise:

unsaturated monomers belonging to the general class of methacrylates, e.g. C_{1-30}alkyl irrespective of the functionality;

unsaturated monomers belonging to the general class of acrylates, e.g. C_{1-30}alkyl irrespective of the functionality;

unsaturated hydrocarbon monomers like e.g. butadiene, isoprene, styrene, vinyl toluene, α-methyl styrene, tert.-butyl styrene etc.;

unsaturated monomers belonging to the class of vinyl halides, vinyl esters, vinyl ethers;

multi-olefinically unsaturated monomers such as di-allylphthalate, allylmethacrylate; and/or

any multi unsaturated monomers of any of the aforementioned types.

Preferably the monomers that are other than of Formula 1 are also derived from a bio-renewable source.

Improved properties of beads of the present invention may include heat resistance, colloidal stability, pigment compatibility, surface activity, blocking resistance and reduced MFFT depending on the monomers used.

The monomer system used for the preparation of the vinyl polymer beads may comprise in addition to those of Formula 1 any suitable combination of olefinically unsaturated monomers which is amenable to copolymerisation (including the bio-renewable monomers described herein which may of course also be acid-functional, crosslinkable etc at described below).

Acid-functional olefinically unsaturated monomers include a monomer bearing an acid-forming group which yields, or is subsequently convertible to, such an acid-functional group (such as an anhydride, e.g. methacrylic anhydride or maleic anhydride). Examples of such acid functional monomers have already been given as component (b) previously and may also be used in this aspect of the invention.

Other, non-acid functional, non-crosslinking monomers which may be copolymerised with the acid monomers include acrylate and methacrylate esters and styrenes; also dienes such as 1,3-butadiene and isoprene, vinyl esters such as vinyl acetate, and vinyl alkanoates. Methacrylates include normal or branched alkyl esters of C1 to C12 alcohols and methacrylic acid, such as methyl methacrylate, ethyl methacrylate, and n-butyl methacrylate, and (usually C5 to C12) cycloalkyl methacrylates acid such as isobornyl methacrylate and cyclohexyl methacrylate. Acrylates include normal and branched alkyl esters of C1 to C12 alcohols and acrylic acid, such as methyl acrylate, ethyl acrylate, n-butyl acrylate, and 2-ethylhexyl acrylate, and (usually C5-C12) cycloalkyl acrylates such as isobornyl acrylate and cyclohexylacrylate. Styrenes include styrene itself and the various substituted styrenes, such as .alpha.-methyl styrene and t-butyl styrene. Nitriles such as acrylonitrile and methacrylonitrile may also be polymerised, as well as olefinically unsaturated halides such as vinyl chloride, vinylidene chloride and vinyl fluoride.

Functional monomers which impart crosslinkability (crosslinking monomers for short) include epoxy (usually glycidyl) and hydroxyalkyl (usually C1-C12, e.g. hydroxyethyl)methacrylates and acrylates, as well as keto or aldehyde functional monomers such as acrolein, methacrolein and vinyl methyl ketone, the acetoacetoxy esters of hydroxyalkyl (usually C1-C12) acrylates and methacrylates such as acetoacetoxyethyl methacrylate and acrylate, and also keto-containing amides such as diacetone acrylamide. The purpose of using such functional monomer is to provide subsequent crosslinkability in the resulting polymer system as discussed. (In principle the functional monomer used for imparting crosslinkability could be acid-bearing monomer, but this is not usual) and for the purpose of this invention acid-bearing monomers are not considered as crosslinking monomers.

In an especially preferred embodiment of the invention is provided a vinyl copolymer prepared via suspension polymerization comprising at least 10 wt-% on total copolymer composition of mono-or diesters of itaconic acid (in addition to the DBI). More preferably the total content of mono- or diesters of itaconic acid (including the DBI) is at least 20 wt-%, more preferably 25 wt-%, even more preferably at least 30 wt-%, most preferably at least 40 wt-%, and especially preferably at least 50 wt-% .

The vinyl polymer beads made according to the present invention preferably have a molecular weight in the range of from preferably 5,000 to 100,000 g/mol.

The vinyl polymer beads made according to the present invention preferably have a glass transition temperature in the range of from 35°C to 150°C and more preferably in the range of from 50°C to 115°C.

The vinyl polymer beads made according to the present invention preferably have a an average particle size of about 50 to 500 μm (micron) more preferably from 200 to 500 μm (micron).

The vinyl polymer beads made according to the present invention in one embodiment preferably have an acid value of from 0 to 20 mgKOH/g.

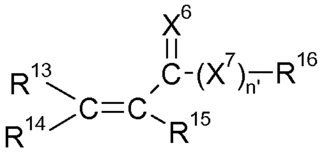
The vinyl polymer beads of the invention may be used in coating compositions but also in printing compositions and/or personal care compositions

The vinyl polymer beads made according to the present invention in another embodiment preferably have an acid value of from 45 to 65 mgKOH/g when used for printing compositions.

The vinyl polymer beads made according to the present invention in another embodiment preferably have an acid value of from 100 to 150 mgKOH/g when used for personal care compositions.

The term “activated unsaturated moiety”, is used herein to denote a species comprising at least one unsaturated carbon to carbon double bond in chemical proximity to at least one activating moiety. Preferably the activating moiety comprises any group which activates an ethylenically unsaturated double bond for addition thereon by a suitable electrophillic group. Conveniently the activating moiety comprises oxy, thio, (optionally organo substituted)amino, thiocarbonyl and/or carbonyl groups (the latter two groups optionally substituted by thio, oxy or (optionally organo substituted) amino). More convenient activating moieties are (thio)ether, (thio)ester and/or (thio)amide moiet(ies). Most convenient “activated unsaturated moieties” comprise an “unsaturated ester moiety” which denotes an organo species comprising one or more "hydrocarbylidenyl(thio)carbonyl(thio)oxy” and/or one or more “hydrocarbylidenyl(thio)- carbonyl(organo)amino” groups and/or analogous and/or derived moieties for example moieties comprising (meth)acrylate functionalities and/or derivatives thereof. “Unsaturated ester moieties” may optionally comprise optionally substituted generic α,β-unsaturated acids, esters and/or other derivatives thereof including thio derivatives and analogs thereof.

Preferred activated unsaturated moieties are those represented by a radical of Formula 4.



Formula 4

where n’ is 0 or 1, X^6 is oxy or, thio; X^7 is oxy, thio or NR^{17} (where R^{17} represents H or optionally substituted organo), R^{13}, R^{14}, R^{15} and R^{16} each independently represent a bond to another moiety in Formula 1, H, optional substituent and/or optionally substituted organo groups, where optionally any of R^{13}, R^{14}, R^{15} and R^{16} may be linked to form a ring; where at least one of R^{13}, R^{14}, R^{15} and R^{16} is a bond; and all suitable isomers thereof, combinations thereof on the same species and/or mixtures thereof.

The terms “activated unsaturated moiety”; “unsaturated ester moiety” and/or Formula 4 herein represents part of a formula herein and as used herein these terms denote a radical moiety which depending where the moiety is located in the formula may be monovalent or multivalent (e.g. divalent).

More preferred moieties of Formula 4 (including isomers and mixtures thereof) are those where n’ is 1; X^6 is O; X^7 is O, S or NR^7.

R^{13}, R^{14}, R^{15} and R^{16} are independently selected from: a bond, H, optional substituents and optionally substituted C_{1-10}hydrocarbo, optionally R^{15} and R^{16} may be linked to form (together with the moieties to which they are attached) a ring; and where present R^{17} is selected from H and optionally substituted C_{1-10}hydrocarbo.

Most preferably n’ is 1, X^6 is O; X^7 is O or S and R^{13}, R^{14}, R^{15} and R^{16} are independently a bond, H, hydroxy and/or optionally substituted C_{1-6}hydrocarbyl.

For example n’ is 1, X^6 and X^7 are both O; and R^3, R^4, R^5 and R^6 are independently a bond, H, OH, and/or C_{1-4}alkyl; or optionally R^5 and R^6 may together form a divalent C_{0-4}alkylenecarbonylC_{0-4}alkylene moiety so Formula 4 represents a cyclic anhydride (e.g. when R^{15} and R^{16} together are carbonyl then Formula 4 represents a maleic anhydride or derivative thereof).

For moieties of Formula 4 where n' is 1 and X^6 and X^7 are both O then when one of (R^{13} and R^{14}) is H and also R^{13} is H, Formula 4 represents an acrylate moiety, which includes acrylates (when both R^{13} and R^{14} are H) and derivatives thereof (when either R^{13} and R^{14} is not H). Similarly when one of (R^{13} and R^{14}) is H and also R^{15} is CH_3, Formula 4 represents an methacrylate moiety, which includes methacrylates (when both R^{13} and R^{14} are H) and derivatives thereof (when either R^{13} and R^{14} is not H). Acrylate and/or methacrylate moieties of Formula 5 are particularly preferred.

Conveniently moieties of Formula 4 are those where n' is 1; X^6 and X^7 are both O; R^{13} and R^{14} are independently a bond, H, CH_3 or OH, and R^{15} is H or CH_3; R^{16} is H or R^{15} and R^{16} together are a divalent C=O group.

More conveniently moieties of Formula 4 are those where n' is 1; X^6 and X^7 are both O; R^{13} is OH, R^4 is CH_3, and R^{15} is H and R^6 is a bond and/or tautomer(s) thereof (for example of an acetoacetoxy functional species).

Most convenient unsaturated ester moieties are selected from: $-OCO-CH=CH_2$; $-OCO-C(CH_3)=CH_2$; acetoacetoxy, $-OCOCH=C(CH_3)(OH)$ and all suitable tautomer(s) thereof.

It will be appreciated that any suitable moieties represented by Formula 4 could be used in the context of this invention such as other reactive moieties.

VINYL POLYMER

Whilst the term vinyl polymer is commonly used to refer to thermoplastic polymers derived by polymerization from compounds containing the vinyl group ($CH_2=CH-$), the term "vinyl polymer" is used herein more broadly to denote any polymer (whether thermoplastic or not) that comprises (e.g. as repeat units therein) and/or is derived from monomers and/or polymer precursors comprising one or more of the following moieties: activated unsaturated moieties (such as acrylates and/or methacrylates); any olefinically unsaturated moieties (such as vinyl moieties); mixtures thereof; and/or combinations thereof within the same moiety.

There is an increasing demand to use bio-renewable monomers in order to improve the sustainability of the polymers used in for example coating applications. In view of concerns about depletion of fossil fuel resources or an increase in carbon dioxide in the air that poses a global-scale environmental problem in recent years, methods for producing raw materials of these polymers from biomass resources have attracted al lot of attention. Since these resources are renewable and therefore have a carbon-neutral biomass, such methods are expected to gain in particular importance in future. It is therefore a preferred feature of the present invention and the aspects described herein that where possible the monomers (especially the higher itaconate diesters such as DBI) as far as possible are biorenewable.

Preferably at least 30 wt-%, more preferably at least 50 wt-%, and especially 70 wt-% of the olefinically unsaturated monomers used to form the polymers of the invention are derived from at least one bio-renewable olefinically unsaturated monomer. Bio-renewable monomers may be obtained fully or in part from bio-renewable sources. Thus it is preferred to also measure the carbon-14 content to determine the biorenewability.

The content of carbon-14 (C-14) is indicative of the age of a bio-based material. It is known in the art that C-14, which has a half life of about 5,700 years, is found in bio-renewable materials but not in fossil fuels. Thus, "bio-renewable materials" refer to organic materials in which the carbon comes from non-fossil biological sources. Examples of bio-renewable materials include, but are not limited to, sugars, starches, corns, natural fibres, sugarcanes, beets, citrus fruits, woody plants, cellulosics, lignocelluosics, hemicelluloses, potatoes, plant oils, other polysaccharides such as pectin, chitin, levan, and pullulan, and a combination thereof.

C-14 levels can be determined by measuring its decay process (disintegrations per minute per gram carbon or dpm/gC) through liquid scintillation counting. In one embodiment of the present invention, polymer A, polymer B and/or the olefinically unsaturated monomer(s) that are used to obtain polymer A and/or polymer B may considered sufficiently biorenewable for the purposes of this embodiment of the invention when the respective polymer A, polymer B and/or olefinically unsaturated monomer comprise an amount of carbon-14 to produce a decay of at least about 1.5 dpm/gC (disintegrations per minute per gram carbon), more preferably at least 2 dpm/gC, most preferably at least 2.5 dpm/gC, and especially at least 4 dpm/gC.

It is preferred that the higher itaconate diesters such as DBI are biorenewable, however other monomers used in the present invention may also be biorenewable. Examples of bio-renewable monomers include but are not limited to bio-based acrylics obtained by for example using bio-derived alcohols such as bio-butanol and include (meth)acrylic acid and alkyl (meth)acrylate, where alkyl is preferably selected from methyl, ethyl, butyl or 2-ethylhexyl.

Acrylic acid can be made from glycerol, as is disclosed by Arkema, or from lactic acid as described by US7687661. Methacrylic acid can be prepared from ethene, methanol and carbon monoxide (all bio-renewable), as disclosed by Lucite International Ltd.

Olefinically unsaturated bio-renewable monomers which may additionally provide a contribution to improved coating properties include α-methylene butyrolactone, α-methylene valerolactone, α-methylene γ-R^3 butyrolactone (R^3 can be an optionally substituted alkyl or optionally substituted aryl); itaconates such as dialkyl itaconates (including DBI) and monoalkyl itaconates, itaconic acid, itaconic anhydride, crotonic acid and alkyl esters thereof, citraconic acid and alkyl esters thereof, methylene malonic acid and its mono and dialkyl esters, citraconic anhydride, mesaconic acid and alkyl esters thereof.

Other non-acid functional, non-crosslinking monomers include diesters of itaconic acid. Preferred examples of such monomers include dimethyl itaconate, diethyl itaconate, di-n-propyl itaconate, di-i-propyl itaconate, di-n-butyl itaconate, di-i-butyl itaconate, and di-2-ethyl hexyl itaconate.

Another useful set of useful bio-renewable monomers include N-R^2, α-methylene butyrolactam (R^2 can be an optionally substituted alkyl or optionally substituted aryl); N-R^2, α-methylene γ-R^1 butyrolactam; N-alkyl itaconimids; itaconmonoamids; itacondiamids; ialkyl itaconamides, mono alkyl itaconamides; furfuryl (meth)acrylate; fatty acid functional (meth)acrylates such as DAPRO FX-522 from Elementis and Visiomer ® MUMA from Evonik.

It is appreciated that certain features of the invention, which are for clarity described in the context of separate embodiments may also be provided in combination in a single embodiment. Conversely various features of the invention, which are for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

The object of the present invention is to solve some or all of the problems or disadvantages (such as identified throughout the application herein) with the prior art.

Unless the context clearly indicates otherwise, as used herein plural forms of the terms herein are to be construed as including the singular form and vice versa.

The term “comprising” as used herein will be understood to mean that the list following is non exhaustive and may or may not include any other additional suitable items, for example one or more further feature(s), component(s), ingredient(s) and/or substituent(s) as appropriate.

The terms ‘effective’, ‘acceptable’ ‘active’ and/or ‘suitable’ (for example with reference to any process, use, method, application, preparation, product, material, formulation, compound, monomer, oligomer, polymer precursor, and/or polymers described herein as appropriate) will be understood to refer to those features of the invention which if used in the correct manner provide the required properties to that which they are added and/or incorporated to be of utility as described herein. Such utility may be direct for example where a material has the required properties for the aforementioned uses and/or indirect for example where a material has use as a synthetic intermediate and/or diagnostic tool in preparing other materials of direct utility. As used herein these terms also denote that a functional group is compatible with producing effective, acceptable, active and/or suitable end products.

Preferred utility of the present invention comprises as a coating composition.

In the discussion of the invention herein, unless stated to the contrary, the disclosure of alternative values for the upper and lower limit of the permitted range of a parameter coupled with an indicated that one of said values is more preferred than the other, is to be construed as an implied statement that each intermediate value of said parameter, lying between the more preferred and less preferred of said alternatives is itself preferred to said less preferred value and also to each less preferred value and said intermediate value.

For all upper and/or lower boundaries of any parameters given herein, the boundary value is included in the value for each parameter. It will also be understood that all combinations of preferred and/or intermediate minimum and maximum boundary values of the parameters described herein in various embodiments of the invention may also be used to define alternative ranges for each parameter for various other embodiments and/or preferences of the invention whether or not the combination of such values has been specifically disclosed herein.

Thus for example a substance stated as present herein in an amount from 0 to ‘’x’’ (e.g. in units of mass and/or weight %) is meant (unless the context clearly indicates otherwise) to encompass both of two alternatives, firstly a broader alternative that the substance may optionally not be present (when the amount is zero) or present only in an de-minimus amount below that can be detected. A second preferred alternative (denoted by a lower amount of zero in a range for amount of substance) indicates that the substance is present, and zero indicates that the lower amount is a very small trace amount for example any amount sufficient to be detected by suitable conventional analytical techniques and more preferably zero denotes that the lower limit of amount of substance is greater than or equal to 0.001 by weight % (calculated as described herein).

It will be understood that the total sum of any quantities expressed herein as percentages cannot (allowing for rounding errors) exceed 100%. For example the sum of all components of which the composition of the invention (or part(s) thereof) comprises may, when expressed as a weight (or other) percentage of the composition (or the same part(s) thereof), total 100% allowing for rounding errors. However where a list of components is non exhaustive the sum of the percentage for each of such components may be less than 100% to allow a certain percentage for additional amount(s) of any additional component(s) that may not be explicitly described herein.

In the present invention, unless the context clearly indicates otherwise, an amount of an ingredient stated to be present in the composition of the invention when expressed as a weight percentage, is calculated based on the total amount of monomers in the composition being equivalent to 100% (thus for example components (a) + (b) + (c) + (d) total 100%). For convenience certain non monomer ingredients (such as for example chain transfer agents (CTA)) which fall outside the definitions of any of components (a) to (d) may also be calculated as weight percentages based on total monomer (i.e. where the weight of total monomers alone is set at 100%). As the weight % of monomers (for example for components (a) to (d)) by definition total 100% it will be seen that using monomer based weight % values for the non-monomer ingredients (i.e. those components outside (a) to (d)) will mean the total percentages will exceed 100%. Thus amounts of non-monomer ingredients expressed as monomer based weight percentages can be considered as providing a ratio for the weight amounts for these ingredients with respect to the total weight of monomers which is used only as a reference for calculation rather than as a strict percentage. Further ingredients are not excluded from the composition when (a) + (b) + (c) + (d) total 100% and weight percentages based on total monomers should not be confused with weight percentages of the total composition.

The term ''substantially'' as used herein may refer to a quantity or entity to imply a large amount or proportion thereof. Where it is relevant in the context in which it is used ''substantially'' can be understood to mean quantitatively (in relation to whatever quantity or entity to which it refers in the context of the description) there comprises an proportion of at least 80%, preferably at least 85%, more preferably at least 90%, most preferably at least 95%, especially at least 98%, for example about 100% of the relevant whole. By analogy the term ''substantially-free'' may similarly denote that quantity or entity to which it refers comprises no more than 20%, preferably no more than 15%, more preferably no more than 10%, even more preferably no more than 5%, most preferably no more than 2%, especially no more than 1.5%, for example about 0% (e.g. completely absent or if present only in an undetectable amount) of the relevant whole.

The terms 'optional substituent' and/or 'optionally substituted' as used herein (unless followed by a list of other substituents) signifies the one or more of following groups (or substitution by these groups): carboxy, sulpho, formyl, hydroxy, amino, imino, nitrilo, mercapto, cyano, nitro, methyl, methoxy and/or combinations thereof. These optional groups include all chemically possible combinations in the same moiety of a plurality (preferably two) of the aforementioned groups (e.g. amino and sulphonyl if directly attached to each other represent a sulphamoyl group). Preferred optional substituents comprise: carboxy, sulpho, hydroxy, amino, mercapto, cyano, methyl, halo, trihalomethyl and/or methoxy.

The synonymous terms 'organic substituent' and "organic group" as used herein (also abbreviated herein to "organo") denote any univalent or multivalent moiety (optionally attached to one or more other moieties) which comprises one or more carbon atoms and optionally one or more other heteroatoms. Organic groups may comprise organoheteryl groups (also known as organoelement groups) which comprise univalent groups containing carbon, which are thus organic, but which have their free valence at an atom other than carbon (for example organothio groups). Organic groups may alternatively or additionally comprise organyl groups which comprise any organic substituent group, regardless of functional type, having one free valence at a carbon atom. Organic groups may also comprise heterocyclyl groups which comprise univalent groups formed by removing a hydrogen atom from any ring atom of a heterocyclic compound: (a cyclic compound having as ring members atoms of at least two different elements, in this case one being carbon). Preferably the non carbon atoms in an organic group may be selected from: hydrogen, halo, phosphorus, nitrogen, oxygen, silicon and/or sulphur, more preferably from hydrogen, nitrogen, oxygen, phosphorus and/or sulphur.

Most preferred organic groups comprise one or more of the following carbon containing moieties: alkyl, alkoxy, alkanoyl, carboxy, carbonyl, formyl and/or combinations thereof; optionally in combination with one or more of the following heteroatom containing moieties: oxy, thio, sulphinyl, sulphonyl, amino, imino, nitrilo and/or combinations thereof. Organic groups include all chemically possible combinations in the same moiety of a plurality (preferably two) of the aforementioned carbon containing and/or heteroatom moieties (e.g. alkoxy and carbonyl if directly attached to each other represent an alkoxycarbonyl group).

The term ‘hydrocarbo group’ as used herein is a sub-set of a organic group and denotes any univalent or multivalent moiety (optionally attached to one or more other moieties) which consists of one or more hydrogen atoms and one or more carbon atoms and may comprise one or more saturated, unsaturated and/or aromatic moieties. Hydrocarbo groups may comprise one or more of the following groups. Hydrocarbyl groups comprise univalent groups formed by removing a hydrogen atom from a hydrocarbon (for example alkyl). Hydrocarbylene groups comprise divalent groups formed by removing two hydrogen atoms from a hydrocarbon, the free valences of which are not engaged in a double bond (for example alkylene). Hydrocarbylidene groups comprise divalent groups (which may be represented by “$R_2C=$”) formed by removing two hydrogen atoms from the same carbon atom of a hydrocarbon, the free valences of which are engaged in a double bond (for example alkylidene). Hydrocarbylidyne groups comprise trivalent groups (which may be represented by “$RC\equiv$”), formed by removing three hydrogen atoms from the same carbon atom of a hydrocarbon the free valences of which are engaged in a triple bond (for example alkylidyne). Hydrocarbo groups may also comprise saturated carbon to carbon single bonds (e.g. in alkyl groups); unsaturated double and/or triple carbon to carbon bonds (e.g. in respectively alkenyl and alkynyl groups); aromatic groups (e.g. in aryl groups) and/or combinations thereof within the same moiety and where indicated may be substituted with other functional groups

The term ‘alkyl’ or its equivalent (e.g. ‘alk’) as used herein may be readily replaced, where appropriate and unless the context clearly indicates otherwise, by terms encompassing any other hydrocarbo group such as those described herein (e.g. comprising double bonds, triple bonds, aromatic moieties (such as respectively alkenyl, alkynyl and/or aryl) and/or combinations thereof (e.g. aralkyl) as well as any multivalent hydrocarbo species linking two or more moieties (such as bivalent hydrocarbylene radicals e.g. alkylene).

Any radical group or moiety mentioned herein (e.g. as a substituent) may be a multivalent or a monovalent radical unless otherwise stated or the context clearly indicates otherwise (e.g. a bivalent hydrocarbylene moiety linking two other moieties). However where indicated herein such monovalent or multivalent groups may still also comprise optional substituents. A group which comprises a chain of three or more atoms signifies a group in which the chain wholly or in part may be linear, branched and/or form a ring (including spiro and/or fused rings). The total number of certain atoms is specified for certain substituents for example $C_{1\text{-}N}$organo, signifies a organo moiety comprising from 1 to N carbon atoms. In any of the formulae herein if one or more substituents are not indicated as attached to any particular atom in a moiety (e.g. on a particular position along a chain and/or ring) the substituent may replace any H and/or may be located at any available position on the moiety which is chemically suitable and/or effective.

Preferably any of the organo groups listed herein comprise from 1 to 36 carbon atoms, more preferably from 1 to 18. It is particularly preferred that the number of carbon atoms in an organo group is from 1 to 12, especially from 1 to 10 inclusive, for example from 1 to 4 carbon atoms.

As used herein chemical terms (other than IUAPC names for specifically identified compounds) which comprise features which are given in parentheses – such as (alkyl)acrylate, (meth)acrylate and/or (co)polymer - denote that that part in parentheses is optional as the context dictates, so for example the term (meth)acrylate denotes both methacrylate and acrylate.

Certain moieties, species, groups, repeat units, compounds, oligomers, polymers, materials, mixtures, compositions and/or formulations which comprise and/or are used in some or all of the invention as described herein may exist as one or more different forms such as any of those in the following non exhaustive list: stereoisomers (such as enantiomers (e.g. E and/or Z forms), diastereoisomers and/or geometric isomers); tautomers (e.g. keto and/or enol forms), conformers, salts, zwitterions, complexes (such as chelates, clathrates, crown compounds, cyptands / cryptades, inclusion compounds, intercalation compounds, interstitial compounds, ligand complexes, organometallic complexes, non-stoichiometric complexes, π-adducts, solvates and/or hydrates); isotopically substituted forms, polymeric configurations [such as homo or copolymers, random, graft and/or block polymers, linear and/or branched polymers (e.g. star and/or side branched), cross-linked and/or networked polymers, polymers obtainable from di and/or tri-valent repeat units, dendrimers, polymers of different tacticity (e.g. isotactic, syndiotactic or atactic polymers)]; polymorphs (such as interstitial forms, crystalline forms and/or amorphous forms), different phases, solid solutions; and/or combinations thereof and/or mixtures thereof where possible. The present invention comprises and/or uses all such forms which are effective as defined herein.

Polymers of the present invention may be prepared by one or more suitable polymer precursor(s) which may be organic and/or inorganic and comprise any suitable (co)monomer(s), (co)polymer(s) [including homopolymer(s)] and mixtures thereof which comprise moieties which are capable of forming a bond with the or each polymer precursor(s) to provide chain extension and/or cross-linking with another of the or each polymer precursor(s) via direct bond(s) as indicated herein.

Polymer precursors of the invention may comprise one or more monomer(s), oligomer(s), polymer(s); mixtures thereof and/or combinations thereof which have suitable polymerisable functionality. It will be understood that unless the context dictates otherwise term monomer as used herein encompasses the term polymer precursor and does not necessarily exclude monomers that may themselves be polymeric and/or oligomeric in character.

A monomer is a substantially monodisperse compound of a low molecular weight (for example less than one thousand daltons) which is capable of being polymerised.

A polymer is a polydisperse mixture of macromolecules of large molecular weight (for example many thousands of daltons) prepared by a polymerisation method, where the macromolecules comprises the multiple repetition of smaller units (which may themselves be monomers, oligomers and/or polymers) and where (unless properties are critically dependent on fine details of the molecular structure) the addition or removal one or a few of the units has a negligible effect on the properties of the macromolecule.

A oligomer is a polydisperse mixture of molecules having an intermediate molecular weight between a monomer and polymer, the molecules comprising a small plurality of monomer units the removal of one or a few of which would significantly vary the properties of the molecule.

Depending on the context the term polymer may or may not encompass oligomer.

The polymer precursor of and/or used in the invention may be prepared by direct synthesis or (if the polymeric precursor is itself polymeric) by polymerisation. If a polymerisable polymer is itself used as a polymer precursor of and/or used in the invention it is preferred that such a polymer precursor has a low polydispersity, more preferably is substantially monodisperse, to minimise the side reactions, number of by-products and/or polydispersity in any polymeric material formed from this polymer precursor. The polymer precursor(s) may be substantially un-reactive at normal temperatures and pressures.

Except where indicated herein polymers and/or polymeric polymer precursors of and/or used in the invention can be (co)polymerised by any suitable means of polymerisation well known to those skilled in the art. Examples of suitable methods comprise: thermal initiation; chemical initiation by adding suitable agents; catalysis; and/or initiation using an optional initiator followed by irradiation, for example with electromagnetic radiation (photo-chemical initiation) at a suitable wavelength such as UV; and/or with other types of radiation such as electron beams, alpha particles, neutrons and/or other particles .

The substituents on the repeating unit of a polymer and/or oligomer may be selected to improve the compatibility of the materials with the polymers and/or resins in which they may be formulated and/or incorporated for the uses described herein. Thus the size and length of the substituents may be selected to optimise the physical entanglement or interlocation with the resin or they may or may not comprise other reactive entities capable of chemically reacting and/or cross linking with such other resins as appropriate.

Another aspect of the invention broadly provides a coating composition comprising the polymers and/or beads of the present invention and/or as described herein.

A further aspect of the invention provides a coating obtained or obtainable from a coating composition of the present invention.

A yet other aspect of the invention broadly provides a substrate and/or article having coated thereon an (optionally cured) coating composition of the present invention.

A yet further aspect of the invention broadly provides a method of using polymers of the present invention and/or as described herein to prepare a coating composition.

A still further aspect of the invention broadly provides a method for preparing a coated substrate and/or article comprising the steps of applying a coating composition of the present invention to the substrate and/or article and optionally curing said composition in situ to form a cured coating thereon. The curing may be by any suitable means, such as thermally, by radiation and/or by use of a cross-linker.

Preferred coating compositions are solvent coating compositions or aqueous coating compositions, more preferably are aqueous coating compositions.

Optionally aqueous coating compositions may also comprise a co-solvent. A co-solvent, as is well known in the coating art, is an organic solvent employed in an aqueous composition to ameliorate the drying characteristics thereof, and in particular to lower its minimum film forming temperature. The co-solvent may be solvent incorporated or used during preparation of polymers of the invention or may have been added during formulation of the aqueous composition.

The compositions of the invention are particularly useful as or for providing the principle component of coating formulations (i.e. composition intended for application to a substrate without further treatment or additions thereto) such as protective or decorative coating compositions (for example paint, lacquer or varnish) wherein an initially prepared composition optionally may be further diluted with water and/or organic solvents, and/or combined with further ingredients or may be in more concentrated form by optional evaporation of water and/or organic components of the liquid medium of an initially prepared composition.

The compositions of the invention may be used in various applications and for such purposes may be optionally further combined or formulated with other additives and/or components, such as defoamers, rheology control agents, thickeners, dispersing and/or stabilizing agents (usually surfactants and/or emulsifiers), wetting agents, fillers, extenders, fungicides, bacteriocides, coalescing and wetting solvents or co-solvents (although solvents are not normally required), plasticisers, anti-freeze agents, waxes, colorants, pigments, dyes, heat stabilisers, levelling agents, anti-cratering agents, fillers, sedimentation inhibitors, UV absorbers, antioxidants, reactive diluents, neutralising agents, adhesion promoters and/or any suitable mixtures thereof.

The aforementioned additives and/or components and the like may be introduced at any stage of the production process or subsequently. It is possible to include fire retardants (such as antimony oxide) to enhance fire retardant properties.

The compositions of the invention may also be blended with other polymers such as vinyl polymers, alkyds (saturated or unsaturated), polyesters and or polyurethanes.

The coating composition of the invention may be applied to a variety of substrates including wood, board, metals, stone, concrete, glass, cloth, leather, paper, plastics, foam and the like, by any conventional method including brushing, dipping, flow coating, spraying, and the like. The coating composition of the invention may also be used to coat the interior and/or exterior surfaces of three-dimensional articles. The coating compositions of the invention may also be used, appropriately formulated if necessary, for the provision of films, polishes, varnishes, lacquers, paints, inks and adhesives. However, they are particularly useful and suitable for providing the basis of protective coatings for substrates that comprise wood (e.g. wooden floors), plastics, polymeric materials, paper and/or metal.

The carrier medium may be removed from the compositions of the invention once they have been applied to a substrate by being allowed to dry naturally at ambient temperature, or the drying process may be accelerated by heat. Crosslinking can be developed by allowing to stand for a prolonged period at ambient temperature (several days) or by heating at an elevated temperature (e.g. 50 °C) for a much shorter period of time.

In addition, the present invention relates to the use of copolymers of the present invention optionally in the form of organic particles / beads (optionally nano and/or micro sized) in any of the following uses:

As particles for encapsulating particles of a colorant composition, and to colorant compositions comprising the organic nano particles and/or micro particles of the present invention. Colorant denotes any coloured material (including materials which absorb or reflect UV or IR radiation instead of or in addition to visible light) and includes dyes and pigments. Dyes are generally soluble in the medium to which they are added and are typically (but not exclusively) organic liquids. Pigments are generally insoluble in the medium to which they are added and typically (but not exclusively) inorganic solids. Preferably the colorant is a dye. Encapsulating of particles of colorant composition may take place suspending particles of colorant composition in the solution prior to emulsification or during emulsification, so that particles of colorant composition is encapsulated in the nano particles during curing of the solution. Alternatively, the particles of colorant composition may be added after the curing reaction, so that the encapsulation takes place during the optional agglomeration process.

A non limiting list of other end uses for the copolymers and/or beads of the invention include:

Use in binders for a toner composition, and toner compositions may comprise the particles of the present invention;

As additives for sheet moulded compounds (also denoted herein as SMC), where the presence of the particles (particularly spray dried particles) leads to lower density products;

As plastic pigment, particularly for coatings, such as paper coatings, where the presence of the particles may provide high gloss or tuneable gloss properties of the product;

As fillers in composite materials and particularly in concrete, where for example the use of the particles as micro fillers may increase strength, lower porosity, reduce density and/or prevent water penetration into the structure;

As filler for coatings, where for example the particles may provide anti blocking properties to the coating, increase scratch resistance, lower abrasion, increase drying speed, reduce the required amount of solvent, and reduce shrink;

As filler for waxes, where for example the particles may provide a lubricating effect, reduce weight, reduce abrasion and/or act as a high temperature filler;

Mono disperse particles of the invention may be used for spacers for example in display applications;

As hybrid colorant, where for example a colorant (preferably pigment) particle may interact with the particles of the invention in several ways. In one option pigment particles may be dispersed in the emulsion prior to curing of the resin and monomer. The pigment particles (which are usually hydrophobic) will tend to migrate inside the hydrophobic droplets of the solution. Curing the solution will form particles in which a pigment core is encapsulated within a shell of cured polymer. In another option the pigment particles may be co agglomerated with the nano particles to form micro particles. Both methods can produce pigments which are dispersible in water and which can be either partially accessible or inaccessible for direct contact with ambient atmosphere or other materials.

In adhesives, where for example the particles may be used as a filler or as a shrink reducing agent, since the particles will be inert during curing of the adhesive. As the particles will be strongly connected to the adhesive they will have no detrimental effect on adhesive strength.

As encapsulating agent for active ingredients that may be added to the emulsion prior to curing and remain in the particle upon curing. The resulting particles, which contain the active ingredient, are more easily dispersible and the active ingredient is protected. Examples of active ingredients are dyes and UV blockers.

As an ingredient in compositions suitable for use in personal care and/or as topical medicaments.

It will be appreciated that some of the above uses may overlap.

Depending on the desired properties of the topical medicament and/or personal care composition, particles of the invention (organic nano particles and/or micro particles) may be present in an amount from 0.001 to 99 %, preferably 0.1 to 80%, more preferably 0.5 to 50%, most preferably 1 to 20% by weight of the total composition. Any suitable, conventional ingredients suitable for such applications may be used, such as those well known to a skilled formulator of such compositions.

Topical medicament indicates a composition which is formulated for the delivery of a therapeutically active agent to, or via, the skin. A wide variety of active agents may be delivered using such formulations, including agents that are intended for treatment of the skin, such as anti acne agents, and systemically active agents for which the skin is merely the route of administration, rather than the site of action.

Non limiting examples of personal care compositions (which may or may not be applied topically) include: cosmetic compositions, hair care products, insect repellents, oral hygiene compositions, self tanning products, sunscreens, toiletry compositions, mixtures thereof, and/or combinations in the same composition.

Cosmetic composition indicates a composition that may be used on the body to modify its appearance. Non limiting examples of such compositions may include: after sun compositions, blushers, colour cosmetics, eye shadows, face creams, face masks, foundations, lip balms, lipsticks, moisturisers, powder formulations, temporary tattoos and other forms of body art; and toner cleansers. Cosmetic compositions may be applied as any suitable formulation type, non limiting examples of which include: creams, dispersions, emulsions (such as water in oil (w/o), oil in water (o/w), water in oil in water (w/o/w) and oil in water in oil (o/w/o), although emulsions where the continuous phase is aqueous such as o/w and w/o/w are preferred), gels, lotions, milks, ointments, pastes, powders, roll on, salves, serums, solutions, spray, sticks and suspensions.

Hair care composition indicates a composition that may be used on animal hair, preferably on human hair, most preferably on the human head. Non limiting examples of such a composition may include suitable: conditioners, creams, foams, gels, hair dyes, hair colorants, hair styling products, hot oil treatments, lotions, mascaras, masks, mousses, muds, rinses, shampoos, styling sprays and / or waxes.

Oral hygiene composition indicates a composition that may be suitable for use in oral hygiene, dental treatment and/or be otherwise applied to the buccal and/or oral cavity. Non limiting examples of such a composition may include suitable: chewing gums, dentifrices, denture cleansing formulations, flosses, glass ionomer cements, lozenges, mouth sprays, mouthwashes, tooth paints, tooth pastes and / or toothpowders.

Sunscreen indicates a composition that may be used on the body to provide protection against the sun's rays or other UV sources. Non limiting examples of such compositions may also include: sun blockers and / or tanning lotions.

Toiletry composition indicates a composition that may be used on the body to clean, scour, wash, perfume and / or reduce odour. Non limiting examples of such a composition may include suitable: anti microbial compositions, bath products (e.g. bath foams and bath salts), deodorants, detergents, perfumes, soaps and / or shower gels. Cleaning compositions (e.g. formulated domestic cleaning) may also be considered as toiletry compositions.

Many other variations embodiments of the invention will be apparent to those skilled in the art and such variations are contemplated within the broad scope of the present invention.

Further aspects of the invention and preferred features thereof are given in the claims herein.

TESTS

MINIMUM FILM FORMING TEMPERATURE

The minimum film forming temperature (MFFT) of a dispersion as used herein is the temperature where the dispersion forms a smooth and crack free coating or film using DIN 53787 and when applied using a Sheen MFFT bar SS3000.

SPOT TESTS

Coating films formed by blends of the invention can be tested in well known conventional spot tests (such as ASTM D1308-02e1) to determine the resistance of the film to various liquid reagents such as water, ethanol, detergent (e.g. that available commercially from Unilever under the trade mark Andy) and coffee. In one such test a standard volume (e.g. 0.5 ml) of the liquid reagent may be applied to the film to form a spot thereon (e.g. by pipette) which is then covered with a watch glass. After the time specified (e.g. in the tables herein) the film can be assessed and rated visually on a scale of 1 to 5 as described below.

KOENING HARDNESS

Koenig hardness as used herein is a standard measure of hardness, being a determination of how the viscoelastic properties of a film formed from the dispersion slows down a swinging motion deforming the surface of the film, and is measured according to DIN 53157 NEN5319.

GLASS TRANSITION TEMPERATURE (Tg)

As is well known, the glass transition temperature of a polymer is the temperature at which it changes from a glassy, brittle state to a plastic, rubbery state. The glass transition temperatures may be determined experimentally using Differential Scanning Calorimetry (DSC), taking the peak of the derivative curve as Tg, or calculated from the Fox equation. Thus the Tg, in degrees Kelvin, of a copolymer having "n" copolymerised comonomers is given by the weight fractions W of each comonomer type and the Tgs of the homopolymers (in degrees Kelvin) derived from each comonomer according to the equation:

$$\frac{1}{Tg} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2} + \dots\dots\dots\dots \frac{W_n}{Tg_n}$$

The calculated Tg in degrees Kelvin may be readily converted to °C.

SOLIDS CONTENT

The solids content of an aqueous dispersion of the invention is usually within the range of from about 20 to 65 wt-% on a total weight basis, more usually 30 to 55 wt-%. Solids content can, if desired, be adjusted by adding water or removing water (e.g. by distillation or ultrafiltration).

pH VALUE

The pH value of the dispersion of the invention can be from 2 to 10 and mostly is from 6 to 9.5.

BLOCKING

Block Resistance Measurement [Includes Blocking and Early Blocking]:

Step 1: Blocking:

A 100 micron wet film of the aqueous emulsion of the invention to which 10% butyldiglycol is added is cast on to a paper substrate and dried for 16 hours at 52 °C.

Step 1: Early Blocking:

A 250 micron wet film of the aqueous emulsion of the invention to which 10% butyldiglycol was added, is cast on to a paper substrate and dried for 24 hours at room temperature.

Step 2: Blocking and Early Blocking:

After cooling down to room temperature two pieces of coated film are placed with the coated side against each other under a load of 1 Kg/cm.sup.2 for 4 hours at 52 °C. After this time interval the load on the samples is removed and the samples are left to cool down to room temperature (22+-2 °C). When the two coatings can be removed from each other without any damage to the film (do not stick) the block resistance is very good and assessed as a 5. When they however completely stick together, block resistance is very bad and assessed as a 0.

Gas Chromatography Mass Spectrometry (GCMS)

to confirm polymerisation is substantially complete the content of free itaconate ester monomers content can be determined by GCMS. The GCMS analyses were performed on a Trace GC – DSQ MS (Interscience, Breda, the Netherlands) equipped with a CTC combi Pal robotic autosampler for head space has been used. The carrier gas was Helium and a CP Sil 5 low bleed/MS, 25 m x 0.25 mm i.d., 1.0 µm (CP nr. 7862) column has been used.

The GC-oven was programmed from 50°C (5 min) followed by different sequential temperature ramps of 5°C/min to 70°C (0 min), 15°C/min to 220°C (0 min), and ending with 25°C/min to 280°C (10 min). A continuous Helium flow of 1.2 ml/min was used. A hot split injection at 300°C was performed on a programmed temperature vaporizer (PTV). The injection volume was 1µl. The MS transfer line and ion source were both kept at 250°C. The samples were measured with single ion monitoring (SIM). For the specific case of dibutyl itaconate (DBI) the masses 127.0 and

59.0 Da were used, for the internal standard (iso butyl acrylate) the masses 55.0 and 73.0 were applied. The sample solutions were approximately 500 mg in 3 ml of internal standard solution (iso butyl acrylate in acetone). The calibration was performed with 5 different concentration levels from 0 to 500 ppm. The calculation was performed using Microsoft Excel with a linear calibration curve.

MOLECULAR WEIGHT

Unless the context clearly dictates otherwise the term molecular weight of a polymer or oligomer as used herein denotes weight average molecular weight (also denoted as M_w). M_w may be measured by any suitable conventional method for example by Gas Phase Chromatography (GPC – performed similarly to the GCMS method described above) and/or by the SEC method described below. GPC method is preferred

Determination of molecular weight of a polymer using SEC

The molecular weight of a polymer may also be determined using Size Exclusion Chromatography (SEC) with tetrahydrofuran as the eluent or with 1,1,1,3,3,3 hexafluoro isopropanol as the eluent.

1) tetrahydrofuran

The SEC analyses were performed on an Alliance Separation Module (Waters 2690), including a pump, auto injector, degasser, and column oven. The eluent was tetrahydrofuran (THF) with the addition of 1.0 vol% acetic acid. The injection volume was 150µl. The flow was established at 1.0 ml/min. Three PL MixedB (Polymer Laboratories) with a guard column (3µm PL) were applied at a temperature of 40°C. The detection was performed with a differential refractive index detector (Waters 410). The sample solutions were prepared with a concentration of 20 mg solids in 8 ml THF (+ 1vol% acetic acid), and the samples were dissolved for a period of 24 hours. Calibration is performed with eight polystyrene standards (polymer standard services), ranging from 500 to 4,000,000 g/mol. The calculation was performed with Millennium 32 software (Waters) with a third order calibration curve. The obtained molar masses are polystyrene equivalent molar masses (g/mol).

2) 1,1,1,3,3,3 hexafluoro isopropanol

The SEC analyses were performed on a Waters Alliance 2695 (pump, degasser and autosampler) with a Shodex RI-101 differential refractive index detector and Shimadzu CTO-20AC column oven. The eluent was 1,1,1,3,3,3 hexafluoro isopropanol (HFIP) with the addition of 0.2M potassium trifluoro acetate (KTFA). The injection volume was 50µl. The flow was established at 0.8 ml/min. Two PSS PFG Linear XL columns (Polymer Standards Service) with a guard column (PFG PSS) were applied at a temperature of 40°C. The detection was performed with a differential refractive index detector. The sample solutions were prepared with a concentration of 5 mg solids in 2 ml HFIP (+ 0.2M KTFA), and the samples were dissolved for a period of 24 hours. Calibration is performed with eleven polymethyl methacrylate standards (polymer standard services), ranging from 500 to 2,000,000 g/mol. The calculation was performed with Empower Pro software (Waters) with a third order calibration curve. The molar mass distribution is obtained via conventional calibration and the molar masses are polymethyl methacrylate equivalent molar masses (g/mol).

STANDARD CONDITIONS

As used herein, unless the context indicates otherwise, standard conditions (e.g. for drying a film) means a relative humidity of 50% ±5%, ambient temperature (which denotes herein a temperature of 23°C ±2°) and an air flow of ≤ (less than or equal to) 0.1m/s.

The following examples are provided to further illustrate the processes and compositions of the present invention. These examples are illustrative only and are not intended to limit the scope of the invention in any way. Unless otherwise specified all parts, percentages, and ratios are on a weight basis. The prefix C before an example indicates that it is comparative.

Various registered trademarks, other designations and/or abbreviations are used herein to denote some of ingredients used to prepare polymers and compositions of the invention. These are identified below by chemical name and/or trade-name and optionally their manufacturer or supplier from whom they are available commercially. However where a chemical name and/or supplier of a material described herein is not given it may easily be found for example in reference literature well known to those skilled in the art: such as: 'McCutcheon's Emulsifiers and Detergents', Rock Road, Glen Rock, N.J. 07452-1700, USA, 1997 and/or Hawley's

Condensed Chemical Dictionary (14th Edition) by Lewis, Richard J., Sr.; John Wiley & Sons.

In the examples the following abbreviations / monomers may be used:

BA = n-butyl acrylate (may be biorenewable)
BMA = n-butyl methacrylate (may be prepared using bio-renewable alkanols)
DBI denotes di(n-butyl) itaconate (also known as dibutyl 2-methylidenebutanedioate) (may be bio-renewable)
DDM denotes n-dodecyl mercaptane
DMI = dimethyl itaconate (may be bio-renewable)
DMW denotes dematerialized water
EDTA = ethylene diamine tetraacetic acid
HFIP denotes hexafluoro isopropanol
KTFA denotes potassium trifluoro actetate
MMA = methyl methacrylate (may be prepared using bio-renewable alkanols)
MAA = methacrylic acid (may be biorenewable)
NS denotes sodium sulfate
PAA denotes polyacrylic acid
STY denotes styrene;
D(iB)I denotes di(iso-butyl) itaconate (also known as di(tert-butyl)itaconate)
DPI denotes di(pentyl) itaconate
DHI denotes di(hexyl) itaconate
DHpI denotes di(heptyl) itaconate
DOI denotes di(n-octyl) itaconate
D(EH)I denotes di(2-ethylhexyl) itaconate
DDI denotes di(decyl) itaconate
DBzI denotes di(benzyl) itaconate
DPhI denotes di(phenyl) itaconate
BPI denotes butyl pentyl itaconate
BHI denotes butyl hexyl itaconate
HOI denotes hexyl n-octyl itaconate
IA denotes itaconic acid
MSA denotes the sulphonic acid of α-methyl styrene
DPrI denotes di(propyl) itaconate
CEA denotes beta carboxy ethyl acrylate

PA denotes propyl acrylate

OA denotes n-ocyl acrylate

MBI denotes the mono acid butyl itaconate (i.e. half ester)

IAn denotes itaconic anhydride

MMalA denotes methylene malonic acid,

MalAn denotes maleic anhydride, i

PHEMA denotes phosphated hydroxyl ethyl methacrylate

AMPS denotes 2-acrylamido-2-methylpropane sulfonic acid

URED denotes the monomer N-[2-(2-Oxo-1-imidazolidinyl)ethyl] methacrylate

MSTY denotes alpha methyl styrene

EXAMPLES 1 to 3 (Sequential vinyl polymers)

Example 1

To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer 84.853 parts of water, 0.253 parts of sodium bicarbonate, and 1.786 parts of a 30 wt-% solution of sodium lauryl sulphate in water are added and this mixture is heated to 50 °C. At 50 °C, 10 % of a first monomer feed consisting of 20.93 parts of water, 4.285 of a 30 wt-% solution of sodium lauryl sulphate in water, 0.726 parts of sodium bicarbonate, 0.246 parts of ammonium persulphate, 1.340 parts of methacrylic acid, 26.811 parts of dibutyl itaconate, and 25.456 parts of methyl methacrylate is added and the reactor contents are heated to 90 °C. After the reaction temperature has been reached, the reactor contents are stirred for 15 minutes.

Next, the remainder of the first monomer feed is added over a period of 210 minutes. When the feed is completed, the feed tank is rinsed with 1.885 parts of water.

The batch is kept at 90 °C for 30 minutes and cooled the batch to 70 °C. Next, a slurry comprising 0.289 parts of a 70 wt-% solution of t-butyl hydroperoxide in water and 1.228 parts of water is added and the batch is stirred for 5 minutes. Next, a second monomer feed, comprising 2.681 parts of methacrylic acid, 4.932 parts of methyl methacrylate, 15.117 parts of butyl acrylate, and 30.877 parts of butyl methacrylate is added over a period of 240 minutes. Simultaneously, a catalyst feed comprising 11.943 parts of water, 0.120 parts of i-ascorbic acid, and 1.071 parts of a 30 wt-% solution of sodium lauryl sulphate, is fed over the same period. After the second monomer feed is finished, the feed tank is rinsed with 1.885 parts of water.

The reactor contents are stirred at 70 °C for another 30 minutes, after which the batch is cooled to 30 °C. The pH of the emulsion is adjusted to 7 using 0.6 parts of a 25 % solution of ammonia in water or part of it. Simultaneously, 0.623 parts of water are added. The solids content of the emulsion is adjusted to 45 % using water.

The resulting emulsion has a solids content of 45 %, and a pH of 7.0.

Example 2

To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer 84.853 parts of water, 0.253 parts of sodium bicarbonate, and 1.786 parts of a 30 wt-% solution of sodium lauryl sulphate in water are added and this mixture is heated to 50 °C. At 50 °C, 10 % of a first monomer feed consisting of 20.93 parts of water, 4.285 of a 30 wt-% solution of sodium lauryl sulphate in water, 0.726 parts of sodium bicarbonate, 0.246 parts of ammonium persulphate, 1.340 parts of methacrylic acid, 14.044 parts of butyl methacrylate, 24.123 parts of dimethyl itaconate, and 14.100 parts of methyl methacrylate is added and the reactor contents are heated to 90 °C. After the reaction temperature has been reached, the reactor contents are stirred for 15 minutes.

Next, the remainder of the first monomer feed is added over a period of 210 minutes. When the feed is completed, the feed tank is rinsed with 1.885 parts of water.

The batch is kept at 90 °C for 30 minutes and cooled the batch to 70 °C. Next, a slurry comprising 0.289 parts of a 70 wt-% solution of t-butyl hydroperoxide in water and 1.228 parts of water is added and the batch is stirred for 5 minutes. Next, a second monomer feed, comprising 2.681 parts of methacrylic acid, 4.932 parts of methyl methacrylate, 15.117 parts of butyl acrylate, 18.762 parts of dibutyl itaconate, and 12.115 parts of butyl methacrylate is added over a period of 240 minutes. Simultaneously, a catalyst feed comprising 11.943 parts of water, 0.120 parts of i-ascorbic acid, and 1.071 parts of a 30 wt-% solution of sodium lauryl sulphate, is fed over the same period. After the second monomer feed is finished, the feed tank is rinsed with 1.885 parts of water.

The reactor contents are stirred at 70 °C for another 30 minutes, after which the batch is cooled to 30 °C. The pH of the emulsion is adjusted to 7 using 0.6 parts of a 25 % solution of ammonia in water or part of it. Simultaneously, 0.623 parts of water are added. The solids content of the emulsion is adjusted to 45 % using water.

The resulting emulsion has a solids content of 45 %, and a pH of 7.0.

Example 3

To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer 84.853 parts of water, 0.253 parts of sodium bicarbonate, and 1.786 parts of a 30 wt-% solution of sodium lauryl sulphate in water are added and this mixture is heated to 50 °C. At 50 °C, 10 % of a first monomer feed consisting of 20.93 parts of water, 4.285 of a 30 wt-% solution of sodium lauryl sulphate in water, 0.726 parts of sodium bicarbonate, 0.246 parts of ammonium persulphate, 1.340 parts of methacrylic acid, 14.044 parts of butyl methacrylate, and 38.223 parts of methyl methacrylate is added and the reactor contents are heated to 90 °C. After the reaction temperature has been reached, the reactor contents are stirred for 15 minutes.

Next, the remainder of the first monomer feed is added over a period of 210 minutes. When the feed is completed, the feed tank is rinsed with 1.885 parts of water.

The batch is kept at 90 °C for 30 minutes and cooled the batch to 70 °C. Next, a slurry comprising 0.289 parts of a 70 wt-% solution of t-butyl hydroperoxide in water and 1.228 parts of water is added and the batch is stirred for 5 minutes. Next, a second monomer feed, comprising 2.681 parts of methacrylic acid, 4.932 parts of methyl methacrylate, 2.673 parts of diacetone acrylamide, 12.444 parts of butyl acrylate, 26.803 parts of dibutyl itaconate, and 4.074 parts of butyl methacrylate is added over a period of 240 minutes. Simultaneously, a catalyst feed comprising 11.943 parts of water, 0.120 parts of i-ascorbic acid, and 1.071 parts of a 30 wt-% solution of sodium lauryl sulphate, is fed over the same period. After the second monomer feed is finished, the feed tank is rinsed with 1.885 parts of water.

The reactor contents are stirred at 70 °C for another 30 minutes, after which the batch is cooled to 30 °C. The pH of the emulsion is adjusted to 7 using 0.6 parts of a 25 % solution of ammonia in water or part of it. Simultaneously, 0.623 parts of water are added. The solids content of the emulsion is adjusted to 45 % using water.

The resulting emulsion has a solids content of 45 %, and a pH of 7.0.

EXAMPLES 4 to 7 (Vinyl oligomer -polymers)

Example 4

Oligomer 4A

To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer 549.0 parts of water and 0.7 parts of Aerosol GPG were charged. This mixture was heated to 70 °C. At 70 °C 10 % of a monomer feed consisting of 100.8 parts of water, 44.1 parts of methyl methacrylate, 136.2 parts of dimethyl itaconate, 14.6 parts of diacetone acrylamide, 24.3 parts of diethyl itaconate, 24.3 parts of methacrylic acid, 2.0 parts of Aerosol GPG, and 5.8 parts of 3-mercaptopropionic acid was added and the reactor contents were further heated to 85 °C. At 80 °C a solution consisting of 0.2 parts of ammonium persulphate and 11.3 parts of water was added.

At 85 °C, the remainder of the monomer feed was added over a period of 260 minutes. A catalyst feed, comprising 0.5 parts of ammonium persulphate and 33.5 parts of water was fed to the reactor in period of 250 minutes. At the end of the addition of the monomer feed 5.0 parts of water were used to rinse the feed tank and were added to the reactor. A temperature of 85 °C was maintained for 20 minutes after which the reaction mixture was cooled to 80 °C. At 80 °C the emulsion was neutralized using 19.4 parts of a 25 % solution of ammonia in water mixed with 21.2 parts of water. The reaction mixture was subsequently kept at 80 °C for another 20 minutes before it was cooled to room temperature. The solids content of the emulsion was adjusted to 25 % with water.

The resulting emulsion had a solids content of 25.1 % and a pH of 8.0.

<u>Polymer emulsion 4B</u>

To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer were added 15.2 parts of water and 498.1 parts of an oligomer prepared as described in Oligomer 4A. The contents of the reactor were heated to 60 °C.

33 % of a monomer feed consisting of 13.9 parts of water, 13.9 parts of diethyl itaconate, 156.0 parts of dibutyl itaconate, 135.9 parts of butyl acrylate, and 6.2 parts of diacetone acrylamide was added after which the emulsion was stirred for 15 minutes. Next, 0.4 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 1.2 parts of water, followed by 33 % of a solution of 0.7 parts of i-ascorbic acid in 13.8 parts of water.

After the temperature had reached 66 °C, the batch was stirred for 10 minutes, 45.5 parts of water were added and the batch was cooled to 60 °C. Next, 50 % of the remaining monomer feed was added, followed by 0.4 parts of a 70 wt-% slurry of t-butyl hydroperoxide, 1.2 parts of water, and 50 % of the remaining i-ascorbic acid solution. After the temperature had reached 62 °C, the batch was stirred for 10 minutes, 56.4 parts of water were added and the batch was cooled to 60 °C. The remainder of the monomer feed and 5.1 parts of water were added, followed by 0.4 parts of a 70 wt-% slurry of t-butyl hydroperoxide, 1.8 parts of water, and the remaining i-ascorbic acid solution. After the temperature had reached 61 °C after approximately 15 minutes, the batch was stirred for an additional 10 minutes. Next, 0.5 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 0.7 parts of water were added, followed by a solution of 0.3 parts of i-ascorbic acid in 4.6 parts of water. After the emulsion was allowed to stir for 30 minutes, the batch was cooled to 30 °C after which 6.2 parts of adipic dihydrazide and 17.8 parts of water were added. The solids content of the emulsion was corrected to 44 % using water.

The resulting emulsion had a solids content of 44.0 % and a pH of 7.8.

Example 5

Oligomer 5A

To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer 1087.6 parts of water and 1.3 parts of Aerosol GPG were charged. This mixture was heated to 70 °C. At 70 °C 10 % of a monomer feed consisting of 211.7 parts of water, 416.9 parts of methyl methacrylate, 39.0 parts of diacetone acrylamide, 32.2 parts of methacrylic acid, 3.9 parts of Aerosol GPG, and 11.7 parts of lauryl mercaptane was added and the reactor contents were further heated to 85 °C. At 80 °C a solution consisting of 0.4 parts of ammonium persulphate and 28.8 parts of water was added.

At 85 °C, the remainder of the monomer feed was added over a period of 60 minutes. A catalyst feed, comprising 1.0 parts of ammonium persulphate and 67.3 parts of water was fed to the reactor in period of 70 minutes. At the end of the addition of the monomer feed 31.3 parts of water were used to rinse the feed tank and were added to the reactor. A temperature of 85 °C was maintained for 20 minutes after which the reaction mixture was cooled to 80 °C. At 80 °C the emulsion was neutralized using 24.4 parts of a 25 % solution of ammonia in water mixed with 41.4 parts of water. The reaction mixture was subsequently kept at 80 °C for another 20 minutes before it was cooled to room temperature. The solids content of the emulsion was adjusted to 25 % with water.

The resulting emulsion had a solids content of 25.1 % and a pH of 8.0.

Polymer emulsion 5B

To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer were added: 1.50 parts of water, and 49.11 parts of an oligomer prepared as described in Oligomer 5A above. The contents of the reactor were heated to 60 °C.

33 % of a monomer feed consisting of 2.77 parts of dimethyl itaconate, 11.08 parts of butyl acrylate, and 13.84 parts of dibutyl itaconate was added after which the emulsion was stirred for 15 minutes. Next, 0.03 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 0.13 parts of water were added, followed by 30 % of a solution of 0.07 parts of i-ascorbic acid in 2.73 parts of water. After the temperature had reached 73 °C, the batch was stirred for 10 minutes and cooled to 60 °C. Next, 50 % of the remaining monomer feed was added, followed by 4.74 parts of water, and the emulsion was allowed to stir for 15 minutes. A slurry of 0.03 parts of a 70 wt-% slurry of t-butyl hydroperoxide, 0.13 parts of water was added followed by 30 % of the i-ascorbic acid solution. The temperature reached 69 °C after which the mixture was mixed for another 10 minutes. 6.71 parts of water were added and the batch was cooled to 60 °C. Next, the remainder of the monomer feed was added, the mixture was stirred for 15 minutes and 0.03 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 0.13 parts of water were added, followed by 30 % of the i-ascorbic acid solution. After the reaction mixture had reached a temperature of 68 °C, the emulsion was allowed to stir for 30 minutes at this temperature after which the emulsion was cooled to 65 °C.

A second monomer feed, consisting of 0.06 parts of diacetone acrylamide, 2.03 parts of butyl acrylate, and 0.98 parts of methyl methacrylate, was added. Next, 0.01 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 0.04 parts of water were added, followed by the remaining i-ascorbic acid solution. The temperature was allowed to drift for 15 minutes, after which the batch was again cooled to 65 °C. At 65 °C a slurry of 0.04 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 0.06 parts of water was added, followed by a solution of 0.03 parts of i-ascorbic acid in 1.30 parts of water. The batch was cooled to 30 °C and 0.50 parts of water were added. At 30 °C 0.61 parts of adipic dihydrazide were added together with 0.90 parts of water. The solids content of the emulsion was corrected to 44 % using water.

The resulting emulsion had a solids content of 44.0 % and a pH of 7.8.

Example 6

Polymer emulsion 6B

To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer, were added 1.50 parts of water, and 49.11 parts of an oligomer prepared as described in Oligomer 5A above. The contents of the reactor were heated to 60 °C.

33 % of a monomer feed consisting of 2.77 parts of monobutyl itaconate, 11.08 parts of butyl acrylate, and 6.41 parts of dimethyl itaconate, 7.43 parts of dibutyl itaconate was added after which the emulsion was stirred for 15 minutes. Next, 0.03 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 0.13 parts of water were added, followed by 30 % of a solution of 0.07 parts of i-ascorbic acid in 2.73 parts of water. After the temperature had reached 73 °C, the batch was stirred for 10 minutes and cooled to 60 °C. Next, 50 % of the remaining monomer feed was added, followed by 4.74 parts of water, and the emulsion was allowed to stir for 15 minutes. A slurry of 0.03 parts of a 70 wt-% slurry of t-butyl hydroperoxide, 0.13 parts of water was added followed by 30 % of the i-ascorbic acid solution. The temperature reached 69 °C after which the mixture was mixed for another 10 minutes. 6.71 parts of water were added and the batch was cooled to 60 °C. Next, the remainder of the monomer feed was added, the mixture was stirred for 15 minutes and 0.03 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 0.13 parts of water were added, followed by 30 % of the i-ascorbic acid solution. After the reaction mixture had reached a temperature of 68 °C, the emulsion was allowed to stir for 30 minutes at this temperature after which the emulsion was cooled to 65 °C.

A second monomer feed, consisting of 0.06 parts of diacetone acrylamide, 2.03 parts of butyl acrylate, and 0.98 parts of methyl methacrylate, was added. Next, 0.01 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 0.04 parts of water were added, followed by the remaining i-ascorbic acid solution. The temperature was allowed to drift for 15 minutes, after which the batch was again cooled to 65 °C. At 65 °C a slurry of 0.04 parts of a 70 wt-% slurry of t-butyl hydroperoxide, and 0.06 parts of water was added, followed by a solution of 0.03 parts of i-ascorbic acid in 1.30 parts of water. The batch was cooled to 30 °C and 0.50 parts of water were added. At 30 °C

0.61 parts of adipic dihydrazide were added together with 0.90 parts of water. The solids content of the emulsion was corrected to 44 % using water.

The resulting emulsion had a solids content of 44.0 % and a pH of 7.8.

Example 7

An emulsion was prepared exactly as described in Example 6 above except in preparing the polymer component (Polymer Emulsion 7B) the monomer feed consisted of: 11.08 parts of butyl acrylate, 4.86 parts of dimethyl itaconate, and 8.98 parts of dibutyl itaconate.

The resulting emulsion had a solids content of 44.0 % and a pH of 7.8.

EXAMPLE 8 (Vinyl beads)

Example 8

To a round-bottomed flask equipped with a condenser, thermometer, nitrogen inlet and mechanical stirrer are charged 950 parts of demineralised water (DMW), 1.6 parts of sodium sulphate (NS), and 7.9 parts of a 20 wt-% solution of polyacrylic acid (PAA) (weight average molecular weight (M_W) = 100,000 g/mole). Under constant stirring and nitrogen purge a dispersed phase consisting of 253 parts of methyl methacrylate (MMA), 190 parts of dibutyl itaconate (DBI), 190 parts of styrene (STY), 9.48 parts of dilauryl peroxide (DLP), and 1.58 parts of dodecyl mercaptane (DDM) are added. The reactor contents are heated to 75 °C and allowed to polymerize for a period of 5 hours. Next, the temperature is increased to 90 °C and the reactor contents are allowed to stir for another hour. Next, the resulting polymerization mixture is cooled down to room temperature.

The polymer beads are separated from the continuous phase and washed with water and left to dry at 40 °C. The polymer thus obtained has a mean particle size of 267 mm and a Tg, as determined with DSC, of 61 °C.

FURTHER EXAMPLES

Examples 9 to 38

Further examples for the various embodiments can be prepared according the Common methods E, F and G below and with reference to the Tables 1 to 3 below. The percentages in the tables are mostly quoted to the nearest percentage and/or to 2 significant figures and thus may not total 100% due to rounding errors.

COMMON METHOD E (for sequential vinyl polymers)

The total weight of monomer used in Examples 9 to 18 herein can be the same as the total amount used to prepare Example 1 and so for convenience the amount of monomers used in these examples can be expressed as a weight percent of the total monomers used in both the first and second monomer feeds. The first monomer feed (used to prepare the low Tg part of the polymer) consists of the same ingredients described in Example 1 (or with consequent modification), other than the monomers which can be:z1 % of Monomer Z1, y1 % of Monomer Y1, x1% of Monomer X1 and/or w1% of Monomer W1. To the equipment described in Example 1 and the pre-feed described therein the same initial amount of the first monomer feed can be added under the conditions described therein and then the remainder of the first monomer feed can be added and the reaction continued as described in Example 1 (or with consequent modification) until the second monomer feed can be added. The second monomer feed (used to prepare the high Tg part of the polymer) consists of the same ingredients described in Example 1 (or with consequent modification), other than the monomers which can be:z2 % of Monomer Z2, y2 % of Monomer Y2, x2% of Monomer X2 and/or w2% of Monomer W2.

The rest of the process can be followed as described in Example 1 (or with consequent modification) with reference to Table 1 to obtain vinyl sequential polymers analogous to that described in Example 1. The relative weight ratio (R) of the respective total amount of low Tg polymer A to the total amount of high Tg polymer B is also given in Table 2 and if necessary the method described in Example 1 can be modified according by adjusting the weight of the total amount of monomers used to prepare polymer B relative to the weight of the total amount of monomers used to prepare polymer A.

The total amount of monomer of Formula 1 (as a percentage T of the total amount of monomers A + B is also given in Table 1)

COMMON METHOD F for oligomer / polymer

The total weight of monomer used in Examples 19 to 28 can be the same as the total amount used to prepare each part of Example 4 (oligomer Ex 4A and polymer Ex 4B). So for convenience the amount of monomers used in these examples is expressed as a weight percent of the respective total monomers for the oligomer (in method F1) and the polymer (in method F2).

Oligomer (F1)

A monomer feed (used to prepare the oligomer) consists of the same ingredients described in Example 4A (or with consequent modification), other than the monomers which can be: z3 % of Monomer Z3, y3 % of Monomer Y3, x3% of Monomer X3 and/or w3% of Monomer W3. To the equipment described in Example 4A under the conditions described therein the monomer feed can be added and the reaction continued as described in Example 4A (or with consequent modification) with reference to Table 2 to obtain oligomer analogous to that described in Example 4A which can be used in step F2 below.

Polymer emulsion (F2)

A monomer feed (used to prepare the polymer) consists of the same ingredients described in Example 4B (or with consequent modification), other than the monomers which can be: z4 % of Monomer Z4, y4 % of Monomer Y4, x4% of Monomer X4 and/or w4% of Monomer W4. To the equipment described in Example 4B under the conditions described therein the monomer feed can be added together with an oligomer from step F1 and the reaction continued as described in Example 4B (or with consequent modification) with reference to Table 2 to obtain oligomer-polymers analogous to that described in Example 4.

The total amount of monomer of Formula 1 (as a percentage T' of the total amount of monomers C + D is also given in Table 2)

Common method G (for beads)

The total weight of monomer used in Examples 29 to 38 can be the same as the total amount used to prepare Example 8 and so for convenience the amount of monomers used in these examples could also be expressed as a weight percent of the total monomers or as an absolute mass.

To the equipment described in Example 8 a monomer mixture (used to prepare the polymeric beads) can be added consisting of the same ingredients described in Example 8 (or with consequent modification), other than the monomers which can be: z5 % of Monomer Z4, y5 % of Monomer Y5, x5% of Monomer X5 and/or w5% of Monomer W5. The rest of the process can be followed as described in

Example 8 with reference to Table 3 to obtain polymeric beads analogous to those described in Example 8.

Table 1 Examples 9 to 18 – sequential polymers (see method E)

Ex	Low Tg polymer A (% of A)								High Tg polymer B (% of B)								R	T % (of A+B)
	z1%	Z1	y1%	Y1	x1%	X1	W1%	W1	z2%	Z2	y2 %	Y2	x2%	X2	w2%	W2	(A to B)	
9	10	MAA	40	MMA	50	DPI	-	-	5	MAA	10	MMA	30	DMI	55	BMA	40/60	20
10	0.1	AA	39.9	MA	60	DHI	-	-	10	MAA	10	MMA	20	DEI	60	BMA	45/55	27
11	0.5	MSA	20	EA	65	DOI	14.5	BA	15	MA	5	EMA	50	DPrI	30	OA	50/50	23.5
12	1	CEA	36	PA	30	DBI	33	MA	60	DBzI	30	BA	10	DEI	-	-	55/45	43.5
13	2	MBI	80	MMA	18	EMA	-	-	85	DPhI	10	EMA	5	DMI	-	-	60/40	34
14	4	IA	22	BA	74	DBI	-	-	90	DHI	10	URED	-	-	-	-	65/35	79.6
15	6	IAn	20	MMA	64	DBI	10	EA	5	MAA	10	BA	65	DMI	20	BA	70/30	44.8
16	7.5	MMalA	40	EMA	52.5	BPI	-	-	10	AA	40	EHA	10	DEI	40	BMA	75/25	39.4
17	8	PHEMA	30	MMA	42	BHI	20	EA	1	MMA	49	OA	50	DMI			80/20	33.6
18	3	AMPS	35	PA	62	HOI	-	-	2	MSA	30	DBI	30	DEI	38	EA	90/10	58.8

Table 2 Examples 19 to 28 – oligomer-polymers (see method F1 and F2)

Ex	Oligomer C (% of C)								Polymer D (% of D)								R’ (C to D)	T % (of C+ D)
	z3%	Z3	y3%	Y3	x3%	X3	w3%	W3	z4%	Z4	y4%	Y4	x4%	X4	w4%	W4		
19	20	AA	80	EMA	-	-	-	-	80	D(EH)I	20	DEI	-	-	-	-	5:95	76
20	10	AA	10	DBI	70	DMI	10	DAAM	50	DBI	40	BA	10	DAAM	-	-	10:90	46
21	5	MSA	70	MMA	20	DEI	5	DAAM	30	DOI	55	OA	5	DAAM	10	BA	30:70	21
22	20	CEA	50	MA	30	DMI	-	-	40	DHI	60	BMA	-	-	-	-	40:60	24
23	5	MBI	20	EA	70	DPrI	5	DAAM	50	DPI	40	BA	10	DEI	-	-	50:50	25
24	3	IA	10	MMA	80	DBI	7	DAAM	50	DMI	40	EA	10	MA			60:40	48
25	4	IAn	30	MMA	60	DBI	6	DAAM	50	DBI	40	PA	10	MMA			70:30	57
26	5	MMalA	50	MMA	40	DPI	5	DAAM	50	DBI	40	DMI	10	BMA			75:25	42.5
27	2	PHEMA	60	MMA	30	DMI	8	DAAM	50	DBI	20	EA	20	BMA	10	DAAM	50:50	25
28	40	AMPS	20	MMA	40	DBI	-	-	50	DEI	40	MMA	10	BMA			50:50	20

Table 3 Examples 29 to 38 - polymer beads (see method G)

Ex	z3%	Z3	y3%	Y3	x3%	X3	w3%	W3
29	40	MMA	30	DBI	20	STY	10	BA
30	10	AA	50	DHI	20	MSTY	10	OA
31	30	EMA	40	DOI	30	OA	-	-
32	35	MMA	20	DBzI	25	STY	10	DBI
33	10	EA	60	DPhI	30	STY	-	-
34	20	MA	30	DBI	30	STY	10	DMI
35	25	MMA	35	DBI	25	STY	5	DEI
36	40	MMA	30	BPI	20	MSTY	-	-
37	40	EMA	30	BHI	30	MSTY	-	-
38	35	MMA	25	HOI	30	STY	-	-

Examples 39 to 43 and Comparative Examples Comp I to V

Example 39 DBI polymer containing wet-adhesion promoting monomer

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 559.2 parts of demineralized water, 5.5 parts of sodium bicarbonate, 29.4 parts of a 30 wt-% solution of sodium lauryl sulphate in water, and 1.1 parts of sodium persulphate. The reactor contents were heated to 70 °C. At 50 °C, 10 % of a monomer feed consisting of 510.3 parts of demineralized water, 12.5 parts of a 30 wt-% solution of sodium lauryl sulphate in water, 516.7 parts of butyl acrylate, 33.0 parts of methacrylic acid, 494.7 parts of dibutyl itaconate, and 110.0 parts of a 50 wt-% solution of N-(2-methacryloyloxyethyl)ethylene urea in water (Plex 6852-0, ex.Evonik), was added. Due to the exothermic nature of the polymerizing monomers, the temperature increased to 85 °C (if the exotherm would be insufficient the mixture could be heated slightly to reach a temperature of 85 °C). At 85 °C, the monomer feed, comprising the remaining 90 % of the original feed, and the initiator feed, consisting of 124.5 parts of demineralized water, 4.4 parts of sodium persulphate, and 2.2 parts of a 30 wt-% solution of sodium lauryl sulphate in water, were started. Both feeds were added over a period of 120 minutes. At the end of the monomer feed, the feed tank was rinsed with 19.7 parts of demineralized water and the mixture was stirred at 85 °C for another 35 minutes.

Next, the emulsion was cooled to 45 °C, and a solution of 0.7 parts of iso-ascorbic acid in 12.5 parts of demineralized water was added, followed by 1.0 part of a 70 wt-% solution of t-butyl hydroperoxide in water, 1.5 parts of demineralized water, and 0.3 parts of a 30 wt-% solution of sodium lauryl sulphate in water. The entire reactor contents were stirred for 30 minutes at 45 °C.

The emulsion was cooled to room temperature, and 55.0 parts of an equal mixture of a 25 % solution of ammonia in water and demineralized water were added. The solids content of the emulsion was adjusted to 45 % using demineralized water.

Example 40 DBI and styrene containing polymer

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 644.0 parts of demineralized water, 0.5 parts of sodium bicarbonate, 13.3 parts of a 30 wt-% solution of sodium lauryl sulphate in water, and 0.8 parts of sodium persulphate. The reactor contents were heated to 80 °C and stirred for 5 minutes at 80 °C. Next, 10 % of a monomer feed, consisting of 132.9 parts of demineralized water, 13.0 parts of a 30 wt-% solution of sodium lauryl sulphate in water, 23.3 parts of methacrylic acid, 280.1 parts of dibutyl itaconate, and 280.1 parts of styrene, was added, after the temperature rose to approximately 90 °C due to the exothermic nature of the polymerization. As soon as the temperature of 90 °C was reached, the remaining monomer feed and the initiator feed, consisting of 58.7 parts of demineralized water, 2.5 parts of sodium persulphate, and 3.7 parts of a 30 wt-% solution of sodium lauryl sulphate in water, were started. Both feeds were added over a period of 2 hours. At the end of the monomer feed the feed tank was rinsed with 10.4 parts of demineralized water. The temperature of the reactor contents were cooled to 80 °C, after which a solution of 1.8 parts of iso-ascorbic acid dissolved in 26.5 parts of demineralized water (which was brought to a pH of 8.5 using an ammonia solution) was fed over a period of 30 minutes, during which a mixture of 2.8 parts of t-butyl hydroperoxide and 5.6 parts of demineralized water was added in two shots; one at the start of the iso-ascorbic acid feed and 15 minutes later.

At the end of the feed, the mixture was stirred at 80 °C for 30 minutes, and the pH was raised to 7.2 using a 25 wt-% solution of ammonia in water. After stirring for another 30 minutes, the batch was cooled to room temperature. The solids content was adjusted to 40 % using demineralized water.

Comparative example Comp I BA and styrene containing polymer

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 639.5 parts of demineralized water, 0.5 parts of sodium bicarbonate, and 13.3 parts of a 30 wt-% solution of sodium lauryl sulphate in water. The reactor contents were heated to 80 °C, after which a solution of 0.8 parts of sodium persulphate in 4.5 parts of demineralized water were added and stirred for 5 minutes at 80 °C. Next, 10 % of a monomer feed, consisting of 132.9 parts of demineralized water, 13.0 parts of a 30 wt-% solution of sodium lauryl sulphate in water, 23.3 parts of methacrylic acid, 280.1 parts of butyl acrylate, and 280.1 parts of styrene, was added, after the temperature rose to approximately 90 °C due to the exothermic nature of the polymerization. As soon as the temperature of 90 °C was reached, the remaining monomer feed and the initiator feed, consisting of 58.7 parts of demineralized water, 2.5 parts of sodium persulphate, and 3.7 parts of a 30 wt-% solution of sodium lauryl sulphate in water, were started. Both feeds were added over a period of 2 hours. At the end of the monomer feed the feed tank was rinsed with 10.4

parts of demineralized water. The temperature of the reactor contents were cooled to 80 °C, after which a solution of 1.8 parts of iso-ascorbic acid dissolved in 26.5 parts of demineralized water (which was brought to a pH of 8.5 using an ammonia solution) was fed over a period of 30 minutes, during which a mixture of 2.8 parts of t-butyl hydroperoxide and 5.6 parts of demineralized water was added in two shots; one at the start of the iso-ascorbic acid feed and 15 minutes later.

At the end of the feed, the mixture was stirred at 80 °C for 30 minutes, and the pH was raised to 7.2 using a 25 wt-% solution of ammonia in water. After stirring for another 30 minutes, the batch was cooled to room temperature. The solids content was adjusted to 40 % using demineralized water.

Example 41 DBI and MMA containing polymer

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 639.5 parts of demineralized water, 0.5 parts of sodium bicarbonate, and 13.3 parts of a 30 wt-% solution of sodium lauryl sulphate in water. The reactor contents were heated to 80 °C, after which a solution of 0.8 parts of sodium persulphate in 4.5 parts of demineralized water were added and stirred for 5 minutes at 80 °C. Next, 10 % of a monomer feed, consisting of 132.9 parts of demineralized water, 13.0 parts of a 30 wt-% solution of sodium lauryl sulphate in water, 23.3 parts of methacrylic acid, 280.1 parts of dibutyl itaconate, and 280.1 parts of methyl methacrylate, was added, after the temperature rose to approximately 90 °C due to the exothermic nature of the polymerization. As soon as the temperature of 90 °C was reached, the remaining monomer feed and the initiator feed, consisting of 58.7 parts of demineralized water, 2.5 parts of sodium persulphate, and 3.7 parts of a 30 wt-% solution of sodium lauryl sulphate in water, were started. Both feeds were added over a period of 2 hours. At the end of the monomer feed the feed tank was rinsed with 10.4 parts of demineralized water. The temperature of the reactor contents were cooled to 80 °C, after which a solution of 1.8 parts of iso-ascorbic acid dissolved in 26.5 parts of demineralized water (which was brought to a pH of 8.5 using an ammonia solution) was fed over a period of 30 minutes, during which a mixture of 2.8 parts of t-butyl hydroperoxide and 5.6 parts of demineralized water was added in two shots; one at the start of the iso-ascorbic acid feed and 15 minutes later.

At the end of the feed, the mixture was stirred at 80 °C for 30 minutes, and the pH was raised to 7.2 using a 25 wt-% solution of ammonia in water.

After stirring for another 30 minutes, the batch was cooled to room temperature. The solids content was adjusted to 40 % using demineralized water.

Comparative example Comp II BA and MMA containing polymer

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 639.5 parts of demineralized water, 0.5 parts of sodium bicarbonate, and 13.3 parts of a 30 wt-% solution of sodium lauryl sulphate in water. The reactor contents were heated to 80 °C, after which a solution of 0.8 parts of sodium persulphate in 4.5 parts of demineralized water were added and stirred for 5 minutes at 80 °C. Next, 10 % of a monomer feed, consisting of 132.9 parts of demineralized water, 13.0 parts of a 30 wt-% solution of sodium lauryl sulphate in water, 23.3 parts of methacrylic acid, 280.1 parts of butyl acrylate, and 280.1 parts of methyl methacrylate, was added, after the temperature rose to approximately 90 °C due to the exothermic nature of the polymerization. As soon as the temperature of 90 °C was reached, the remaining monomer feed and the initiator feed, consisting of 58.7 parts of demineralized water, 2.5 parts of sodium persulphate, and 3.7 parts of a 30 wt-% solution of sodium lauryl sulphate in water, were started. Both feeds were added over a period of 2 hours. At the end of the monomer feed the feed tank was rinsed with 10.4 parts of demineralized water. The temperature of the reactor contents were cooled to 80 °C, after which a solution of 1.8 parts of iso-ascorbic acid dissolved in 26.5 parts of demineralized water (which was brought to a pH of 8.5 using an ammonia solution) was fed over a period of 30 minutes, during which a mixture of 2.8 parts of t-butyl hydroperoxide and 5.6 parts of demineralized water was added in two shots; one at the start of the iso-ascorbic acid feed and 15 minutes later.

At the end of the feed, the mixture was stirred at 80 °C for 30 minutes, and the pH was raised to 7.2 using a 25 wt-% solution of ammonia in water. After stirring for another 30 minutes, the batch was cooled to room temperature. The solids content was adjusted to 40 % using demineralized water.

Comparative example Comp III DMI containing copolymer

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 639.5 parts of demineralized water, 0.5 parts of sodium bicarbonate, and 13.3 parts of a 30 wt-% solution of sodium lauryl sulphate in water. The reactor contents were heated to 80 °C, after which a solution of 0.8 parts of sodium persulphate in 4.5 parts of demineralized water were added and stirred for 5 minutes at 80 °C. Next, 10 % of a monomer feed, consisting of 132.9 parts of demineralized water, 13.0 parts of a 30 wt-% solution of sodium lauryl sulphate in water, 23.3 parts of methacrylic acid, 414.3 parts of dimethyl itaconate, and 145.9 parts of ethyl acrylate, was added, after the temperature rose to approximately 90 °C due to the exothermic nature of the polymerization. As soon as the temperature of 90 °C was reached, the remaining monomer feed and the initiator feed, consisting of 58.7 parts of demineralized water, 2.5 parts of sodium persulphate, and 3.7 parts of a 30 wt-% solution of sodium lauryl sulphate in water, were started. Both feeds should be added over a period of 2 hours.

After 110 minutes of the monomer feed, the emulsion gelled, showing that higher itaconates, such as DBI, yield superior properties over lower itaconates, such as DMI.

Example 42 DBI containing h/s sequential copolymer

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 426.6 parts of demineralized water, 0.4 parts of sodium bicarbonate, 31.3 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), and 0.4 parts of a 25 wt-% ammonia solution. The reactor contents were heated to 80 °C, after which a solution of 0.4 parts of sodium persulphate in 7.9 parts of demineralized water were added, followed by 10 % of a first monomer feed consisting of 115.1 parts of demineralized water, 35.9 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), 0.6 parts of sodium bicarbonate, 15.7 parts of acrylic acid, 90.1 parts of dibutyl itaconate, and 286.0 parts of methyl methacrylate. Due to the heat formed as a result of the polymerizing monomers, the temperature rose to 90 °C, after which adding the remainder of the first monomer feed was started. The first monomer feed was added over a period of 45 minutes. Simultaneously, 60 % of an initiator feed, consisting of 36.3 parts of demineralized water, 0.2 parts of sodium bicarbonate, and 2.0 parts of sodium persulphate, was fed over a period of 45 minutes. At the end of the monomer feed, the feed tank was rinsed with 7.6 parts of demineralized water.

Next, a mixture of 0.9 parts of a 25 wt-% ammonia solution and 1.2 parts of demineralized water was fed over a period of 15 minutes. 45 minutes after the end of the first monomer feed, a second monomer feed, consisting of 76.7 parts of demineralized water, 23.9 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), 0.4 parts of sodium bicarbonate, 10.5 parts of acrylic acid, 198.5 parts of dibutyl itaconate, and 52.2 parts of butyl acrylate, was started. This feed, and the remainder of the initiator feed that was fed simultaneously, were added over a period of 30 minutes. After completion of the second monomer feed, the feed tank was rinsed with 15.3 parts of demineralized water and the mixture was allowed to stir at 90 °C for another 30 minutes.

Finally, the emulsion was cooled to room temperature, the solids content was corrected to 45 % using demineralized water, and the pH was corrected to 7.5 using a 25 wt-% ammonia solution.

Comparative example Comp IV DBI free h/s sequential copolymer

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 426.6 parts of demineralized water, 0.4 parts of sodium bicarbonate, 31.3 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), and 0.4 parts of a 25 wt-% ammonia solution. The reactor contents were heated to 80 °C, after which a solution of 0.4 parts of sodium persulphate in 7.9 parts of demineralized water were added, followed by 10 % of a first monomer feed consisting of 115.1 parts of demineralized water, 35.9 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), 0.6 parts of sodium bicarbonate, 15.7 parts of acrylic acid, 90.1 parts of butyl acrylate, and 286.0 parts of methyl methacrylate. Due to the heat formed as a result of the polymerizing monomers, the temperature rose to 90 °C, after which adding the remainder of the first monomer feed was started. The first monomer feed was added over a period of 45 minutes. Simultaneously, 60 % of an initiator feed, consisting of 36.3 parts of demineralized water, 0.2 parts of sodium bicarbonate, and 2.0 parts of sodium persulphate, was fed over a period of 45 minutes. At the end of the monomer feed, the feed tank was rinsed with 7.6 parts of demineralized water.

Next, a mixture of 0.9 parts of a 25 wt-% ammonia solution and 1.2 parts of demineralized water was fed over a period of 15 minutes. 45 minutes after the end of the first monomer feed, a second monomer feed, consisting of 76.7 parts of demineralized water, 23.9 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), 0.4 parts of sodium bicarbonate, 10.5 parts of acrylic acid, and 250.7 parts of butyl acrylate, was started. This feed, and the remainder of the initiator feed that was fed simultaneously, were added over a period of 30 minutes. After completion of the second monomer feed, the feed tank was rinsed with 15.3 parts of demineralized water and the mixture was allowed to stir at 90 °C for another 30 minutes.

Finally, the emulsion was cooled to room temperature, the solids content was corrected to 45 % using demineralized water, and the pH was corrected to 7.5 using a 25 wt-% ammonia solution.

Example 43 DBI containing s/h sequential

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 426.6 parts of demineralized water, 0.4 parts of sodium bicarbonate, 31.3 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), and 0.4 parts of a 25 wt-% ammonia solution. The reactor contents were heated to 80 °C, after which a solution of 0.4 parts of sodium persulphate in 7.9 parts of demineralized water were added, followed by 10 % of a first monomer feed consisting of 114.3 parts of demineralized water, 37.9 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), 0.6 parts of sodium bicarbonate, 18.3 parts of acrylic acid, 420.6 parts of dibutyl itaconate, 18.3 parts of a 50 wt-% solution of N-(2-methacryloyloxyethyl)ethylene urea in water (Plex 6852-0 ex. Evonik), and 9.1 parts of methyl methacrylate. Due to the heat formed as a result of the polymerizing monomers, the temperature rose to 90 °C, after which adding the remainder of the first monomer feed was started. The first monomer feed was added over a period of 45 minutes. Simultaneously, 60 % of an initiator feed, consisting of 36.3 parts of demineralized water, 0.2 parts of sodium bicarbonate, and 2.0 parts of sodium persulphate, was fed over a period of 45 minutes. At the end of the monomer feed, the feed tank was rinsed with 7.6 parts of demineralized water.

Next, a mixture of 0.9 parts of a 25 wt-% ammonia solution and 1.2 parts of demineralized water was fed over a period of 15 minutes.45 minutes after the end of the first monomer feed, a second monomer feed, consisting of 77.5 parts of demineralized water, 21.9 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), 0.4 parts of sodium bicarbonate, 7.8 parts of acrylic acid, 45.0 parts of dibutyl itaconate, and 143.0 parts of methyl methacrylate, was started. This feed, and the remainder of the initiator feed that was fed simultaneously, were added over a period of 30 minutes. After completion of the second monomer feed, the feed tank was rinsed with 15.3 parts of demineralized water and the mixture was allowed to stir at 90 °C for another 30 minutes.

Finally, the emulsion was cooled to room temperature, the solids content was corrected to 45 % using demineralized water, and the pH was corrected to 7.5 using a 25 wt-% ammonia solution.

Comparative example Comp V DBI free s/h sequential

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer were charged 426.6 parts of demineralized water, 0.4 parts of sodium bicarbonate, 31.3 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), and 0.4 parts of a 25 wt-% ammonia solution. The reactor contents were heated to 80 °C, after which a solution of 0.4 parts of sodium persulphate in 7.9 parts of demineralized water were added, followed by 10 % of a first monomer feed consisting of 114.3 parts of demineralized water, 37.9 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), 0.6 parts of sodium bicarbonate, 18.3 parts of acrylic acid, 420.6 parts of butyl acrylate, 18.3 parts of a 50 wt-% solution of N-(2-methacryloyloxyethyl)ethylene urea in water (Plex 6852-0 ex. Evonik), and 9.1 parts of methyl methacrylate. Due to the heat formed as a result of the polymerizing monomers, the temperature rose to 90 °C, after which adding the remainder of the first monomer feed was started. The first monomer feed was added over a period of 45 minutes. Simultaneously, 60 % of an initiator feed, consisting of 36.3 parts of demineralized water, 0.2 parts of sodium bicarbonate, and 2.0 parts of sodium persulphate, was fed over a period of 45 minutes. At the end of the monomer feed, the feed tank was rinsed with 7.6 parts of demineralized water. Next, a mixture of 0.9 parts of a 25 wt-% ammonia solution and 1.2 parts of demineralized water was fed over a period of 15 minutes.

45 minutes after the end of the first monomer feed, a second monomer feed, consisting of 77.5 parts of demineralized water, 21.9 parts of a 20 wt-% aqueous solution of a phosphate functional surfactant (Fosfodet FAZ109V, ex. KAO), 0.4 parts of sodium bicarbonate, 7.8 parts of acrylic acid, 45.0 parts of butyl acrylate, and 143.0 parts of methyl methacrylate, was started. This feed, and the remainder of the initiator feed that was fed simultaneously, were added over a period of 30 minutes. After completion of the second monomer feed, the feed tank was rinsed with 15.3 parts of demineralized water and the mixture was allowed to stir at 90 °C for another 30 minutes.

Finally, the emulsion was cooled to room temperature, the solids content was corrected to 45 % using demineralized water, and the pH was corrected to 7.5 using a 25 wt-% ammonia solution.

To illustrate the invention, film properties were determined for a selection of the polymer emulsions described above. The polymer emulsions were formulated with 8 % of butyl diglycol to make them film forming. The films were cast, dried at ambient temperature for 4 hours, and next dried for 34 hours at 50 °C. The results are shown below in Table 4.

Table 4

Film properties; “5” means excellent resistance properties, no damage to the film, ”1” indicated completely destroyed film

	Water spot test		Blocking resistance	Stain resistance (16 hrs)*			König hardness (s)
	1 hr	16 hrs		EtOH	Andy	Coffee	
Ex 40	5	5	3	5	4	5	201
Comp I	5	4	1	4	2	5	110
Ex 41	5	5	5	4	4	5	173
Comp II	5	3	3	3	2	4	115
Comp III	Could not be prepared due to instable processing.						
Ex 42	5	5	5	3	4	5	70
Comp IV	5	5	3	3	2	4	60
Ex 43	5	5	4	3	3	5	115
Comp V	5	5	0	3	2	4	8

* Determined as spot test.

In all cases (except Comp III), the water spot was good. Blocking resistance and König hardness were in all cases better for the polymers according to the invention compared to their most similar comparative examples. While resistance to coffee and ethanol were comparable between polymers according to the invention and the comparatives, the resistance to soap (Andy) was clearly better for the polymers according to the invention.

Example 44 MMA/DMI/AA

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer are charged 394.0 parts of 2-butanone. The reactor contents are heated to 80 °C. As soon as the polymerization temperature is reached, 13.3 parts of azobis(2-methyl butyronitrile) are added and the monomer feed and catalyst feed are started. The monomer feed consists of 244.4 parts of methyl methacrylate, 244.4 parts of dimethyl itaconate, and 244.4 parts of acrylic acid. The catalyst feed consists of 31.1 parts of azobis(2-methyl butyronitrile) dissolved in 125.9 parts of 2-butanone. Both feeds are added over a period of 180 minutes.

At the end of the feeds 2.5 parts of azobis(2-methyl butyronitrile) are added and the mixture is stirred at 80 °C for another 150 minutes. The mixture is cooled to room temperature.

To 615.8 parts of the polymer solution is added a mixture of 99.6 parts of a 25 wt-% of ammonia in water, and 1080.5 parts of water. Next, the 2-butanone is removed at 50 °C under reduced pressure. The solids content is corrected to 22.5 % using demineralized water and the pH is corrected to 8.6-8.8 using a 25 wt-% solution of ammonia in water.

The final polymer solution has a solids content of 22.5 % and a pH of 8.7.

Example 45 S/DMI/AA

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer are charged 394.0 parts of 2-butanone. The reactor contents are heated to 80 °C. As soon as the polymerization temperature is reached, 13.3 parts of azobis(2-methyl butyronitrile) are added and the monomer feed and catalyst feed are started. The monomer feed consists of 244.4 parts of styrene, 244.4 parts of dimethyl itaconate, and 244.4 parts of acrylic acid. The catalyst feed consists of 31.1 parts of azobis(2-methyl butyronitrile) dissolved in 125.9 parts of 2-butanone. Both feeds are added over a period of 180 minutes.

At the end of the feeds 2.5 parts of azobis(2-methyl butyronitrile) are added and the mixture is stirred at 80 °C for another 150 minutes. The mixture is cooled to room temperature.

To 546.1 parts of polymer solution is added a mixture of 105.4 parts of a 25 wt-% of ammonia in water, and 1144.1 parts of water. Next, the 2-butanone is removed at 50 °C under reduced pressure. The solids content is corrected to 22.5 %

using demineralized water and the pH is corrected to 8.6-8.8 using a 25 wt-% solution of ammonia in water.

The final polymer solution has a solids content of 22.4 % and a pH of 8.6.

Example 46 MMA/DMI/AA

To a high pressure reactor equipped with a thermometer, and a stirrer are charged 500.0 parts of 2-butanone. The reactor contents are heated to 140 °C. As soon as the polymerization temperature is reached, 2.9 parts of di-t-butyl peroxide and 40 parts of 2-butanone are added. 5 minutes later the monomer feed is started. The monomer feed consists of 331.8 parts of methyl methacrylate, 331.8 parts of dimethyl itaconate, 331.8 parts of acrylic acid, 5.7 parts of di-t-butyl peroxide, and 6.6 parts of t-butyl perbenzoate, and is added over a period of 180 minutes at 140 °C.

At the end of the feed the feed tank is rinsed with 90.9 parts of 2-butanone. 45 minutes after completion of the monomer feed 2.5 parts of t-butyl perbenzoate dissolved in 40 parts of 2-butanone are added and the mixture is stirred at 140 °C for another 45 minutes. Next, 2.5 parts of t-butyl perbenzoate dissolved in 40 parts of 2-butanone are added and the mixture is stirred for another 135 minutes at 140 °C.

The mixture is cooled to room temperature.

To 619.3 parts of the polymer solution is added a mixture of 99.3 parts of a 25 wt-% of ammonia in water, and 1077.3 parts of water. Next, the 2-butanone is removed at 50 °C under reduced pressure. The solids content is corrected to 22.5 % using demineralized water and the pH is corrected to 8.6-8.8 using a 25 wt-% solution of ammonia in water.

The final polymer solution has a solids content of 22.5 % and a pH of 8.6.

Example 47 S/DMI/AA

To a high pressure reactor equipped with a thermometer, and a stirrer are charged 500.0 parts of 2-butanone. The reactor contents are heated to 140 °C. As soon as the polymerization temperature is reached, 4.4 parts of di-t-butyl peroxide and 40 parts of 2-butanone are added. 5 minutes later the monomer feed is started. The monomer feed consists of 331.8 parts of styrene, 331.8 parts of dimethyl itaconate, 331.8 parts of acrylic acid, 8.6 parts of di-t-butyl peroxide, and 10.0 parts of t-butyl perbenzoate, and is added over a period of 180 minutes at 140 °C.

At the end of the feed the feed tank is rinsed with 90.9 parts of 2-butanone. 45 minutes after completion of the monomer feed 2.5 parts of t-butyl perbenzoate dissolved in 40 parts of 2-butanone are added and the mixture is stirred at 140 °C for another 45 minutes. Next, 2.5 parts of t-butyl perbenzoate dissolved in 40 parts of 2-butanone are added and the mixture is stirred for another 135 minutes at 140 °C.

The mixture is cooled to room temperature.

To 617.8 parts of the polymer solution is added a mixture of 99.4 parts of a 25 wt-% of ammonia in water, and 1078.6 parts of water. Next, the 2-butanone is removed at 50 °C under reduced pressure. The solids content is corrected to 22.5 % using demineralized water and the pH is corrected to 8.6-8.8 using a 25 wt-% solution of ammonia in water.

The final polymer solution has a solids content of 22.5 % and a pH of 8.7.

Example 48 Sequential polymerization using the polymer from Example 44

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer are charged 128.9 parts of the alkaline solution obtained from Example 44. The mixture is heated to 80 °C ± 2 °C.

As soon as the reaction temperature is reached, a mixture of 0.2 parts of sodium persulphate and 0.4 parts of demineralized water is added. After 5 minutes, the monomer feed, consisting of 43.8 parts of methyl methacrylate and 43.8 parts of butyl acrylate, and the initiator feed, consisting of 10.8 parts of demineralized water and 0.4 parts of sodium persulphate (corrected to a pH of 8 using a 25 wt-% ammonia solution) are started. Both feeds should take 120 minutes. At the end of the monomer feed, the feed tank is rinsed with 1.2 parts of water. After both feeds are completed, the batch is stirred at 80 °C for another 30 minutes, after which it is cooled to 50 °C.

At 50 °C, one third of a mixture consisting of 0.1 part of a 70 wt-% solution of t-butyl hydroperoxide is added followed by one third of a solution of 0.1 part of iso-ascorbic acid in 2.9 parts of water. 15 minutes later and 30 minutes later similar portions are added and the batch is stirred at 50 °C for another 15 minutes.

The pH is checked and, if necessary, adjusted to 8.4 ± 0.1 using a 25 wt-% solution of ammonia in water. The batch is cooled to room temperature, after which the solids content is adjusted to 48.5 % ± 1 % using demineralized water.

Example 49 Sequential polymerization using the polymer from Example 45

Example 49 was prepared analogously to the method described in Example 48, replacing Example 44 with the alkaline solution obtained from Example 45. The final emulsion obtained was highly viscous, requiring a dilution to a solids content of 35 %.

Example 50 Sequential polymerization using the polymer from Example 46

Example 50 was prepared analogously to the method described in Example 48, replacing Example 44 with the alkaline solution obtained from Example 46.

Example 51 Sequential polymerization using the polymer from Example 47

Example 51 was prepared analogously to the method described in Example 48, replacing Example 44 with the alkaline solution obtained from Example 47.

Results (Table 5)

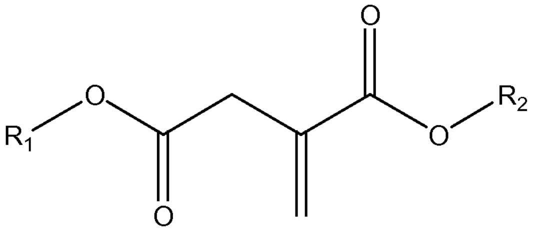
	SC (%)	Viscosity (mPa.s)	pH
Example 48	47.6	208	8.4
Example 49	34.8	1006	8.4
Example 50	48.1	35	8.5
Example 51	48.1	201	8.4

CLAIMS

1 Use of a copolymer composition in one or more of the following uses: as an ingredient in a topical composition and/or personal care composition, as a binder for toner, as an encapsulating agent for a colorant, as a hybrid colorant, as additive for sheet moulding compounds, as a plastic pigment, as a filler for composite materials such as concrete, as a filler for coatings and/or waxes; and/or as a spacer in a display;

where the copolymer composition [which is optionally substantially free of styrene (< 1.5 wt-% of copolymer)] comprises:

(a) at least 23 % by weight of at least one monomer represented by Formula 1

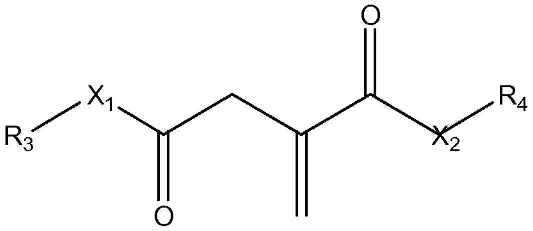


Formula 1

where both R_1 and R_2 independently represent an optionally substituted hydrocarbo moiety having from 4 to 10 carbon atoms.

(b) optionally at least one hydrophilic monomer also in an amount sufficient that the resultant polymer has an acid value less than 150 mg KOH per g of polymer,

(c) optionally of one or more monomers represented by Formula 2



Formula 2

where R_3 and R_4 independently represent H or an optionally substituted hydrocarbo moiety having from 1 to 20 carbon atoms

X_1 and X_2 independently represents O or NR_5 where R_5 denotes H or an optionally substituted hydrocarbo moiety having from 1 to 20 carbon atoms with the proviso that when X_1 and/or X_2 are O then the respective R_3 and/or R_4 attached to the oxy group independently represent an optionally substituted hydrocarbo having from 1 to 3 carbon atoms

(d) optionally less than 77% by weight of monomers other than components (a), (b) or (c).

where the percentages or amounts of (a), (b) (c) (d) are by weight calculated as a proportion of the total weight of (a) + (b) + (c) + (d) and thus total 100%; where independently at least one of the components(a), (b) (c) and/or (d) and/or the copolymer obtained from them are biorenewable defined as comprising an amount of carbon-14 sufficient to produce a decay of at least about 1.5 dpm/gC (disintegrations per minute per gram carbon).

2 Use of a copolymer as claimed in claim 1, in which the copolymer comprises

(a) component (a) is from 24 % to 70% by weight of one or more monomers represented by Formula 1

(b) component (b) is one or more acid functional monomer(s) in an amount from 0.5 % to 15 % by weight, in an amount also sufficient that the resultant polymer has an acid value of from 3 to 100 mg KOH per g of polymer,

(c) component (c) is from 0.01 % to 10% by weight of one or more monomers represented by Formula 2 in which X_1 and X_2 are both O and R_3 and/or R_4 independently represent an optionally substituted hydrocarbo having from 1 to 3 carbon atoms.

(d) component (d) if present is less than 75% wt-% by weight of monomer(s) other than components (a), (b) or (c) and does not contain stryene. butyl acrylate, 2-ethyl hexyl acrylate and/or mixtures thereof;

where the weight percentages or amounts of (a), (b) (c) (d) are calculated as a proportion of the total amount of (a) + (b) + (c) + (d) which thus totals 100%; with the provisos that

where the copolymer is prepared by an emulsion polymerisation a chaser monomer is not used;

the copolymer is not prepared in the presence of a seed polymer comprising a poly(itaconate ester);

the copolymer is not prepared in the presence of an initiator system comprising an organoborane amine complex.

3 Use of a copolymer as claimed in either preceding claim, in which the copolymer comprises a component (a) that comprises dibutyl itaconate;

4 Use of a copolymer as claimed in any preceding claim, in which in the copolymer:

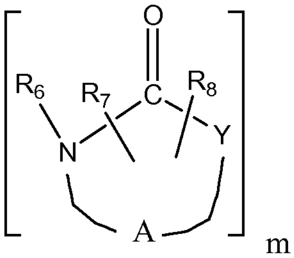
(a) component (a) is present in an amount of from 30 to 65 wt-% and is dibutyl itaconate;

(b) optional component (b) if present is present in an amount of up to 10 wt-% and comprises an acid functional ethylenically unsaturated monomer and/or anhydride thereof;

(c) optional component (c) if present is present in an amount of from 1 to 25 wt-% and is dimethyl itaconate and/or diethyl itaconate;

(d) optional component (d) if present is present in an amount such that (a) and (d) [and (b) and (c) where present] total 100% by weight.

5 Use of a copolymer as claimed in any preceding claim, in which in the copolymer component (d) comprises at least one polymer precursor(s) of Formula 3



Formula 3,

where Y denotes an electronegative group,

R_6 is H, OH or an optionally hydroxy substituted C_{1-10}hydrcarbo

R_7 is H or a C_{1-10}hydrocarbo;

R_8 is a C_{1-10}hydrocarbo group substituted by at least one activated unsaturated moiety; and; either:

A represents a divalent organo moiety attached to both the –HN- and –Y- moieties so the –A-, -NH-, -C(=O)- and –Y- moieties together represent a ring of 4 to 8 ring atoms, and R_7 and R_8 are attached to any suitable point on the ring; or

A is not present (and Formula 3 represents a linear and/or branched moiety that does not comprise a heterocyclic ring) in which case R_7 and R_8 are attached to R_6; and

m is an integer from 1 to 4.

6 Use of a copolymer as claimed in any preceding claim as an ingredient in a topical composition and/or personal care composition where the composition is selected from:

a topical medicament, cosmetic composition, hair care composition, oral hygiene composition, sunscreen composition and/or toiletry composition.

7 Use of a copolymer as claimed in any preceding claim, in which in the copolymer is prepared by a process comprising the step of

polymerising polymer precursors in a polymerisation method the polymer precursors comprising component (a), component (b) and optionally components (c) and/or component (d) as described in the preceding claims, to obtain a copolymer,

where optionally the polymerisation method is selected from aqueous emulsion polymerisation and suspension polymerisation and where the method does not comprise a chaser monomer step.

8 A composition comprising a copolymer as described in any of claims 1 to 7, together with a suitable carrier medium, the composition being formulated to be useful in any of the uses described in any of claims 1 to 7.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/052174

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L35/02 C08F222/14 A61K8/81 C09D135/02
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)
C08L C08F A61K 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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/144265 A1 (DURANT YVON [US]) 16 June 2011 (2011-06-16) cited in the application paragraphs [0005], [0014], [0016], [0029] -----	1-8
A	WO 2011/073417 A1 (DSM IP ASSETS BV [NL]; NABUURS TIJS [NL]; OVERBEEK GERARDUS CORNELIS [) 23 June 2011 (2011-06-23) cited in the application page 1, lines 3-15 page 17, lines 14-21 -----	1-8

☐ 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 18 March 2013	Date of mailing of the international search report 25/03/2013
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 Plehiers, Mark

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/052174

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011144265 A1	16-06-2011	CA 2784024 A1	23-06-2011
		EP 2513174 A1	24-10-2012
		US 2011144265 A1	16-06-2011
		WO 2011075567 A1	23-06-2011
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		EP 2513176 A1	24-10-2012
		US 2013065070 A1	14-03-2013
		WO 2011073417 A1	23-06-2011

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A61K 8/81(2006.01)
C09D 135/02(2006.01)

权利要求书3页 说明书63页

(54) **发明名称**

聚合物组合物的用途

(57) **摘要**

本发明描述了生物可再生共聚物在以下应用中一种或多种中的用途：用于局部和／或个人护理组合物，用作用于调色剂的粘合剂，用作用于着色剂的包封剂，用作混杂着色剂，用作用于片材模塑组合物的添加剂，用作塑料颜料，用作用于复合材料诸如混凝土的填料，用作用于涂料和／或蜡的填料；和／或用作用于显示器中的间隔物，其中所述生物可再生共聚物包含(a)至少8.5重量％、优选地＞＝20重量％的高级衣康酸二酯（优选地衣康酸二丁酯-DBI）；(b)小于23重量％酸单体，且足以具有小于150mg KOH/g聚合物的酸值，(c)任选地具有小于50重量％的其他衣康酸酯单体，和(d)任选地小于77重量％的非(a)至(c)的其他单体。DBI可以是生物可再生的。一个实施方式是两相的乙烯基序列聚合物的水性分散体，所述两相为：A)40至90重量％的Tg从-50到30℃的乙烯基聚合物A；和B)10至60重量％的Tg从50到130℃的乙烯基聚合物B；其中DBI用于制备A和／或B，并且聚合物A具有0.1至10重量％的至少一种酸官能烯属不饱和单体。

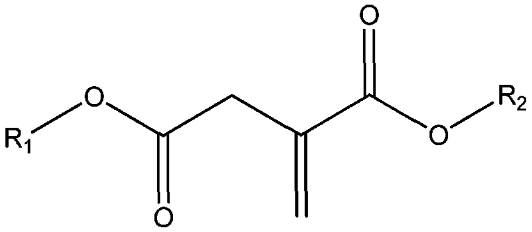
CN 104204080 A

1. 共聚物组合物在如下使用中的一个或多个中的用途，所述使用为：

用作局部组合物和／或个人护理组合物中的成分、用作调色剂的粘合剂、用作着色剂的包封剂、用作混杂着色剂、用作片材模制复合物的添加剂、用作塑料颜料、用作复合材料诸如混凝土的填料、用作涂料和／或蜡的填料；和／或用作显示器中的间隔物

其中所述共聚物组合物［其可选地基本上不含苯乙烯（＜共聚物的 1.5 重量％）］包含：

(a) 至少 23 重量％的至少一种由式 1 表示的单体

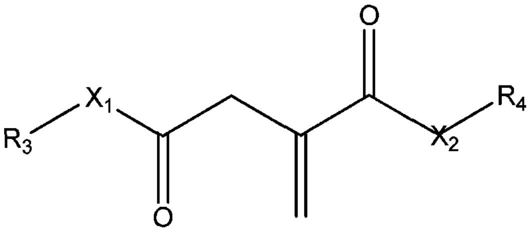


式 1

其中 R_1 和 R_2 二者独立地表示可选地被取代的具有 4 至 10 个碳原子的烃片段，

(b) 可选地至少一种亲水性单体，而且其量足以使所得到的聚合物具有小于 150mg KOH 每 g 聚合物的酸值，

(c) 可选地一种或多种由式 2 表示的单体，



式 2

其中 R_3 和 R_4 独立地表示 H 或可选地被取代的具有 1 至 20 个碳原子的烃片段，

X_1 和 X_2 独立地表示 O 或 NR_5，其中 R_5 表示 H 或可选地被取代的具有 1 至 20 个碳原子的烃片段，前提是当 X_1 和／或 X_2 为 O 时，与氧基相连的各个 R_3 和／或 R_4 独立地表示可选地被取代的具有 1 至 3 个碳原子的烃，

(d) 可选地小于 77 重量％的非组分 (a)、(b) 或 (c) 的单体，

其中 (a)、(b)、(c)、(d) 的百分数或量以重量计被计算为基于 (a)+(b)+(c)+(d) 的总重量的比例，因此总计为 100％；

其中组分 (a)、(b)、(c) 和／或 (d) 中至少一个和／或由它们所获得的共聚物独立地为生物可再生的，所述生物可再生被定义为含有的碳 -14 的量足以产生至少约 1.5dpm/gC（每克碳每分钟衰变）的衰变。

2. 如权利要求 1 所述的共聚物的用途，其中所述共聚物包含：

(a) 组分 (a) 是 24 重量％至 70 重量％的一种或多种由式 1 表示的单体，

(b) 组分 (b) 是以 0.5 重量％至 15 重量％的量的一种或多种酸官能单体，而且其量也足以使所获得的聚合物具有 3 至 100mg KOH 每 g 聚合物的酸值，

(c) 组分 (c) 是 0.01 重量％至 10 重量％的一种或多种由式 2 表示的单体，其中 X_1 和 X_2 均为 O 并且 R_3 和／或 R_4 独立地表示可选地被取代的具有 1 至 3 个碳原子的烃，

(d) 如果存在的话，组分 (d) 是小于 75％重量％的非组分 (a)、(b) 或 (c) 的单体，并且

不包括苯乙烯、丙烯酸丁酯、丙烯酸2-乙基己酯和/或其混合物；其中(a)、(b)、(c)、(d)的重量百分数或量被计算为基于(a)+(b)+(c)+(d)的总量的比例，因此总计为100%；

前提是当所述共聚物通过乳液聚合制备时，不使用追加单体；

所述共聚物不是在包含聚（衣康酸酯）的种子聚合物存在下制得的；

所述共聚物不是在含有有机硼烷胺络合物的引发剂体系存在下制得的。

3. 如前面权利要求中任意一项所述的共聚物的用途，其中所述共聚物包含含有衣康酸二丁酯的组分(a)。

4. 如前面权利要求中任意一项所述的共聚物的用途，其中在所述共聚物中：

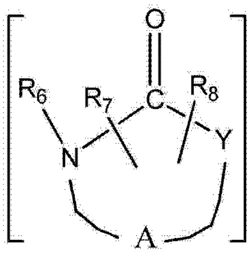
(a) 组分(a)以30至65重量%的量存在并且是衣康酸二丁酯；

(b) 如果存在的话，可选的组分(b)以至多10重量%的量存在，并且包含酸官能烯属不饱和单体和/或其酸酐；

(c) 如果存在的话，可选的组分(c)以1至25重量%的量存在，并且是衣康酸二甲酯和/或衣康酸二乙酯；

(d) 如果存在的话，可选的组分(d)以使得(a)和(d)[以及(b)和(c)，当存在时]总计100重量%的量存在。

5. 如前面权利要求中任意一项所述的共聚物的用途，其中在所述共聚物中，组分(d)包含至少一种式3的聚合物前体



式3，

其中Y表示电负性基团，

R_6是H、OH或可选地羟基取代的C_{1-10}烃

R_7是H或C_{1-10}烃；

R_8是被至少一个经活化的不饱和片段取代的C_{1-10}烃基；并且；

要么A代表既与-HN-又与-Y-片段相连的二价有机片段，因此-A-、-NH-、-C(=O)-和-Y-片段一起表示具有4至8个环原子的环，并且R_7和R_8与所述环上的任何合适的点相连；

要么A不存在（从而式3表示不含杂环的直链和/或支链片段），在这种情况下R_7和R_8与R_6相连；并且

m是1至4的整数。

6. 如前面权利要求中任意一项所述的共聚物的用途，所述共聚物用作局部组合物和/或个人护理组合物中的成分，其中所述组合物选自：局部药物、化妆品组合物、毛发护理组合物、口部清洁组合物、防晒组合物和/或梳洗组合物。

7. 如前面权利要求中任意一项所述的共聚物的用途，其中所述共聚物是通过包括在聚合方法中使聚合物前体聚合的步骤的工艺来制备的，所述聚合物前体包含在前面权利要求中所描述的组分(a)、组分(b)和可选地组分(c)和/或组分(d)，从而获得共聚物，

其中可选地，所述聚合方法选自水性乳液聚合物和悬浮聚合，并且其中所述方法不包括追加单体步骤。

8. 组合物，其包含如权利要求1-7中任意一项中所描述的共聚物以及合适的载体介质，所述组合物被配制成适用于权利要求1至7中任意一项中所描述的任意一个用途。

聚合物组合物的用途

[0001] 本发明涉及由某些2-偏亚甲基丁二酸二酯(2-methylidenebutanedioate diester)单体（本文中也称为高级衣康酸二酯，higher itaconate diesters）获得和/或能够获得的聚合物和聚合材料，还涉及制备这种聚合物的方法以及它们用于制备例如涂料、墨和/或粘合剂的用途。优选的是本发明的聚合物和/或高级衣康酸二酯是由生物可再生来源获得的。

[0002] 许多传统聚合物通常饱受不适当的水敏感性。对于水基聚合物乳液来说尤其更是如此，与它们的溶剂型对应物相比水基聚合物乳液具有更高的水敏感性。处理此问题的一个常用方法是掺入非常疏水的单体，例如丙烯酸丁酯(BA)或丙烯酸2-乙基己酯(EHA)。然而，由于由这些单体获得均聚物具有极低的Tg，因此掺入大量这些单体会产生通常过于软（低Tg）的组合物，而如果为了产生满意的Tg这些单体的量足够低的话，则所产生的组合物疏水性就会不足。可以通过引入高Tg疏水性单体诸如苯乙烯等来反过来缓解此问题。然而，由于苯乙烯固有的UV敏感性，含苯乙烯单体的聚合物组合物具有较低的户外耐久性。

[0003] 令人惊奇的是，我们现已发现上面所描述的困境是可以被解决的。通过引入高级酯衣康酸酯诸如衣康酸二丁酯(DBI)作为疏水性单体，可以实现与高硬度和高断裂伸长率组合的良好的耐水性和低的水敏感性。即使这些单体非常疏水，但是申请人已经出人意料地发现，由高级衣康酸酯制得的聚合物并不会产生与由高浓度的典型疏水性单体（诸如丙烯酸丁酯(BA)和/或丙烯酸2-乙基己酯(EHA)）所制得的共聚物通常观察到的硬度降低相同的硬度降低。

[0004] 衣康酸酯单体已经被研究了很多年。然而，它们并没有广泛用于制备商业的乙烯基聚合物，因为它们很昂贵并且难于加工。现有技术文件仅以一般性术语来描述衣康酸酯的用途，并且通常描述了或举例说明了低级衣康酸二酯，例如衣康酸二甲酯(DMI)。很少有文件描述下文所述的高级衣康酸酯。

[0005] US4206292(Kureha Kagaku Kogyo Kabushiki Kaisha)描述了具有光滑表面的氯乙烯树脂涂料。该涂料包含：(1)100份的氯乙烯聚合物；和(2)0.1至30份的聚合物加工助剂，该聚合物加工助剂包含：(A)10至100份的共聚物，该共聚物含有20至99％的甲基丙烯酸烷基酯、1至70％的衣康酸二烷基酯和0至60％的可共聚单体；和(B)0至90份的共聚物，该共聚物含有80至100％的甲基丙烯酸烷基酯和0至20％的可共聚单体。氯乙烯树脂不是由生物基来源或其他环境友好来源制备的。在实施例中使用的DBI的最大量为30重量％。

[0006] US4547428(Monsanto)描述了一种三元共聚物，其包含衍生自烯烃、可加成聚合的不饱和二羧酸的二酯和增溶性单体的重复单元，其中增溶性单体促进三元共聚物与卤乙烯聚合物之间的相容性。还公开了该加工助剂的颗粒形式及其制备方法。这些聚合物不适合涂料应用，并且在实施例中DBI的最高浓度为17重量％。

[0007] US4588776(Monsanto)描述了包含氯乙烯聚合物与颗粒状三元共聚物的共混物的聚合物组合物，该三元共聚物具有至少100000的分子量和至少50℃的玻璃化转变温度。该三元共聚物包含衍生自烯烃、可加成聚合的不饱和二羧酸的二酯和增溶性单体的重复单

元，其中增溶性单体促进三元共聚物与卤乙烯聚合物的相容性。这些聚合物用于制备成形的塑料制品，而不能用于涂料应用。在实施例中使用的 DBI 的最高浓度为 17 重量%。

[0008] US6951909(3M) 描述了一种可聚合体系，其包含有机硼烷、至少一种可聚合单体和工作寿命延长剂。这些组合物不适合用于涂料应用，并且在实施例中使用的 DBI 的最高浓度为 17 重量%。

[0009] WO11/073417(DSM) 公开了一种水性乳液，其至少包含乙烯基聚合物，所述乙烯基聚合物包含 ：a)45 至 99 重量%的具有式 (I) 的衣康酸酯单体，其中 R 和 R′ 独立地为烷基和芳基 ；b)0.1 至 15 重量%的离子或潜离子不饱和单体 ；c)0 至 54 重量%的不同于 a) 和 b) 的不饱和单体 ；和在单体 a)、b) 和 c) 聚合之后接着加入并聚合的占总单体的 0.9 至 54.9 重量%的追加 (chaser) 单体组合物 ；其中 a)+b)+c) 和追加单体组合物总计 100 重量%；并且其中基于水性乳液的总重量，水性乳液包含小于 0.5 重量%的式 I 的游离衣康酸酯单体。尽管该发明所声称的目标是提供具有高总浓度的衣康酸酯单体的乙烯基聚合物 (参见第 2 页第 14-17 行)，但是实际上较大比例的这种衣康酸酯是低级衣康酸酯 (即小烷基的酯，诸如 DMI)。该文件并没有教导希望使用高浓度的高级衣康酸酯 (即大烷基的酯，诸如 DBI)。事实上，WO11/073417 指出衣康酸酯难于加工 (参见第 2 页第 23-25 行)，这与实施例的教导组合在一起使读者不会将大量疏水的高级衣康酸酯诸如 DBI 掺入到共聚物中。

[0010] WO11/073417 中描述 DBI 单体的使用的仅有的实施例是实施例 2、4、5 和 6。制备这些实施例所使用的 DBI 和其他单体的量在下表 A 中给出。可以看出，DBI 仅以低的浓度在这些实施例中所制备的最终共聚物中用作共聚单体 (最大 22.7 重量%)，每一个实施例还使用了显著量的另一种疏水性单体丙烯酸丁酯 (BA) 来制备。苯乙烯追加单体总是存在于最终产物中 (至少 1.5 重量%)。这些实施例教导了不要使用 DBI 或其他高级衣康酸酯来替换常用的疏水性单体诸如 BA、EHA 和 / 或苯乙烯。在该文件中所制得的共聚物的膜性质诸如硬度和水敏感性方面，没有观察到明显改善。

[0011] GB 1009486(Borden) 描述了复合聚合颗粒的胶乳，其中核和壳可以包含偏氯乙烯与 α 不饱和脂肪酸的酯的共聚物 (酯在壳中的量比在核中大)。一个实施例 (实施例 3) 描述了衣康酸二丁酯 (DBI) 以总单体的 17 重量%的总量 (在外壳中 5%和在内部非核层中 12%) 用作酯。这些复合多层聚合物颗粒解决了为纸或类似物提供水蒸汽阻隔涂层的问题，并且他们使用的 DBI 量比本发明中低得多。

[0012]

表 A（WO11/073417 的现有技术 DBI 实施例）

WO11/073417 的实施例	组成	单体 / 重量%（1 d.p.）									
		AA	BA	MMA	Plex 652	DAAM	MAA	DMI	DBI	S (追加)	总衣康酸酯
Ex 2	初始进料	2.0	28.0	-	-	-	-	45.0	25.0	-	60.0
	单相共聚物	1.8	25.2	-	-	-	-	40.5	22.5	10.0	63.0
Ex 4	第一次进料	4.4	32.4	13.2	-	-	-	20.0	30.0	-	50.0
	第二次进料	5.0	11.0	34.0	-	-	-	45.0	5.0	-	50.0
	序列共聚物	4.1	25.5	15.8	-	-	-	22.7	22.7	9.1	45.4
Ex 5	第一次进料	4.2	30.0	9.5	8.4	-	-	19.1	28.7	-	47.8
	第二次进料	4.7	9.3	28.8	9.5	-	-	42.9	4.7	-	47.6
	序列共聚物	3.9	23.6	12.2	7.9	-	-	21.8	21.8	8.7	43.6
Ex 6	Olg 初始进料	35.4	-	-	-	8.0	5.0	51.6	-	-	51.6
	Olg-plr 初始进料	-	41.2	-	--	-	-	17.6	41.2	-	58.8
	聚合物-低聚物	26.8	10.7（inc 2.2 BA 追加)	-	-	6.1	3.8	42.7	8.5	1.5	51.2

在 WO11/073417 的实施例 2、4 和 5 中，追加单体为 100 重量%苯乙烯，在实施例 6 中，追加单体组合物为苯乙烯（40 重量%）和 BA（60 重量%）的混合物。

[0013] US3766112 描述了用于地板蜡的高光泽胶乳，其包含具有聚乙烯吡咯烷酮保护胶体的氯化石蜡。用于制备胶体的四种单体组分：苯乙烯（70 至 85％），丙烯酸 2- 乙基己酯

(EHA)(5至15%),(甲基)丙烯酸(3至10%)和第四单体(1至5%),所有百分数均为聚乙烯吡咯烷酮的总单体的重量百分数。建议作为第四单体的七个单体中的一个是DBI。这些聚合物解决了提供高光泽地板涂层的问题,并且以比本发明中低得多的量使用DBI。

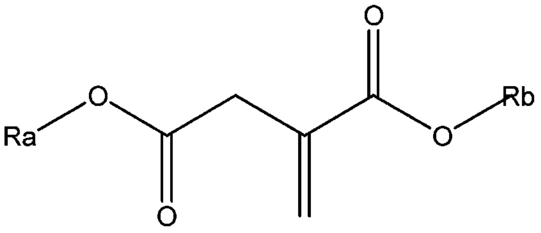
[0014] US2011-144265(Durant Yvon)描述了为了控制颗粒尺寸通过在种子颗粒的存在下将衣康酸的酯聚合而制得的聚合物颗粒。

[0015] WO2002-068479(3M)描述了使用有机硼烷胺络合物和活化剂的两部分引发剂体系的(甲基)丙烯酸单体的聚合。许多不同实例中的一个(实施例6)是由少量DBI(20重量%)制备的,并且该实施例未使用任何其他衣康酸二酯单体。

[0016] WO 2007-026949(Nippon Cat.)描述了具有≤0℃的最低成膜温度(MFT)并且不含挥发性有机化合物(VOC)的乳液型树脂组合物。这些组合物是通过将具有高玻璃化转变温度(高Tg)的聚合物与具有低Tg的聚合物混合来获得的。这些聚合物可以是水可分散性的,并且暗示了各种各样的羧酸官能的酸单体(包括衣康酸、衣康酸单甲酯和衣康酸单丁酯)赋予了这种水溶性(参见第12页第12-14行)。没有描述其他衣康酸衍生的单体,并且该文章的读者没有理由掺入(非羧酸官能的)衣康酸二酯单体。

[0017] 2-偏亚甲基丁二酸的酯(包括单酯和二酯)(本文中也统称为衣康酸酯)可以由式A表示:

[0018]



(A)

[0019] 其中Ra和Rb可以独立地为H或者是任何可选地被取代的烃片段(例如任何脂族、脂环族或芳族片段),前提是Ra和Rb不能同时为H(均为H时,其不是酯而是衣康酸)。

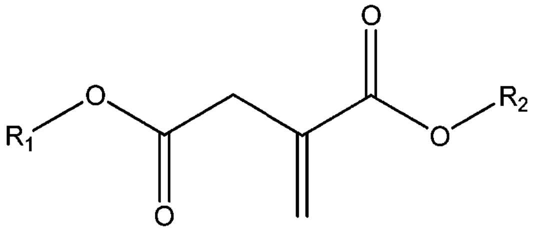
[0020] 已经发现某些疏水的衣康酸二酯(例如大烷基的二酯)难以用于常规的聚合方法中(尤其用于水性乳液聚合中),并且也很昂贵。因此,在这种方法中在高浓度下使用这种疏水性高级衣康酸酯已经成为很不情愿的事。

[0021] 本发明的一个目的是解决本文中所指出的一些或所有问题,例如通过提供由较大量的高级衣康酸酯(例如DBI)任选地与其他烯属不饱和单体(也任选地由生物可再生来源获得)一起制得的聚合材料。所得到的聚合物可以具有各种额外的优点以及本文中已经描述过的那些优点诸如在室温下良好的成膜性,并且形成的膜具有高柔韧性(弹性)和良好的耐粘连性。

[0022] 因此,广义地根据本发明,提供了共聚物组合物,其包含(优选地基本上由以下组成):

[0023] (a)超过8.5重量%、有用地≥15重量%、优选地至少20重量%、更优选地至少24重量%、更优选地至少30重量%、例如至少45重量%的至少一种由式1表示的单体,

[0024]



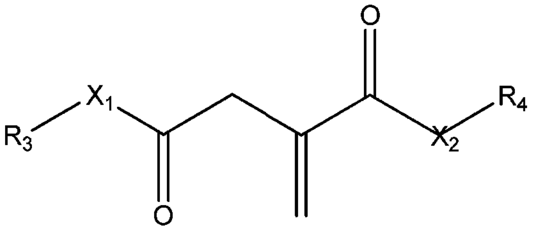
式 1

[0025] 其是 R_1 和 R_2 独立地表示可选地被取代的具有 4 至 10 个碳原子的烃片段，

[0026] (b) 可选地至少一种亲水性单体，优选地以小于 23 重量％、更优选地 0.5 至 15 重量％的量，而且其量足以使所得到的聚合物具有 0 至 150mgKOH/g、优选地小于 150mg KOH/g、更优选地 3 至 100mg KOH/g 聚合物的酸值，

[0027] (c) 可选地小于 50 重量％、例如 0.01 至 10 重量％和／或一种或多种由式 2 表示的单体，

[0028]



式 2

[0029] （式 2 包括除式 1 所表示的那些衣康酸二酯单体外的衣康酸二酯单体）

[0030] 其中 R_3 和 R_4 独立地表示 H 或可选地被取代的具有 1 至 20 个碳原子的烃片段，

[0031] X_1 和 X_2 独立地表示 O 或 NR_5，其中 R_5 表示 H 或可选地被取代的具有 1 至 20 个碳原子的烃片段，前提是当 X_1 和／或 X_2 为 O 时，与氧基相连的各个 R_3 和／或 R_4 独立地表示可选地被取代的具有 1 至 3 个碳原子的烃，

[0032] (d) 可选地小于 80 重量％、有用地小于 77 重量％、优选地小于 75 重量％、更优选地＜ 70 重量％、最优选地＜ 65 重量％的非组分 (a)、(b) 或 (c) 的单体。

[0033] 其中 (a)、(b)、(c)、(d) 的量的重量百分数（本文中也称为“重量％”和／或“wt-％”）被计算为基于 (a)+(b)+(c)+(d) 的总（重）量的比例，因此总计为 100％。

[0034] 本发明的共聚物还可以由下列可选的附加条件中的一个或多个来限制：

[0035] (I) 当组分 (a) 由以小于总单体的 30 重量％的量的 DBI 组成时，则共聚物基本上不含任何氯基团；和

[0036] (II) 当组分 (a) 由以小于总单体的 23 重量％的量的 DBI 组成时，共聚物不是通过其中使用追加 (chaser) 单体的乳液聚合方法制得的；和

[0037] (III) 当组分 (a) 由以小于总单体的 23 重量％的量的 DBI 组成时，那么如果存在组分 (d) 的话，组分 (d) 不是苯乙烯或者由丙烯酸丁酯（混合物的 60 重量％）和苯乙烯（混合物的 40 重量％）组成的混合物；

[0038] (IV) 共聚物基本上不含苯乙烯（优选地不含苯乙烯），更优选地如果存在的话组分 (d) 不是苯乙烯或者由丙烯酸丁酯（混合物的 60 重量％）和苯乙烯（混合物的 40 重量％）组成的混合物，更优选地如果存在的话组分 (d) 不是苯乙烯 (S)、丙烯酸丁酯 (BA)、丙烯酸 2- 乙基己酯 (EHA) 或其混合物。

[0039] (V) 所述共聚物不是通过其中使用追加单体的乳液聚合方法制得的；和

[0040] (VI) 只有当组分 (a) 由优选地以总单体 (a)+(b)+(c)+(d) 的 8.5 重量％至 15 重量％的量的 DBI 组成时，共聚物不是通过其中使用追加单体的乳液聚合方法制得的。

[0041] (VII) 当组分 (a) 由 DBI 组成时，则组分 (a) 不以总单体组合物的 8.5 重量％、21.8 重量％、22.5 重量％或 22.7 重量％的量存在，优选地不以 8 重量％至 23 重量％的量存在，

[0042] (VIII) 当组分 (a) 由 DBI 组成时，则组分 (a) 不以总单体组合物的 4.7 重量％、5.0 重量％、8.5 重量％、21.8 重量％、22.5 重量％、22.7 重量％、25.0 重量％、28.7 重量％、30.0 重量％或 41.2 重量％的量存在，优选地不以 4 重量％至 42 重量％的量存在，

[0043] (IX) 共聚物不是在聚衣康酸二乙酯种子聚合物存在下由以 15 比 85 的各自重量比的衣康酸二甲酯 (DMI) 和衣康酸二丁酯 (DBI) 的聚合获得的；更优选地共聚物不是在聚衣康酸二乙酯种子聚合物存在下由衣康酸二烷基酯的聚合获得的；最优选地共聚物不是在聚衣康酸二烷基酯种子聚合物存在下由聚合获得的；

[0044] (X) 如果共聚物的聚合在包含有机硼烷胺络合物和活化剂的引发剂体系存在下进行，那么组分 (a) 以总单体 (a)+(b)+(c)+(d) 的大于 20 重量％、优选地至少 24 重量％的量存在。

[0045] 本文中使用时，术语“种子聚合物”如 US2011144265 中所定义（例如参见第 [007] 段），即聚合物种子颗粒分散于水性介质中从而该种子颗粒吸收又添加的（共聚）单体，并且该种子颗粒存在的浓度使得可以控制该（共聚）单体的颗粒尺寸。

[0046] 优选地，共聚物组合物是乳液共聚物（通常为未使用追加单体时制得的乳液聚合物）、更优选地水性乳液共聚物、最优选地水性涂料组合物。

[0047] 适宜地，组合物基本上不含聚氯乙烯聚合物和／或氯化石蜡，更优选地基本上不含任何含氯基团的单体，最优选地基本上不含任何含有 Cl 的物质（无论是取代基、原子、二分子、离子或其他方式）。

[0048] 广义地，在本发明的另外一个方面中，提供了制备共聚物的方法，其包括在聚合方法中使聚合物前体进行聚合的步骤，其中聚合物前体包含如上所述的组分 (a)、组分 (b) 和可选地组分 (c) 和／或组分 (d)，从而获得共聚物。

[0049] 优选地，聚合方法选自乳液聚合和／或悬浮聚合。

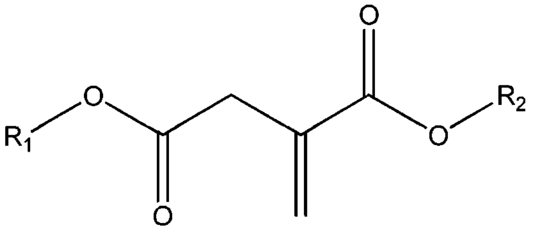
[0050] 优选地，共聚物是乳液共聚物和／或聚合珠粒的分散体。

[0051] 本发明的另一方面广义地提供了通过本发明的方法获得或者能够获得的共聚物。

[0052] 疏水性组分 (a)（高级衣康酸酯）

[0053] 本发明尤其关注由有限种类的衣康酸二酯单体获得和／或能够获得的聚合物，其中衣康酸二酯单体选自式 A 的一般衣康酸酯的广义公开内容。因此，疏水性组分 (a) 包含式 1 的衣康酸二酯：

[0054]



式 1

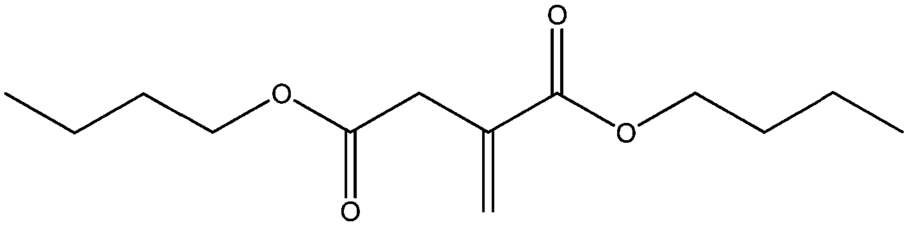
[0055] 其中 R_1 和 R_2 均独立地表示可选地被取代的具有 4 至 10、优选地 4 至 8、更优选地 4 至 6、最优选地 4 个碳原子的烃片段。

[0056] 式 1 的二酯在本文中也被称为高级衣康酸二酯。

[0057] 有用地 R_1 和 R_2 可独立地表示可选地被取代的 C_{4-10} 烷基和 / 或 C_{4-10} 芳基、更有用地 C_{4-8} 烷基和 / 或 C_{4-8} 芳基并且最有用地 C_{4-6} 烷基、甚至更有用地丁基（尤其有用的是正丁基）。

[0058] 虽然 R_1 和 R_2 可以不同，但更适宜地，它们表示相同的片段。式 1 的尤其优选的实例包括 R_1 和 R_2 相同的那些，例如衣康酸二（卞基）酯、衣康酸二（苯基）酯、衣康酸二正丁酯、衣康酸二异丁酯和 / 或衣康酸二 2- 乙基己酯。当 R_1 和 R_2 均表示正丁基时，式 1 表示 2- 偏亚甲基丁二酸二丁酯（在本文中也被称为衣康酸二（正丁基）酯或 DBI），其具有如下结构 ：

[0059]



[0060] 在本发明中，DBI 是最优选的用作组分 (a) 的单体。

[0061] 基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），衣康酸酯官能组分 (a) 以大于 8.5％重量％、有用地≥ 15 重量％、优选地至少 20 重量％、有用地至少 24 重量％、更有用地至少 30 重量％、甚至更有用地至少 35 重量％以及最有用地至少 40 重量％、例如至少 50％的量存在于本发明的组合物和 / 或共聚物中。

[0062] 适宜地，基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），衣康酸酯官能组分 (a) 可以以小于 80 重量％、更适宜地小于 70 重量％、甚至更适宜地小于 65 重量％、最适宜地小于 58 重量％以及例如小于 55 重量％的量存在于本发明的组合物和 / 或共聚物中。

[0063] 优选地，基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），衣康酸酯官能组分 (a) 可以以 20 至 80 重量％、更优选地 24 至 70 重量％、甚至更优选地 30 至 65 重量％、最优选地 35 至 65 重量％、例如 40 至 55 重量％的量存在于本发明的组合物和 / 或共聚物中。

[0064] 亲水性组分 (b)（酸官能单体）

[0065] 组分 (b) 的合适的亲水性单体是能够与组分 (a) 的疏水性单体共聚并且溶于水的那些单体。适宜地，组分 (b) 的至少一种亲水性单体可以包含至少一种如本文中所限定的经活化的不饱和片段。

[0066] 有用地，组分 (b) 的亲水性单体是酸官能的烯属不饱和单体，例如酸官能的丙烯酸类单体。

[0067] 应当理解的是，当在本文中涉及酸官能的组分和 / 或酸性组分时，其指的可以是酸性片段和 / 或在使用条件下可形成酸性基团的潜在酸性片段（例如酸酐）。携带酸的单体可以以游离酸或盐（例如其铵盐和 / 或碱金属盐）形式聚合。因此，本文中提及酸时也

应当理解为包括其合适的盐和／或衍生物（例如其酸酐和／或酰氯）。

[0068] 优选的亲水性单体包含至少一种烯属不饱和羧酸，有利地本质上由至少一种烯属不饱和羧酸组成，但也可以使用其他酸性基团诸如可选地被取代的有机磷酸和／或磺酸。

[0069] 实例包括磷酸化的（甲基）丙烯酸烷基酯、芳基烯烃（arylalkylenes）的磺酸（及其衍生物）、（甲基）丙烯酸烷基酯的磺酸（及其衍生物）和／或其他有机取代的磺酸（例如丙烯酰氨基烷基磺酸（acrylamidoalkyl sulfonic acid））。

[0070] 优选的芳基烯烃磺酸是其中芳基烯烃片段包含可选地烃取代的苯乙烯、适宜地包含可选地 C_{1-10} 烃取代的苯乙烯、更适宜地包含可选地 C_{1-4} 烷基取代的苯乙烯的那些。有用的酸是苯乙烯化合物的磺酸取代的衍生物，该苯乙烯化合物选自由苯乙烯、α－甲基苯乙烯、乙烯基甲苯、叔丁基苯乙烯、二甲基苯乙烯和／或其混合物组成的组。尤其优选的是苯乙烯对磺酸及其相应的酰氯，苯乙烯对磺酰氯。

[0071] 优选的磷酸化的有机酸包括磷酸化的（甲基）丙烯酸酯，其可选地被例如一个或多个羟基取代，例如磷酸化的羟基（甲基）丙烯酸酯及其 C_{1-4} 烷基酯。

[0072] 组分 (b) 的其他优选的亲水性单体包括多价酯的部分酸、更优选地二酯中的半酯、最优选地单酸半衣康酸酯（即，式 A 中要么 R_a 为 H，要么 R_b 为 H 的那些酯）。衣康酸还是也适合用作组分 (b) 的（二）酸官能单体的另一个实例。

[0073] 更优选的酸具有一个烯属基团和一个或两个羧基。最优选地，酸（和／或其合适的酸衍生物）选自由以下组成的组：丙烯酸（及其可共聚的低聚物）、丙烯酸 β－羧基乙酯、柠康酸、中康酸、巴豆酸、富马酸、衣康酸、马来酸、甲基丙烯酸、亚甲基丙二酸、它们的酸酐、它们的盐、它们的酰氯、及其在相同的物种中的组合和／或其混合物。

[0074] 可以构成组分 (b) 的尤其优选的单体选自：丙烯酸、甲基丙烯酸、丙烯酸 β－羧基乙酯、亚甲基丙二酸、马来酸酐、衣康酸、衣康酸酐、磷酸化的甲基丙烯酸羟乙酯（磷酸化的 HEMA）、磷酸化的丙烯酸羟乙酯（磷酸的 HEA）、磷酸化的甲基丙烯酸羟丙酯（磷酸化的 HPMA）、磷酸化的丙烯酸羟丙酯（磷酸化的 HPA）、磺化的苯乙烯（和其氯化物）、2- 丙烯酰氨基 -2- 甲基丙磺酸 (AMPS) 和甲基丙烯酸乙酯 -2- 磺酸。

[0075] 尤其优选的酸单体是丙烯酸、甲基丙烯酸、丙烯酸 β－羧基乙酯、衣康酸和／或衣康酸酐。

[0076] 对于乳液聚合来说，丙烯酸、甲基丙烯酸、丙烯酸 β－羧基乙酯和／或衣康酸可以是便利的。对于 SAD 共聚来说，丙烯酸、甲基丙烯酸和／或衣康酸酐是优选的。

[0077] 亲水性单体组分 (b) 可以可选地不存在于本发明的组合物和／或共聚物中，但如果存在的话，基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），其以大于痕量、有用地大于或等于 0.1 重量％、适宜地大于或等于 0.5 重量％、例如大于 0.8 重量％的量存在。

[0078] 适宜地，基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），如果存在的话，组分 (b) 以小于 23 重量％、更适宜地小于或等于 20 重量％、甚至更适宜地小于或等于 10 重量％、最适宜地≤ 5 重量％、例如≤ 3 重量％、例如≤ 1 重量％的量存在于本发明的组合物和／或共聚物中。

[0079] 优选地，基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），组分 (b) 可以以 0 至 10 重量％、更优选地约 0.1 至约 5 重量％、甚至更优选地约 0.1 至约

3 重量％、最优选地约 0.5 至约 1 重量％的总量使用。

[0080] 适宜地，所使用的组分 (b) 的总量可以足以使所获得的聚合物具有 3 至 100mg KOH 每 g 固体聚合物、优选地 8 至 80mg KOH 每 g 固体聚合物、更优选地 15 至 65mg KOH 每 g 固体聚合物以及最优选地 15 至 45mgKOH 每 g 固体聚合物的酸值 (AV)。

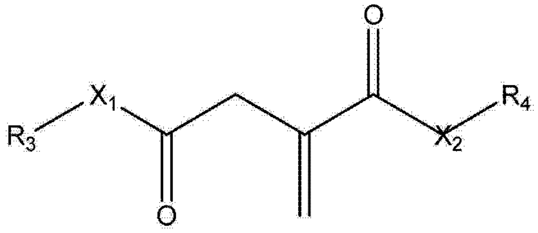
[0081] 有用地，组分 (b) 既满足本文中的酸值 (AV) 限制又满足重量限制，但应当理解的是，根据所使用的单体，本文中所指定的 AV 可以通过使用本文中所给的优选重量％值以外的重量百分数来实现。当本文中在单体或其他组分的任意重量％与指定的酸值之间存在明显的不一致时，应当理解的是满足 AV 通常是更期望的目标。如果必要的话，可以以本领域技术人员所公知的方式适当地修改相关成分的重量％值。

[0082] 组分 (c)（低级衣康酸酯和衣康酸酰胺 (itaconate amide)）

[0083] 组分 (c) 包含一种或多种除式 1 那些之外的其他衣康酸二酯单体，优选地包含其中的 R_a 和 R_b 均不为 H 或不为可选地被取代的 C_{4-10} 烃的式 A 的单体。更优选地，组分 (c) 包含低级衣康酸二酯。本文中使用时，术语“低级衣康酸二酯”指的是其中的 R_a 和 R_b 独立地为可选地被取代的 C_{1-3} 烃基（例如 C_{1-3} 烷基）的式 A 的二酯，其中一个实例是衣康酸二甲酯 (DMI)。

[0084] 有用地，组分 (c) 可以包含低级衣康酸二酯（即除式 1 那些之外的二酯）、和／或高级或低级衣康酸酰胺，并且因此组分 (c) 可以由式 2 来表示，

[0085]



式 2

[0086] 其中 R_3 和 R_4 独立地表示 H 或可选地被取代的具有 1 至 20 个碳原子（例如 1 至 6 个碳原子）的烃片段，优选地 C_{1-20} 烷基、优选地 C_{1-6} 烷基、更优选地 C_{1-4} 烷基、最优选地 C_{1-3} 烷基；

[0087] X_1 和 X_2 独立地表示 O 或 NR_5，其中 R_5 表示 H 或可选地被取代的具有 1 至 20 个碳原子（例如 1 至 6 个碳原子）的烃片段，优选地 C_{1-20} 烷基、优选地 C_{1-6} 烷基、甚至更优选地 C_{1-4} 烷基、例如 C_{1-3} 烷基；

[0088] 前提是当 X_1 和／或 X_2 为 O 时，与氧基相连的各个 R_3 和／或 R_4 独立地表示可选地被取代的具有 1 至 3 个碳原子的烃、优选地 C_{1-3} 烷基。

[0089] 组分 (a)、(b)、(c) 和 (d) 分别是互相排斥的。因此式 2 的化合物与式 1 的那些不同，并且单酸半衣康酸酯也被排除在式 1 和 2 之外，可选地构成亲水性组分 (b) 的一部分。

[0090] 因此，在本发明的一个优选的实施方式中，组分 (a) 和 (b)（和可选地 (c)，如果存在的话）均衍生自衣康酸酯和／或衣康酸和／或其衍生物、更优选地衍生自生物可再生来源。因此，例如，组分 (a) 可以是衣康酸二 (C_{4-6} 二烷基）酯（例如 DBI)，组分 (b) 可以是衣康酸酐、衣康酸和／或衣康酸的 C_{1-4} 烷基单酯，并且当存在时组分 (c) 可以是衣康酸二 (C_{1-3} 二烷基）酯（例如 DMI)。在这样的实施方式中，可选地无组分 (d)，因此，共聚物可以有利地由来自相同衣康酸来源的单体得到。

[0091] 尽管 R_3 和 R_4 可以不同，但更适宜地它们表示相同的片段。

[0092] 尽管 X_1 和 X_2 可以不同，但更适宜地它们表示相同的片段。

[0093] 优选地，组分 (c) 可以以小于 35 重量％、更优选地 0 至 25 重量％的总量使用。

[0094] 基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），如果存在的话，组分 (c) 可以可选地以有用地大于或等于 0.1 重量％、适宜地大于或等于 0.5 重量％、例如大于 1.0 重量％的量存在。

[0095] 适宜地，基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），组分 (c) 以小于 40 重量％、更适宜地小于或等于 35 重量％、甚至更适宜地小于或等于 25 重量％、最适宜地≤ 20 重量％，、例如≤ 15 重量％的量存在于本发明的组合物和／或共聚物中。

[0096] 基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），组分 (c) 可以以 0 至 10 重量％、优选地 0.01 至 10 重量％、更优选地 0.1 至 40 重量％、甚至更优选地 0.5 至 35 重量％、最优选地 1.0 至 30 重量％、例如 1.0 至 25 重量％的总量使用。

[0097] 组分 (d)（其他可共聚单体）

[0098] 优选地，组分 (d) 包含并非组分 (a)、(b) 或 (c) 中部分的单体、更优选地包括可以与它们以任何合适的技术诸如本文中所描述的那些中的任意一种技术（例如以 SAD 和／或乳液聚合）进行共聚的那些单体。

[0099] 组分 (d) 可以包含合适的经活化的不饱和片段（例如烯属不饱和），其中组分 (d) 的结构不与组分 (a)、(b) 或 (c) 中任意一个重叠。

[0100] 优选地，组分 (d) 以小于 50 重量％、更优选地小于 40 重量％的量使用。

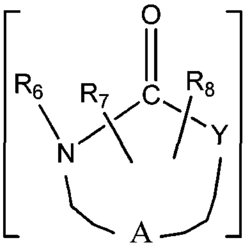
[0101] 组分 (d) 可以包含能够进行交联的单体、能够改善涂料对各种基材的粘附的单体、能够增强聚合物乳液的胶体稳定性的单体、或者能够用来影响 Tg 或聚合物极性的单体。

[0102] 适宜地，组分 (d) 可以包含（甲基）丙烯酸酯单体（该单体具有包含 1 至 20 个碳原子的烷基片段）、苯乙烯、α－甲基苯乙烯、（甲基）丙烯腈、（甲基）丙烯酰胺或烷基化的（甲基）丙烯酰胺、双丙酮丙烯酰胺、甲基丙烯酸乙酰乙酰氧基乙酯、（甲基）丙烯酸羟乙酯、（甲基）丙烯酸羟丙酯；硅烷官能单体，例如 3- 甲基丙烯酰氧基丙基三甲氧基硅烷 (Geniosil GF31，ex Wacker)；脲基官能单体诸如 Plex 6852-0（来自 Evonik)，（甲基）丙烯酸异冰片酯、聚乙二醇（甲基）丙烯酸酯、聚丙二醇（甲基）丙烯酸酯。

[0103] 组分 (d) 还可以包含能够诱导共聚物组合物交联的交联单体。交联能够如下发生：在室温下（使用例如与己二酸二酰肼结合的双丙酮丙烯酰胺）、高温下（烘烤条件，其中例如共聚的（甲基）丙烯酸羟乙酯与六甲氧基甲基蜜胺反应）进行，作为 2C 组合物（共聚的（甲基）丙烯酸羟乙酯与多异氰酸酯反应，例如 Bayhydur 3100)，或者作为 UV 涂料（当具有多个不饱和基团的聚合物或低聚物混合时。典型的实例包括二官能或三官能的多官能丙烯酸酯，诸如三羟甲基丙烷三丙烯酸酯或者其乙氧基化物或丙氧基化物）。

[0104] 可选地，组分 (d) 还可以包含至少一种式 3 的聚合物前体

[0105]


式 3

[0106] 其中 Y 表示电负性基团，

[0107] R_6 是 H、OH 或可选地羟基取代的 C_{1-10} 烃

[0108] R_7 是 H 或 C_{1-10} 烃；

[0109] R_8 是被至少一个经活化的不饱和片段取代的 C_{1-10} 烃基；并且；

[0110] 要么 A 代表既与 -HN- 又与 -Y- 片段相连的二价有机片段，因此 -A-、-NH-、-C(＝O)- 和 -Y- 片段一起表示 4 至 8 个环原子的环，并且 R_7 和 R_8 与环上的任何合适的点相连；

[0111] 要么 A 不存在（并且式 3 表示不含杂环的直链和/或支链片段），在这种情况下 R_7 和 R_8 与 R_6 相连；并且

[0112] m 是 1 至 4 的整数。

[0113] 式 3 的一个或多个环片段均与 R_8 相连，并且在式 3 中当 m 是 2、3 或 4 时 R_8 是多价的（取决于 m 的值）。如果 m 不为 1，则 R_7 和 -Y- 可以分别表示在每个环中的相同或不同的片段、优选地在每个环中的相同的相应片段。R_7 和 R_8 可与环上的任意合适的位置相连。

[0114] 式 3 的优选单体包含其中具有以下特征的那些、适宜地本质上由其中具有以下特征的那些组成，所述特征为：A 表示可选的经取代的二价 C_{1-5} 亚烃基；和

[0115] -Y- 是二价 -NR_9-（其中 R_9 是 H、OH、可选地羟基取代的 C_{1-10} 烃或 R_8）或二价 O。

[0116] 式 3 的更优选单体包含其中具有以下特征的那些，所述特征为：m 为 1 或 2，

[0117] -Y- 是 -NR_8-（即其中式 2 经环氮与 R_8 相连），A 表示二价 C_{1-3} 亚烃基；R_6 是 H，R_7 是 C_{1-10} 烃；并且

[0118] R_8 包括（甲基）丙烯酰氧基烃基或其衍生物（例如马来酸酐）。

[0119] 式 3 所表示的单体包括通俗地被称为脲基单体的一些单体。式 3 的其他合适的脲基单体描述于"Novel wet adhesion monomers for use in latex paints"，Singh 等，Progress in Organic Coatings，34(1998)，214-219，（尤其参见第 2.2&2.3 部分）和 EP 0629672(National Starch) 中，二者均通过引用并入本文。适宜地，式 3 的单体可以以基本上纯的化合物（或化合物的混合物）形式使用或者可以溶解于合适的溶剂中，例如合适的（甲基）丙烯酸酯或丙烯酸衍生物，例如甲基丙烯酸甲酯。

[0120] 其他组分 (d) 和/或额外组分 (d) 可以用于需要较高的分子量的那些情况中，例如合适的多官能（甲基）丙烯酸酯或二乙烯基芳烃。典型的实例包括二官能、三官能或四官能的（甲基）丙烯酸酯，尤其是二官能的（甲基）丙烯酸酯和二乙烯基苯。典型的浓度为基于总单体的小于 10 重量％、更优选地小于 5 重量％、甚至更优选地 0.05 重量％至 4 重量％、最优选地 0.1 至 2.5 重量％以及甚至最优选的 0.15 重量％至 1.5 重量％。

[0121] 基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100％），组分 (d) 可以任选地以有用地大于或等于 0.1 重量％、适宜地大于或等于 0.5 重量％、例如大于 1.0 重量％的量存在。

[0122]　适宜地，基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100%），组分 (d) 以小于 77 重量%、更适宜地小于或等于 50 重量%、甚至更适宜地小于或等于 40 重量%、最适宜地≤ 30 重量%、例如≤ 25 重量%的量存在于本发明的组合物和 / 或共聚物中。

[0123]　优选地，基于用于制备共聚物的单体 (a)、(b)、(c) 和 (d) 的总重量（为 100%），组分 (d) 可以以 0 至 77 重量%、更优选地约 0.1 重量%至约 50 重量%、甚至更优选地约 0.5 重量%至约 40 重量%、最优选地约 1.0 重量%至约 30 重量%的总量使用。

[0124]　本发明的其他方面

[0125]　本发明的一个方面涉及水性序列乙烯基聚合物分散体，其包含 30 重量%（优选地至少 40 重量%）的由一种或多种高级衣康酸二酯获得或者能够获得的聚合物。

[0126]　本发明的另一方面涉及水性乙烯基聚合物涂料组合物，其包含低聚组分和聚合组分的共混物、共聚物和 / 或其混合物，其中该聚合组分包含 30 重量%（优选地至少 40 重量%）的由一种或多种高级衣康酸二酯获得或者能够获得的材料。

[0127]　本发明的另外一个方面涉及乙烯聚合物珠粒，其包含 30 重量%（优选地至少 40 重量%）的由一种或多种高级衣康酸二酯获得或者能够获得的聚合物。

[0128]　可构成组分 (a)、(b)、(c) 或 (d) 中的所有或部分的合适单体的其他实例可以描述于本申请后面描述的本发明的各种其他方面中。可以理解的是，上面未提到的那些合适单体也可以用作本发明上述方面中的组分。

[0129]　聚合方法

[0130]　可以使用多种方法来形成本发明的共聚物。这些方法包括乳液聚合、悬浮聚合、本体聚合和溶液聚合。这些方法都是极其公知的并且不需要非常详细地描述。

[0131]　在一个实施方式中，使用乳液聚合来形成本发明的共聚物。

[0132]　传统的乳液方法包括，将单体分散于水性介质中，并使用自由基引发剂（通常水溶性的）、适当加热（例如 30 至 120℃）和搅拌来进行聚合。

[0133]　可以采用常规乳化剂（表面活性剂）来实现水性乳液聚合，被使用的常规乳化剂例如为阴离子型和 / 或非离子型乳化剂。基于所添加的全部单体的重量，所使用的量优选地很低、优选地 0.3 至 2 重量%、更常用地 0.3 至 1 重量%。

[0134]　水性乳液聚合可以采用常规的自由基引发剂，诸如本领域中所公知的过氧化物、过硫酸盐和氧化还原体系。基于所添加的全部单体的重量，所使用的引发剂的量通常为 0.05 至 3%。

[0135]　可以使用“一锅法”("all in one") 批处理方法（即在聚合开始时要使用的所有组分均存在于聚合介质中的方法）或者半 - 批处理方法（在半 - 批处理方法中，一种或多种所采用的组分（通常至少一种单体）在聚合时全部或部分地进料到聚合介质中）来进行水性乳液聚合方法。尽管不优选，但原则上也可以使用完全连续的方法。优选地，采用半 - 批处理方法。

[0136]　所采用的聚合技术可以使得形成低分子量聚合物，例如通过采用链转移剂，诸如选自硫醇（巯醇）、某些卤代烃和 α - 甲基苯乙烯的链转移剂；或者通过催化链转移聚合，使用例如非常常规的钴螯合物络合物。或者，可以使用受控的自由基聚合方法，例如通过利用合适的硝基氧化合物 (nitroxide) 或硫代羰基硫 (thiocarbonylthio) 化合物，诸如二硫

代酯、二硫代氨基甲酸酯、三硫代碳酸酯和黄原酸酯，从而经由例如氮氧介导的聚合(NMP)、可逆加成断裂链转移方法(RAFT)或原子转移自由基聚合(ATRP)来介导聚合。

[0137] 当本发明的共聚物是乳液聚合物时，其可以与各种其他聚合物乳液混合，例如与不包含DBI(或高级衣康酸酯)的那些聚合物乳液。这种第二聚合物乳液的例子可以是聚氨酯乳液、聚氨酯-聚(甲基)丙烯酸酯乳液、醇酸乳液、聚酯乳液和/或聚乙烯类乳液。后面的这些共聚物乳液集合可包括低聚物-聚合物乳液、梯度形态乳液、序列聚合的(sequentially polymerized)乳液或单相共聚物乳液。

[0138] 可以经由乳液聚合或者经由被称为溶剂辅助分散(SAD)聚合的方法来生产根据上面描述的乳液。

[0139] 当经由乳液聚合来生产共聚物乳液时，这可以根据单次进料方法、顺序进料多相共聚方法、低聚物支持的乳液聚合方法或粉末进料方法来进行，得到梯度颗粒形态。

[0140] 在溶剂辅助分散聚合方法或SAD聚合的情况下，聚合在有机溶剂中进行。接下来，加入碱和/或表面活性剂，并且将聚合物溶液乳化。优选地，在整个方法结束时经由蒸发将溶剂去除。

[0141] 可以经由单次进料溶液聚合或者通过顺序进料多相聚合，来生产SAD聚合物乳液。也可以设想，在可选地去除溶剂之前或者之后，将SAD聚合物乳液用作乳液聚合阶段的种子。在这种情况下，将根据SAD方法制得的聚合物乳液用作批处理或半-批处理聚合方法中的种子。

[0142] 优选的聚合方法是乳液聚合。

[0143] 优选地，含DBI的共聚物的重均分子量(M_w)(如本文中所述用GPC测定)为大于2000g/mol、更优选地大于10000g/mol、甚至更优选地大于25000g/mol、最优选地大于40000g/mol、以及甚至更优选地大于100000g/mol。

[0144] 在经由乳液聚合制备低聚物-聚合物乳液的情况下，可能期望的是较低的分子量。在那些情况下，可以使用链转移剂。典型的链转移剂可以是硫醇诸如月桂硫醇、巯基乙酸异辛酯或3-巯基丙酸，或者卤化物诸如溴甲烷、溴乙烷。在这些情况下，典型的链转移剂浓度足以使低聚物相的重均分子量降低至500和100000g/mol之间、更优选地1000和60000g/mol之间、甚至更优选地2500和50000g/mol之间、以及最优选地5000和25000之间。典型的链转移剂浓度低于总单体的5重量%、更优选地低于2.5重量%、以及最优选地在0.5和2.5重量%之间。在低聚物与高分子量聚合物组合的情况下，高分子量部分的优选分子量将会如前面所述。

[0145] 在共聚物乳液包含多相或者由多个单体进料(顺序、低聚物-聚合物或粉末进料)制成的那些情况下，共聚物相中的一个优选地构成用于制备顺序、粉末进料和/或低聚物-聚合物组合物的总单体的10至80重量%、更优选地15至50重量%、以及最优选地20至40重量%。这种具体的共聚物相具有高于40℃、更优选地高于60℃、以及更优选地高于80℃的Tg，该Tg使用Fox方程计算。其他共聚物相可以构成用于制备顺序、粉末进料和/或低聚物-聚合物组合物的总单体的20至90重量%、更优选地总单体的50至85重量%且最优选地60至80重量%。这些具体共聚物相具有小于40℃、更优选地小于20℃、以及最优选地小于0℃的Tg，该Tg使用Fox方程计算。

[0146] 在这种乳液中高Tg相与低Tg相之间的Tg差值为优选地至少20℃、更优选地至少

30℃、以及最优选地至少 40℃。

[0147] 在特殊情况下，设想，可以使用具有酸酐反应性基团的化学物质对在 SAD 共聚方法中进行共聚的衣康酸酐进行后修饰。在这些情况下，目的是引入特殊官能团诸如交联基团或粘合促进基团，同时保持能够用于胶体稳定化的酸官能团。

[0148] 可以使用任何亲核官能团来进行酸酐基团的修饰。优选的官能团包括羟基、酰肼基、肼基、半 - 卡巴肼基和胺基。在所有情况下，修饰可以导致引入与羟基、酰肼基、肼基、半 - 卡巴肼基或胺基相连的片段，并且同时引入酸基团。随后可以使用酸基团来乳化共聚物。

[0149] 可以使用单官能的羟基、酰肼、或肼、或者伯胺或仲胺来进行修饰，也可以使用双官能或更高官能的羟基、肼、酰肼、半 - 卡巴肼或者伯胺或仲胺来进行修饰。潜在的羟基官能团可以包括 C1-C20 脂族、芳族、或脂环族的单官能、双官能或高官能的醇。脂族、芳族、或脂环族基团可以包含其他官能团，例如能够用于改善粘合、交联或其他目的官能团。这种官能团的典型实例可以包括磷酸酯 / 盐、膦酸酯 / 盐、硫酸酯 / 盐、磺酸酯 / 盐、酮、硅烷、(环状) 脲基、(环状) 碳酸酯 / 盐、酰肼、肼、半 - 卡巴肼、聚氨酯 (urethane)、脲、氨基甲酸酯 / 盐和三聚氰胺。

[0150] 优选的 (多) 胺、(多) 肼或 (多) 酰肼可以通过相同的描述来表征。

[0151] 在经由乳液聚合物制备共聚物组合物的情况下，可以优选地使用有机或无机碱来提高乳液的 pH。典型的实例包括氨、伯有机胺和仲有机胺、氢氧化锂、氢氧化钠或氢氧化钾、碳酸钠或碳酸氢钠。通常，仅在制造过程结束时提高 pH，但是也可以设想在聚合开始时已经提高了水相的 pH(缓冲) 或者在例如序列单体进料之间提高聚合混合物的 pH。在经由乳液聚合制备共聚物的情况下，优选地在制造过程结束时提高 pH，优选地使用氨或氢氧化锂。

[0152] 通常，pH 提高到大于 5 的值、更优选地大于 6、并且最优选地 6 至 9 的值。

[0153] 当经由 SAD 聚合方法制备共聚物乳液时，可以通过添加表面活性剂来进行乳化，但优选地通过先中和聚合物酸基团来进行乳化。这可以通过以下来实现 ：向溶液聚合的聚合物中添加碱，然后添加水 ；或者向水相中添加碱，然后添加聚合物溶液。在这两种情况下，合适的碱与前面描述相同。优选的碱是氨、氢氧化锂或二甲基乙醇胺、甲基二乙醇胺、乙基二乙醇胺、二乙基乙醇胺以及类似物。通常，碱与酸基团的摩尔比为 0.5 至 1.3、更优选地 0.6 至 1.2、最优选地 0.6 至 1。

[0154] 水性共聚物乳液中挥发性有机化合物 (VOC) 的浓度优选地是低的。在优选的情况下，VOC 水平小于 20 重量％、更优选地小于 10 重量％、甚至更优选地小于 5 重量％、最优选地小于 1 重量％、甚至最优选地小于 0.5 重量％。有意地，在将共聚物乳液配制成漆之前，共聚物乳液的 VOC 水平接近 0 重量％、典型地小于 0.1 重量％。

[0155] 当经由 SAD 聚合制备共聚物组合物时，需要溶剂用于溶液聚合方法。典型的溶剂包括本领域技术人员公知的有机溶剂，例如丙酮、甲基乙基甲酮、乙醇、甲醇、异丙醇、异辛醇、二甲苯、乙二醇醚、乙二醇酯。优选地，使用 (高压下聚合后) 能够通过蒸发从乳液中去除的溶剂。在此方面，优选的溶剂是丙酮和甲基乙基甲酮。

[0156] 需要引发剂来开始自由基聚合。这些也是本领域技术人员公知的。水性乳液聚合可以采用常规自由基引发剂，诸如过氧化物、过硫酸盐和氧化还原体系。有用的实例包括无机过氧化物诸如过硫酸铵、过硫酸钠、过硫酸钾，AZO 引发剂诸如偶氮二异丁腈 (AIBN)、2,

2′ -偶氮二(2-甲基丁腈)(AMBN),和有机过氧化物和氢过氧化物。(氢)过氧化物可以很容易地与合适的还原剂组合使用。优选地,引发剂以总单体的0.05至6重量%、更优选地0.5至4重量、最优选地0.5至3重量%的量使用。

[0157] 如本领域技术人员已知的,在乳液聚合物中使用表面活性剂。典型的表面活性剂已经在各种专利申请中广泛地描述了。表面活性剂的选择和浓度对于本发明来说并不关键。可以使用常规乳化剂(表面活性剂)例如阴离子型和/或非离子型乳化剂,来实现水性乳液聚合。基于用来制备聚合物所添加的全部单体的重量,所使用的量优选地很低、优选地0.3至2重量%、更常见地0.3至1重量%。

[0158] 在SAD共聚物乳液的情况下,可以通过选择合适的阴离子型、非离子型和混合的阴离子/非离子型表面活性剂,来辅助乳化。通常,以小于总单体的5重量%、更优选地小于3重量%、以及最优选地0.2至2.5重量%的量使用表面活性剂。

[0159] 优选地(并且受限于本文中的限制),在本发明的一个实施方式中,制备本发明的共聚物乳液的方法包括使用WO2011073417中所描述的追加单体组合物。在另一个实施方式中,可以可选地不使用追加单体。

[0160] 在一个优选的情况下,共聚物乳液的剩余单体含量小于2000mg/L、更优选地小于1500mg/L、最优选地小于1000mg/L、以及尤其优选地小于550mg/L。

[0161] 水性涂料组合物得到的涂料具有至少30s、更优选地至少40s、甚至更优选地至少50s、以及最优选地至少60s的典型的König硬度值。

[0162] 在另一个实施方式中,可以使用本体聚合方法来制备本发明的聚合物。烯属不饱和单体的本体聚合详细描述于EP 0156170、WO82/02387和US4414370中,这些专利的内容通过引用并入本文。

[0163] 通常,在本体聚合方法中,将两种或更多种单体的混合物连续加入到包含熔融的乙烯基聚合物的反应区域中,该乙烯基聚合物具有与单体混合物相同比例的乙烯基单体。将熔融的混合物保持在预定的温度下,以提供具有所期望分子量的乙烯基聚合物。以与将单体加入到反应区域的速度相同的速度,将产物从反应区域泵出,从而在体系中提供固定水平的乙烯基单体和乙烯基聚合物。所选择的具体流速取决于反应温度、乙烯基单体、所期望的分子量和所期望的多分散性。

[0164] 对于本发明的聚合物来说,尤其是用于涂料组合物的那些,在其上提供氨官能基团也可以是有用的,因为这种基团提供对某些基材(诸如木材和醇酸树酯)增强的粘附性。可以通过使用羧基官能前体来将氨基引入到聚合物中,所述羧酸官能前体例如通过采用烯属不饱和酸官能单体诸如丙烯酸或甲基丙烯酸制得。至少一些羧基官能团可以通过与亚烷基亚胺(诸如亚乙基亚胺、亚丙基亚胺或亚丁基亚胺)反应转化成氨基(作为氨基酯基团的一部分)。这种反应在本领域中已经得到广泛接受,被称为亚胺化(imination)反应,并且其详细内容教导于例如US 7049352中,其内容通过引用并入本文。因此,如本文中所述,本发明的另一个方面包括,本发明的所有共聚物的亚胺化形式。

[0165] 如果期望交联聚合物(例如在聚合物分散体中),相关聚合物可以带有官能基团诸如羟基,并且分散体随后与诸如多异氰酸酯、三聚氰胺或甘脲的交联剂一起配制;或者在一种聚合物或两种聚合物上的官能基团可以包括酮羰基或醛羰基,并且在步骤c)中随后配制的交联剂可以是多胺(polyamine)或多酰肼(polyhydrazide),例如己二酸二酰肼、草

酸二酰肼、邻苯二甲酸二酰肼、对苯二甲酸二酰肼、异佛尔酮二胺和 4,7- 二氧杂癸烷 -1,10 二胺。需要注意的是，由于形成共价键，这种交联剂会影响交联。

[0166] 下文描述本发明的另一个方面，其包括设计解决的具体额外问题和 / 或子问题以及其他现有技术。

[0167] 传统的涂料是不理想的，因为聚合物膜具有极小的柔韧性，并且在基材（诸如木材）上的涂层在尺寸上是不稳定的 ；易被撕裂和削掉。硬质聚合物分散体的一个缺点是它们仅能用大量成膜助剂的添加来处理，这对于初始耐粘连性 (initial block resistance) 来说是不利的。

[0168] 初始耐粘连性是已经干燥很短时间的新涂覆的涂层粘连的趋势。这种粘连的趋势使得它几乎不可能用于例如快速堆叠的经涂布的基材，况且大量成膜助剂仍存在于粘合剂膜中且在室温下由常规聚合物仅仅逐渐式地释放。当干燥在室温下进行时，经常仅在几天后才达到最终耐粘连性 (final block resistance)。

[0169] EP 387664 公开了最低成膜温度小于 50℃的水性合成树脂分散体，其包含具有由以下组成的核 / 壳结构的乳液聚合物 ：A)65-90 重量％的弱交联的核聚合物，其具有小于 0℃的玻璃化转变温度和至少 150％的断裂伸长率 ；以及 B)10-35 重量％的本质上未交联的壳聚合物，其具有小于 60℃的玻璃化转变温度，其中所述核聚合物的玻璃化转变温度比所述壳聚合物低至少 10℃。

[0170] US 5021469 公开了一种用于水基光泽漆的粘合剂，其包含分散于水相中的多相乳液聚合物的颗粒，该颗粒由以下制成 ：(a) 具有超过 40℃的玻璃化转变温度的核材料和 (b) 具有小于 70℃的玻璃化转变温度的壳材料。

[0171] US 4654397 公开了制备水性聚合物分散体的方法，该分散体具有低的成膜温度但仍给出具有高耐粘连性的膜，以及公开了这些聚合物分散体作为粘合剂用于涂层材料的用途。

[0172] 上面所讨论的公开物均未教导具有如下所述的特征与整数 (integers) 的选定组合的分散体，来产生如上所讨论的有利的性质组合。

[0173] 本发明的这一方面的优选目标是以水性合成树脂分散体的形式提供物理 - 干燥的粘合剂，其在低温下物理干燥，以得到高弹性的膜，该膜从开始时几乎是不粘的。

[0174] 根据本发明这一方面的乳液聚合物解决了本文中所描述的一些或所有问题。

[0175] 以第一相或核材料和第二相或壳材料形式涉及的聚合物相的设计并不意味着本发明应当受胶乳颗粒的任何具体形态限制。术语“聚合物相”应当理解为指的是乳液聚合物的一部分，其在时间上有限的一段乳液聚合中被制得，并且它的分散体与之前的相或之后的相不同。这也称为多阶段聚合。

[0176] 本发明的分散体的两相结构影响当分散体涂布基材后干燥时所形成的膜的性质。

[0177] 本发明的这一方面提供了具有 MFFT 和抗粘连性质的有利组合的水性乙烯基聚合物分散体，其可以至少部分由生物可再生单体（例如生物可再生 DBI）制备。

[0178] 根据本发明的这个方面，提供了最低成膜温度小于 50℃、更优选地小于 30℃的水性聚合物分散体，其包含衍生自烯属不饱和单体的乙烯基聚合物，具有至少两相，包含 ：

[0179] A)40 至 90 重量％、更优选地 50 至 85 重量％以及尤其 60 至 80 重量％的玻璃化转变温度在 -（负）50 至 30℃范围内的乙烯基聚合物 A ；和

[0180] B)10 至 60 重量％、更优选地 15 至 50 重量％以及尤其 20 至 40 重量％的玻璃化转变温度在 50 至 130℃范围内的乙烯基聚合物 B ;其中

[0181] (i) 用于制备乙烯基聚合物 A 和 / 或乙烯基聚合物 B 的单体中的至少一个表示为本文中所描述的式 1(有用地为高级衣康酸酯，诸如 DBI)，用量优选为总单体的 20 至 80 重量％、更优选地 20 至 65 重量％、最优选地 30 至 55 重量％，

[0182] (ii) 可选地用于形成乙烯基聚合物 A 和乙烯基聚合物 B 的单体的总量的 10 重量％ (优选地至少 20 重量％) 衍生自至少一种生物可再生烯属不饱和单体 ;

[0183] 其中 A 和 B 中单体的重量百分数是基于用于制备聚合物 A 和聚合物 B 的烯属不饱和单体的总量 (为 100％) 以 (i) 和 (ii) 形式计算的 ;

[0184] (iii) 乙烯基聚合物 A 包含 0.1 至 10 重量％的至少一种酸官能的烯属不饱和单体，其中酸官能单体的重量百分数是基于用于制备聚合物 A 的烯属不饱和单体的总量 (为 100％) 计算的。

[0185] 在本发明的这个方面中，特征 (i) 和 (iii) 分别对应于本发明的组分 (a) 和 (b)，并且用于制备聚合物 A 和 B 的其他单体对应于可选的组分 (c) 和 / 或 (d)，视情况而定。

[0186] 本发明的这个方面的其他优选特征在下文中给出和 / 或在权利要求书中给出。

[0187] 酸官能的烯属不饱和单体可以选自由丙烯酸、甲基丙烯酸、衣康酸酐、马来酸酐、亚甲基丙二酸、衣康酸、巴豆酸和富马酸组成的组。

[0188] 乙烯基聚合物 A 可以包含 0.1 至 20 重量％的至少一种交联烯属不饱和单体、优选地 0.4 至 6 重量％的至少一种具有湿粘附促进功能的烯属不饱和单体。

[0189] 一种或多种交联单体和一种或多种湿粘附促进单体可以一起用于相同的聚合物组合物中。但是，通常期望在任意相中要么使用一种或多种交联单体要么使用一种或多种湿粘附促进单体。这意味着乙烯基聚合物 A 可以包含一种或多种交联单体或者一种或多种湿粘附促进单体，而乙烯基聚合物 B 包含一种或多种湿粘附促进单体或者一种或多种交联单体。除此之外，还可以在乙烯基聚合物 A 和 / 或乙烯基聚合物 B 中或者在二者中使用一种或多种湿粘附促进单体，且不使用交联单体，或者可以在乙烯基聚合物 A 和 / 或乙烯基聚合物 B 中使用一种或多种交联单体，且不使用湿粘附促进单体。

[0190] 具有湿粘附促进功能的烯属不饱和单体包含湿粘附促进官能团，例如乙酰乙酰氧基和可选地被取代的胺基或脲基 (例如环状脲基)、咪唑基、吡啶基、肼或半 - 卡巴肼 (semicarbazide) 基团。

[0191] 生物可再生的烯属不饱和单体可以包含生物可再生 (甲基) 丙烯酸和 / 或生物可再生 (甲基) 甲基丙烯酸烷基酯 (alkyl(meth)methacrylate)。

[0192] 生物可再生的烯属不饱和单体还可以包含生物可再生的 :α - 亚甲基丁内酯、α - 亚甲基戊内酯、α - 亚甲基 γ -R^1 丁内酯 (R^1 可以是可选地被取代的烷基或可选地被取代的芳基) ;衣康酸酯例如衣康酸二烷基酯和衣康酸单烷基酯，衣康酸，衣康酸酐，巴豆酸及其烷基酯，柠康酸及其烷基酯，亚甲基丙二酸及其单烷基酯和二烷基酯，柠康酸酐，中康酸及其烷基酯。

[0193] 生物可再生单体还可以包含生物可再生的 :N-R^2，α - 亚甲基丁内酰胺 (R^2 可以是可选地被取代的烷基或可选地被取代的芳基) ;N-R^2，α - 亚甲基 γ -R^1 丁内酰胺 ;N- 烷基衣康酰亚胺 (itaconimids) ;衣康单酰胺 (itaconmonoamids) ;衣康二酰胺 (itacondiamids) ;

二烷基衣康酰胺(dialkyl itaconamides),单烷基衣康酰胺(mono alkyl itaconamides);(甲基)丙烯酸糠酯(furfuryl(meth)acrylate);和脂肪酸官能的(甲基)丙烯酸酯。

[0194] 乙烯基聚合物A和乙烯基聚合物B可以包含至少约1.5dpm/gC的碳14。

[0195] 在本发明的另一个方面中,提供了制备水性聚合物分散体(或如上所述的聚合物A和聚合物B)的方法,该方法包括以下步骤:

[0196] a)第一聚合步骤,以形成第一相乙烯基聚合物;

[0197] b)在来自步骤a)的所获得的第一相乙烯基聚合物存在下的第二聚合步骤,以形成第二相乙烯基聚合物。

[0198] 乙烯基聚合物A可以是第一相,在这种情况下,乙烯基聚合物B是第二相。或者乙烯基聚合物B可以是第一相,在这种情况下,乙烯基聚合物A是第二相。优选地,乙烯基聚合物A是第一相。优选地,第二相乙烯基聚合物是在第一相乙烯基聚合物的存在下制备的。

[0199] 可选地,本发明的方法还包括c)中和步骤,在步骤c)之前、之后或步骤c)时使第一聚合物相溶解。

[0200] 可选地,本发明方法还包括d)在聚合步骤a)和/或步骤b)之后添加交联剂,所述交联剂能够在随后干燥涂料分散体时与乙烯基聚合物A和/或乙烯基聚合物B的任何交联官能团反应,以实现共价键交联。

[0201] 可选地,本发明方法包括使用亚烷基亚胺(诸如亚丙基亚胺)的后处理亚胺化步骤e),该步骤能够极大地改善湿粘附性。

[0202] 膜、光泽剂(polish)、清漆(varnish)、亮漆(lacquer)、漆料、墨和/或粘合剂可以包含含有如上所述聚合物A和聚合物B的水性聚合物分散体,并且这些水性聚合物分散体还可以用于木材、塑料、纸和/或金属基材上的保护性涂料。

[0203] 本发明的一个实施方式提供了水性聚合物分散体,其中乙烯基聚合物A和B各自包含至少30重量%、更优选地至少40重量%、最优选地至少60重量%、以及尤其优选地至少70重量%的式1化合物,诸如高级衣康酸二酯,例如DBI。尽管聚合物A和B中的衣康酸酯单体的浓度可以是相似的,但优选的是该浓度是不同的。在上述的那些优选情况中的每一种中,可以设想衣康酸酯单体在其他相中的浓度始终可以低于20重量%或者甚至可以是0重量%。

[0204] 优选地,根据本发明的衣康酸酯在低Tg相中的浓度要比在高Tg相中高至少10重量%、更优选地高至少20重量%。

[0205] 在本发明的另外一个优选实施方式中,提供了根据本发明的水性聚合物乳液,其中组成聚合物A的单体进料或组成聚合物B的进料包含至多20重量%的有机溶剂、更优选地小于10重量、甚至更优选地小于5重量%、以及最优选地0.1至2.5重量%。

[0206] 在本发明的这个方面中,共聚物的改善的性质可以包括耐热性、胶体稳定性、颜料相容性、表面活性、耐粘连性和降低的MFFT,这取决于所使用的单体。

[0207] 用于制备乙烯基聚合物A和乙烯基聚合物B所使用的单体体系是可以适应共聚的烯属不饱和单体(包括本文中所描述的生物可再生单体,当然它们也可以是在下文所述的酸官能的、可交联的等等)的任意合适组合。

[0208] 优选地,乙烯基聚合物A包含0.5至9重量%、更优选地1至8重量%以及尤其1.5至5重量%的至少一种酸官能烯属不饱和单体。

[0209] 优选地，乙烯基聚合物 B 包含小于 5 重量％的任意酸官能单体，并且优选地小于 2 重量％，而且在一些优选实施方式中根本就不含。

[0210] 可以与酸性单体共聚的其他非酸官能的、非交联的单体包括丙烯酸酯和甲基丙烯酸酯和苯乙烯；还有二烯诸如 1，3- 丁二烯和异戊二烯，乙烯基酯诸如乙酸乙烯酯，和烷酸乙烯酯。甲基丙烯酸酯包括 C1 至 C12 醇与甲基丙烯酸的正常的或支链的烷基酯，例如甲基丙烯酸甲酯、甲基丙烯酸乙酯和甲基丙烯酸正丁酯；以及甲基丙烯酸的（通常 C5 至 C12）环烷基酯，诸如甲基丙烯酸异冰片酯和甲基丙烯酸环己酯。丙烯酸酯包括 C1 至 C12 醇与丙烯酸的正常的和支链的烷基酯，例如丙烯酸甲酯、丙烯酸乙酯和丙烯酸正丁酯和丙烯酸 2- 乙基己酯；以及丙烯酸的（通常 C5-C12）环烷基酯，诸如丙烯酸异冰片酯和丙烯酸环己酯。还包括（甲基）丙烯酰胺以及（甲基）丙烯酸的单烷基酰胺或二烷基酰胺。苯乙烯包括苯乙烯本身以及各种取代的苯乙烯，例如 α - 甲基苯乙烯和叔丁基苯乙烯。也可以聚合腈，诸如丙烯腈和甲基丙烯腈，以及烯属不饱和卤化物诸如氯乙烯、偏二氯乙烯和氟乙烯。

[0211] 赋予可交联性能的官能单体（简称交联单体）包括甲基丙烯酸和丙烯酸的环氧基（通常缩水甘油基）酯和羟烷基（通常 C1-C12，例如羟乙基）酯；以及酮或醛官能单体，例如丙烯醛、甲基丙烯醛和甲基乙烯基甲酮，丙烯酸和甲基丙烯酸羟烷基（通常 C1-C12）酯的乙酰乙酰氧酯，例如甲基丙烯酸乙酰乙酰氧基乙酯和丙烯酸乙酰乙酰氧乙酯；以及含酮的酰胺，例如双丙酮丙烯酰胺。使用这种官能单体的目的是为了在所讨论的获得的聚合物体系中提供随后的可交联性能。原则上，用于赋予可交联性能的官能单体可以是带酸的单体，但这并不常见。

[0212] 优选地，乙烯基聚合物 A 包含 0.1 至 3 重量％的包含至少两个烯属不饱和基团的至少一种交联单体。

[0213] 优选地，乙烯基聚合物 A 包含 0.1 至 20 重量％、优选地 1 至 15 重量％以及具体地 1 至 10 重量％的交联单体。

[0214] 粘附促进单体包括氨基、脲基或 N- 杂环基团。本领域技术人员已知的，这种性质还可以通过亚胺化（即酸基团与亚丙基亚胺的反应）来实现。

[0215] 优选地，乙烯基聚合物 A 包含 0.4 至 6 重量％、更优选地 0.5 至 4 重量％的具有湿粘附促进功能的至少一种烯属不饱和单体。

[0216] 乙烯基聚合物 A 优选地具有 20000 至 6000000g/mol、优选地超过 80000g/mol 和最优选地超过 100000g/mol 的使用 GPC 测定的重均分子量 (M_w)。更优选地，上限不超过 4000000g/mol。

[0217] 乙烯基聚合物 B 优选地具有 20000 至 6000000g/mol、优选地超过 80000g/mol 和最优选地超过 100000g/mol 的使用 GPC 测定的重均分子量 (M_w)。更优选地，上限不超过 4000000g/mol。

[0218] 优选地，乙烯基聚合物 A 具有在 -（负号）20 至 20℃范围内的玻璃化转变温度。

[0219] 优选地，乙烯基聚合物 B 具有在 65 至 110℃范围内的玻璃化转变温度。

[0220] 优选地，聚合物分散体包含直径在 30 至 900 纳米 (nm)、具体地 60 至 300nm 的胶乳颗粒。颗粒尺寸分布可以是单峰、双峰或多峰。具有双峰或多峰颗粒尺寸分布的分散体可以根据 DE3147 008 或 US4456726 中所描述的方法来制备。

[0221] 在一个优选的实施方式中，提供了最低成膜温度小于 30℃的水性聚合物分散体，

其包含衍生自烯属不饱和单体的乙烯基聚合物，具有至少两相，包括：

[0222] A)60 至 80 重量％的玻璃化转变温度在 -20 至 20℃范围内的乙烯基聚合物 A；和

[0223] B)20 至 40 重量％的玻璃化转变温度在 65 至 110℃范围内的乙烯基聚合物 B；

[0224] 其中乙烯基聚合物 A 包含 2 至 5 重量％的至少一种酸官能的烯属不饱和单体，并且

[0225] 其中用于形成乙烯基聚合物 A 和乙烯基聚合物 B 的单体组合物的至少 50 重量％由式 1 的衣康酸二酯构成，优选地由生物可再生来源构成。

[0226] 如果乙烯基聚合物 A 是在第二相中制得的，那么优选地乙烯基聚合物 A 的酸值是在第一相中制得的乙烯基聚合物 B 的酸值的至少 80％、更优选地至少 100％和最优选地 110％，这有助于影响颗粒的形态，以获得良好的成膜性。

[0227] 根据本发明的一个实施方式，也提供了获得本文中所限定的水性聚合物分散体的方法，该方法包括以下步骤：

[0228] a) 第一聚合步骤，以形成第一相乙烯基聚合物；

[0229] b) 在来自步骤 a) 的所获得的第一相乙烯基聚合物存在下的第二聚合步骤，以形成第二相乙烯基聚合物。

[0230] 第一相乙烯基聚合物可以使用乳液聚合来形成。这种方法是极其公知的，描述于本说明书的其他地方，并且不需要进一步详细描述。

[0231] 如果期望的话，可以使用合适的碱将聚合物乳液的 pH 调节到较高的值。合适碱的实例包括有机胺例如三烷基胺（诸如三乙胺、三丁胺）、吗啉和烷醇胺，以及无机碱诸如氨、NaOH、KOH 和 LiOH。

[0232] 在本发明的一个实施方式中，也可以使用例如 EP1434803 中所描述的梯度聚合方法来制备第一相和第二相的至少一部分。第二相单体进料优选地在第一相单体进料完成 20 至 80％之后开始。

[0233] 在一个优选实施方式中，当使用＞ 30 重量％的式 1 的单体（诸如 DBI）时，优选地在聚合时将单体进料到反应器中，优选的进料时间＞ 60 分钟、更优选地＞ 120 分钟以及最优选地＞ 150 分钟。

[0234] 优选地，聚合时根据式 1 的未反应单体的浓度小于乳液总重量的 5 重量％、更优选地小于 3 重量％、最优选地小于 1 重量％、并且典型地小于乳液总重量的 0.5 重量％。聚合时除根据式 1 外的未反应单体的浓度小于乳液总重量的 5 重量％、更优选地小于 2.5 重量％、最优选地小于 1 重量％、并且典型地小于 0.3 重量％。

[0235] 优选地，本发明的分散体具有小于 100g/L、更优选地小于 80g/L、最优选地小于 50g/L 以及尤其小于 20g/L 的挥发性有机组分 (VOC) 诸如聚结溶剂的 VOC 水平。

[0236] 如果存在交联单体，则所采用的交联剂的量优选地使得在第一相乙烯基聚合物和第二相乙烯基聚合物（如果采用的话）中存在的交联基团的数目与交联剂中反应性基团（用于交联目的）的数目的比例在 10/1 至 1/3、优选地 2/1 至 1/1.5 的范围内。

[0237] 如果存在的话，与共聚的交联单体具有反应性的交联剂通常与水性分散体组合，这通过在第二相乙烯基聚合物 A 的制备后（并且有时正好在使用分散体之前）将其加入来实现，尽管原则上也可以通过在交联剂的存在下进行第二相乙烯基聚合物聚合来组合。原则上也可以使用两种掺入方式的组合。

[0238] 可以理解，当与交联剂组合时，乙烯基聚合物A和可选地乙烯基聚合物B具有赋予分散体潜在可交联性能的官能基团（即，使得交联在例如涂料形成之后由它们发生）。例如，一种聚合物或两种聚合物可以携带诸如羟基的官能基团，并且分散体随后与诸如多异氰酸酯、三聚氰胺或甘脲的交联剂一起配制；或者在一种聚合物或两种聚合物上的官能基团可以包括酮羰基或醛羰基，并且在步骤c）中随后配制的交联剂可以是多胺或多酰肼，例如己二酸二酰肼、草酸二酰肼、邻苯二甲酸二酰肼、对苯二甲酸二酰肼、异佛尔酮二胺和4，7-二氧杂癸烷-1，10二胺。需要注意的是，由于形成共价键，这种交联剂会影响交联。

[0239] 根据本发明的一个实施方式，提供了生产水性聚合物涂料分散体的方法，该方法包括以下步骤：a’）第一聚合步骤，以形成第一相乙烯基聚合物；b’）在来自步骤a’）的所获得的第一相乙烯基聚合物的存在下的第二聚合步骤，以形成第二相乙烯基聚合物。可选地，该方法包括c’）在步骤b’）之前、之后或步骤b’）时的中和步骤。可选地，该方法包括使用亚烷基亚胺（诸如亚丙基亚胺）的后处理亚胺化步骤d’），这能够极大地改善湿粘附性。可选地，该方法包括e’）在聚合步骤a’）和/或步骤b’）之后并且优选地在可选的亚胺化步骤d’）之后添加交联剂，所述交联剂能够在随后干燥涂料分散体时与乙烯基聚合物A和/或乙烯基聚合物B的任何交联官能团反应，以实现共价键交联（如本文中所描述）。

[0240] 下文描述本发明的另外一个方面，其包括设计要解决的具体额外问题和/或子问题以及其他现有技术。

[0241] 由于使用挥发性有机溶剂所带来的环境毒性和易燃性问题，一直需要使用水基类似物来替代或补充基于溶剂的聚合物涂料组合物。然而，即使已经设计出了水基聚合物组合物，但是它们的生产通常需要中间使用有机溶剂，这些有机溶剂需要随后去除；或者需要在最终组合物中掺入一定量的溶剂，其作用是确保在涂层中适当成膜，也称为聚结溶剂。因此，现如今存在越来越大的在水基聚合物组合物的合成中显著地减少或消除挥发性有机组分(VOC)的压力，以及还提供生物可再生单体的压力。

[0242] 此外，即使能够获得无溶剂的水性聚合物涂料组合物，也已经发现很难获得具有大多数涂料组合物通常所要求的多个良好性质的平衡，尤其是所获得的涂层的可接受的高硬度和低的最低成膜温度(MFFT)。涂料还应该具有良好的耐水性和耐溶剂性。

[0243] EP0758364公开了制备不含有机溶剂的水性可交联聚合物组合物，其包含具有10至125℃的Tg且具有交联官能基团的酸官能聚合物A以及与交联剂组合的具有至少比聚合物A的Tg低25℃的Tg的聚合物B，该组合物具有MFFT和Koenig硬度的有利平衡。

[0244] EP0758347公开了制备不含有机溶剂的水性可交联聚合物组合物的方法，该组合物包含具有小于50℃的Tg且具有交联官能基团的酸官能聚合物A以及与交联剂组合的具有至少比聚合物A的Tg高25℃的Tg的聚合物B，该组合物具有MFFT和Koenig硬度的有利平衡。

[0245] 上面所讨论的公开文本均没有教导使用单体诸如DBI（可选地来自生物可再生来源）来制备乙烯基聚合物以获得具有本发明中下文所限定的特征与整数(integers)的选定组合的乙烯基聚合物涂料组合物，以及前面所讨论的性质的有利组合。

[0246] 在本发明的这个方面，我们提供了水性乙烯基聚合物涂料组合物，该组合物具有MFFT与硬度的有利组合，此外该组合物至少部分由式1的单体（例如衣康酸二（正丁基）酯(DBI)）、优选地来自生物可再生来源的式1的单体来制备。

[0247] 根据本发明的这个方面，提供了水性乙烯基聚合物涂料组合物，其包含至少：

[0248] α[alpha]) 乙烯基聚合物 C，其包含：

[0249] i) 1 至 45 重量％的酸官能烯属不饱和单体；

[0250] ii) 0 至 20 重量％的交联官能烯属不饱和单体；和

[0251] iii) 99 至 50 重量％的非酸官能、非交联单体，其选自由烯属不饱和单体和芳基芳基烯烃 (aryl arylalkylene) 单体组成的组；

[0252] 其中每个 (α[alpha])(i)、(α[alpha])(ii) 和 (α[alpha])(iii) 的重量百分数是基于 (α[alpha])(i)+(α[alpha])(ii)+(α[alpha])(iii) 的总和 (＝100％) 计算得的；并且其中所述聚合物 C 具有在 1000 至 150000g/mol 范围内的分子量和＞5mgKOH/g 的酸值；和

[0253] (β[beta])) 乙烯基聚合物 D，其包含：

[0254] i) 0 至 10 重量％、优选地小于 25 重量％的至少一种酸官能烯属不饱和单体；

[0255] ii) 0 至 25 重量％、优选地小于 25 重量％的交联官能烯属不饱和单体；和

[0256] iii) 0 至 100 重量％的非酸官能、非交联单体，其选自由除式 1 单体之外的烯属不饱和单体和芳基芳基烯烃单体组成的组；

[0257] β[beta](i) 至 (iii) 中的至少一个是存在的；其中

[0258] 每个 (β[beta])(i)、(β[beta])(ii)、(β[beta])(iii) 和 (β[beta])(iv) 的重量百分数是基于 (β[beta])(i)+(β[beta])(ii)+(β[beta])(iii)+(β[beta])(iv) 的总和 (＝100％) 计算得的；并且其中

[0259] 所述聚合物 D 具有至少 80000g/mol 的分子量 (M_w) (由 GPC 测得) 和小于 65mgKOH/g、优选地小于 50mgKOH/g、更优选地小于 30mgKOH/g、最优选地小于 20mgKOH/g、例如小于 10mgKOH/g 的酸值

[0260] 其中

[0261] I) 当基于 (α[alpha])(i)+(α[alpha])(ii)+(α[alpha])(iii)+(β[beta])(i)+(β[beta])(ii)+(β[beta])(iii)+(β[beta])(iv) 的总量 (＝100％) 计算时，用于形成聚合物 C((α[alpha])(i)、(α[alpha])(ii) 和 (α[alpha])(iii) ＝聚合物 C 单体) 和聚合物 D((β[beta])(i)、(β[beta])(ii)、(β[beta])(iii) 和 (β[beta])(iv) ＝聚合物 D 单体) 的单体的重量％具有如下的重量百分数：

[0262] 对于聚合物 C 单体来说，5 至 75％、优选地 5 至 70％；和

[0263] 对于聚合物 D 单体来说，25％至 95％、优选地 30％至 90％

[0264] II) 用于形成聚合物 C 和聚合物 D 的单体 (α[alpha])(i)+(α[alpha])(ii)+(α[alpha])(iii)+(β[beta])(i)+(β[beta])(ii)+(β[beta])(iii)+(β[beta])(iv) 的总量的 20 至 75 重量％、优选地 24 至 60 重量％包含至少一种式 1 的单体 (例如 DBI)；

[0265] III) 可选地用于形成聚合物 C 和聚合物 D 的单体 (α[alpha])(i)+(α[alpha])(ii)+(α[alpha])(iii)+(β[beta])(i)+(β[beta])(ii)+(β[beta])(iii)+(β[beta])(iv) 的总量的至少 10 重量％、优选地至少 20 重量％衍生自至少一种生物可再生烯属不饱和单体；

[0266] IV) 聚合物 C 的酸值比聚合物 D 的酸值大至少 10mgKOH；

[0267]　V) 聚合物 C 和聚合物 D 具有至少 20℃的玻璃化转变温度差值；

[0268]　VI) 聚合物 C 是在聚合物 D 存在下制备的；

[0269]　VII) 干燥后所述涂料组合物具有至少 20sec 的 Koenig 硬度；并且

[0270]　VII) 所述涂料组合物具有＜ 55℃的最低成膜温度。

[0271]　优选地，聚合物 C 是低聚物并且聚合物 D 是非低聚的聚合物。

[0272]　在本发明的这个方面，特征 (β [beta])(iv) 对应于本发明的组分 (a)；特征 (α [alpha])(i) 和 (β [beta])(i) 对应于本发明的组分 (b)，并且剩余特征 (α [alpha])(ii)、(α [alpha])(iii)、(β [beta])(ii) 和 (β [beta])(iii) 适当地对应于本发明的可选组分 (c) 和 / 或 (d)。

[0273]　本发明的这个方面的其他优选特征在下文中给出和 / 或在权利要求书中给出。

[0274]　酸官能和单体可以选自由丙烯酸、甲基丙烯酸、衣康酸酐、马来酸酐、亚甲基丙二酸、衣康酸、巴豆酸和富马酸以及衣康酸单丁酯组成的组。

[0275]　生物可再生单体可以包含生物可再生 (甲基) 丙烯酸和 / 或生物可再生 (甲基) 甲基丙烯酸烷基酯 (以及可选地式 1 的单体)。

[0276]　生物可再生单体还可以包含生物可再生的：α - 亚甲基丁内酯、α - 亚甲基戊内酯、α - 亚甲基 γ -R^1 丁内酯 (R^1 可以是可选地被取代的烷基或可选地被取代的芳基)；衣康酸酯例如衣康酸二烷基酯和衣康酸单烷基酯，衣康酸，衣康酸酐，巴豆酸及其烷基酯，柠康酸及其烷基酯，亚甲基丙二酸及其单烷基酯和二烷基酯，柠康酸酐，中康酸及其烷基酯。

[0277]　其他合适的生物可再生单体可以包含生物可再生的：N-R^2，α - 亚甲基丁内酰胺 (R^2 可以是可选地被取代的烷基或可选地被取代的芳基)；N-R^2，α - 亚甲基 γ -R^1 丁内酰胺；N- 烷基衣康酰亚胺；衣康单酰胺；衣康二酰胺；二烷基衣康酰胺，单烷基衣康酰胺；(甲基) 丙烯酸糠酯；和脂肪酸官能 (甲基) 丙烯酸酯。

[0278]　聚合物 C 和 / 或聚合物 D 可以包含至少约 1.5dpm/gC 的碳 14。

[0279]　组合物可以额外地包含交联剂，该交联剂能够在随后干燥涂料组合物时与聚合物 C 和 / 或聚合物 D 的任何交联官能基团反应，以实现共价键交联。提供交联的官能基团可以选自由环氧基、羟基、酮基和醛基团组成的组。根据聚合物 C 中和聚合物 D 中的的交联官能团，交联剂也可以选自由多异氰酸酯、三聚氰胺、甘脲、多胺和多酰肼组成的组。

[0280]　基于用来制备乙烯基聚合物 C 和乙烯基聚合物 D 的单体的重量，组合物可以包含小于 2 重量的添加的表面活性剂。

[0281]　组合物可以以小于 100g/L 的量包含挥发性有机化合物 (VOC)，优选地基本上不含 VOC。

[0282]　膜、光泽剂 (polish)、清漆 (varnish)、亮漆 (lacquer)、漆料、墨和 / 或粘合剂可以包含聚合物 C 和聚合物 D 的水性涂料组合物，并且这些水性组合物还可以用作木材、塑料、纸和 / 或金属基材上的保护性涂料。

[0283]　在本发明的一个优选实施方式中，基于单体 α [alpha])iii) 和 β [beta])iii) 的组成，单体 α [alpha])iii) 和 β [beta])iii) 独自包含至少 10 重量％、更优选地至少 20 重量％、最优选地至少 30 重量％以及尤其优选地至少 50 重量％的式 2 化合物，例如衣康酸的低级二酯 (补充高级衣康酸二酯或者替代高级衣康酸二酯诸如 DBI)。尽管在 α [alpha]) iii) 和 β [beta])iii) 中衣康酸酯单体的浓度可以相似，但优选的是浓度不同。在上述的

那些优选情况中的每一种中，衣康酸酯单体在其他相中的浓度优选地为 0 重量％。

[0284] 优选地，聚合物 C 起到用于制备聚合物 D 的（辅助）表面活性剂的作用。

[0285] 优选地，基于用于形成聚合物 C 和聚合物 D 的单体的重量，用于形成聚合物 C 的烯属不饱和单体的浓度为 10 至 65 重量％、更优选地 15 至 60 重量％以及尤其 20 至 55 重量％。

[0286] 优选地，基于用于形成聚合物 C 和聚合物 D 的单体的重量，用于形成聚合物 D 的烯属不饱和单体的浓度为 90 至 35 重量％、更优选地 85 至 40 重量％以及尤其 80 至 45 重量％。

[0287] 用于制备聚合物 C 和聚合物 D 的单体体系是适应共聚的烯属不饱和单体（包括本文中所描述的生物可再生单体，如本文所示，其当然也可以是酸官能的、可交联的等等）的任意合适组合。

[0288] 酸官能烯属不饱和单体（聚合物 C 中所使用的，优选地以足以使所获得聚合物具有表面活性的浓度）可以是携带酸形成基团的单体，该酸形成基团产生或者随后转化为酸官能基团（诸如酸酐，如甲基丙烯酸酐或马来酸酐）或者酸。这种酸官能单体的实例已经在前面作为组分 (b) 给出，并且也可以用于本发明的这个方面中。

[0289] 通常，聚合物 C 包含 1 至 45 重量％、优选地 3 至 30 重量％和更优选地 3 至 20 重量％的酸官能单体。

[0290] 聚合物 C 可以包含聚乙二醇（甲基）丙烯酸酯或者它们的甲醚类似物，它们能够使聚合物 C 具有表面活性。当将这些单体共聚时，可以采用较低的酸浓度，例如聚合物可以包含 1 至 10 重量的酸官能单体 .

[0291] 通常，聚合物 D 包含小于 5 重量％、优选地小于 2 重量％的任意酸官能单体，并且在一些优选实施方式中根本不含。

[0292] 聚合物 D 还可以包含聚乙二醇（甲基）丙烯酸酯或者它们的甲醚类似物，它们可有助于降低所获得的组合物的 MFFT。

[0293] 可以与酸性单体共聚的其他非酸官能、非交联单体包括丙烯酸酯和甲基丙烯酸酯和苯乙烯；也包括二烯，例如 1，3- 丁二烯和异戊二烯，乙烯基酯诸如乙酸乙烯酯，和烷酸乙烯酯。甲基丙烯酸酯包括 C1 至 C12 醇与甲基丙烯酸的正常的或支链的烷基酯，例如甲基丙烯酸甲酯、甲基丙烯酸乙酯和甲基丙烯酸正丁酯；以及甲基丙烯酸（通常 C5 至 C12) 环烷基酯，诸如甲基丙烯酸异冰片酯和甲基丙烯酸环己酯。丙烯酸酯包括 C1 至 C12 醇与丙烯酸的正常的和支链的烷基酯，例如丙烯酸甲酯、丙烯酸乙酯和丙烯酸正丁酯和丙烯酸 2- 乙基已酯；以及丙烯酸（通常 C5-C12) 环烷基酯，诸如丙烯酸异冰片酯和丙烯酸环己酯。还包括（甲基）丙烯酰胺以及（甲基）丙烯酸的单烷基酰胺或二烷基酰胺。苯乙烯包括苯乙烯本身以及各种取代的苯乙烯，例如 α－甲基苯乙烯和叔丁基苯乙烯。也可以聚合腈，诸如丙烯腈和甲基丙烯腈，以及烯属不饱和卤化物诸如氯乙烯、偏二氯乙烯和氟乙烯，以及（甲基）丙烯酰胺。

[0294] 通常，聚合物 C 包含 98.5 至 50 重量％、优选地 96 至 65 重量％以及更优选地 96 至 75 重量％的非酸官能、非交联单体。

[0295] 赋予可交联性能的官能单体（简称交联单体）包括甲基丙烯酸和丙烯酸的环氧基（通常缩水甘油基）酯和羟烷基（通常 C1-C12，例如羟乙基）酯；以及酮或醛官能单体，例

如丙烯醛、甲基丙烯醛和甲基乙烯基甲酮；丙烯酸和甲基丙烯酸羟烷基（通常C1-C12）酯的乙酰乙酰氧基酯，例如甲基丙烯酸乙酰乙酰氧基乙酯和丙烯酸乙酰乙酰氧基乙酯；以及含酮的酰胺，例如双丙酮丙烯酰胺。使用这种官能单体的目的是在所讨论的获得的聚合物体系中提供随后的可交联性能。原则上，用于赋予可交联性能的官能单体可以是携带酸的单体，但这并不常见，因此出于本发明的目的，酸官能单体不认为是可交联的单体，尽管它们可以起到这样的作用。

[0296] 优选地，聚合物C包含0.5至25重量％、更优选地0.5至25重量％、最优选地1至15重量％以及尤其1至10重量％的交联单体。

[0297] 优选地，聚合物C具有1500至100000g/mol、更优选地2000至50000g/mol以及具体地3000至40000g/mol的使用GPC测定的重均分子量(M_w)。

[0298] 使用GPC测定的聚合物D的重均分子量(M_w)优选地为大于100000g/mol以及最优选地大于150000g/mol。上限通常不超过5000000g/mol。

[0299] 优选地，聚合物C的重均分子量(Mw)小于聚合物D的重均分子量(Mw)，并且最优选地存在至少30000g/mol、尤其至少50000g/mol并且通常至少100000g/mol的分子量差值。

[0300] 优选地，在聚合物C与聚合物D之间的Tg的差值（表示为摄氏度）为至少40度以及更优选地至少60度。

[0301] 在本发明的这个方面的一个实施方式中，聚合物C的Tg比聚合物D的Tg高。在这个实施方式中，聚合物C的优选的Tg为50至125℃并且具体地70至125℃。那么，聚合物C的Tg应当比聚合物D的Tg高至少20度、更优选地高至少40度（均表示为摄氏度）。优选地，在该实施方式中，聚合物D的Tg为-（负）50至40℃且更优选地-（负）30至30℃且尤其-（负）20至30℃。

[0302] 在本发明的另一个实施方式中，聚合物C的Tg比聚合物D的Tg低。在该实施方式中，聚合物C的优选的Tg为小于50℃且更优选地为-（负）15至49℃。优选地，在该实施方式中，聚合物D的Tg为50至125℃并且具体地70至125℃。

[0303] 可以使用多种方法来形成聚合物C。这些方法包括乳液聚合、悬浮聚合、本体聚合和溶液聚合。这些方法都是极其公知的，且描述于本说明书其他地方，并且不需要进一步详细地描述。

[0304] 在另一个实施方式中，聚合物C是经由本体聚合方法制备的。烯属不饱和单体的本体聚合详细描述于EP 0156170、WO 82/02387和US 4414370。

[0305] 通常，在本体聚合方法中，将两种或更多种单体的混合物连续加入到包含熔融的乙烯基聚合物的反应器区域中，该乙烯基聚合物具有与单体混合物相同比例的乙烯基单体。将熔融的混合物保持在预定的温度下，以提供具有所期望分子量的乙烯基聚合物。以与将单体加入到反应区域的速度相同的速度，将产物从反应区域泵出，从而在体系中提供固定水平的乙烯基单体和乙烯基聚合物。所选择的具体流速取决于反应温度、乙烯基单体、所期望的分子量和所期望的多分散性。

[0306] 根据被装入到反应器中的具体单体，可以改变最低反应温度。为了获得本发明中使用的具有期望的分子量的聚合物C，反应温度优选地维持在约135℃至约310℃、更优选地约150℃至275℃。可以使用常规的产生自由基的引发剂，并且可选地可以添加链转移剂

来控制分子量。

[0307]　或者，可以通过悬浮或微悬浮聚合的手段来制备聚合物 C。在这种方法中，将单体和水引入到聚合反应器中，并且添加聚合引发剂以及其他化学添加剂来引发聚合反应。不断地混合反应容器的内容物，来维持悬浮并确保所获得的聚合物的颗粒尺寸均匀。

[0308]　还可以通过溶液分散体聚合或溶剂辅助分散体聚合 (SAD) 方法来制备聚合物 C，其中该聚合方法能够在有机溶剂存在下进行。可以使用的典型的有机溶剂包括芳香烃诸如苯、甲苯和二甲苯；醚类诸如二乙醚、四氢呋喃、烷氧基化的乙二醇；醇类诸如甲醇、乙醇、丙醇、丁醇和具有至少六个碳的醇如辛醇，以及它们与羧酸的酯，所述羧酸诸如乙酸、丙酸和丁酸；酮类诸如丙酮或甲基乙基甲酮；以及液体叔胺诸如吡啶。也可以使用溶剂的混合物。典型的溶剂当然会包括烷基二醇，诸如丁基二醇或二丙二醇二甲醚 (Dowanol DMM) 或二丙二醇甲醚 (Dowanol DPM)。经常使用的芳族溶剂的实例为 Solvesso 100。优选地，使用生物可再生溶剂（例如可从 Liberty Chemicals 获得的）。

[0309]　通常，反应温度为大约 140℃至 160℃，并且也可以在高温下进行，以使可以使用较低沸点的溶剂。较低沸点的溶剂的一个优点是，它们能够更容易地去除，从而制得低 VOC 水性组合物。

[0310]　优选地，本发明的组合物具有小于 100g/L、更优选地小于 80g/L、最优选地小于 50g/L 以及尤其小于 20g/L 的挥发性有机组分（诸如聚结溶剂）的 VOC 水平。

[0311]　一旦制得了聚合物 C，就在聚合物 C 的存在下制备聚合物 D，并且在制备聚合物 D 之前、之时或之后通过其他方式增溶聚合物 C，来制备水性组合物。聚合物 C 可以起到聚合物 D 的（辅助）乳化剂的作用，没有聚合物 C，聚合物 D 就不能充分分散于本发明的的水性组合物中。“（辅助）乳化剂”指的是，尽管聚合物 C 起到乳化剂的作用，但也可以添加其他乳化剂。

[0312]　因此，聚合物 C 包含足够浓度的酸官能团或足够高浓度的聚乙二醇（甲基）丙烯酸酯，来使聚合物部分地或者更优选地完全溶解于水性介质中，如果必要的话，通过中和聚合物的酸基团，这例如可以通过调节水性介质的 pH 来实现。（如果酸官能聚合物 C 仅部分溶解于乳液的水性介质中，其中就会存在部分分散和部分不溶）。通常，在其中能找到聚合物 C 本身的介质将是酸性的 ($pH < 7$)，并且酸性基团会是羧基，结果可以通过添加碱来提高介质（通常为其中已经制得聚合物 C 的水性聚合介质）的 pH 从而影响溶解和表面活性，其中通过添加碱来提高 pH 是为了中和酸性基团，所述碱例如有机碱或无机碱，其实例包括有机胺例如三烷基胺（诸如三乙胺、三丁胺）、吗啉和烷醇胺，以及无机碱诸如氨、NaOH、KOH 和 LiOH。当然，包含酸官能聚合物 A 的水性介质可以已经是碱性的（或者足够碱性的），结果酸性基团（诸如羧基）被中和，而不需要主动添加碱来提高 pH，或者酸性基团可以是或包含非常强的酸性基团诸如磺酸基 (pKa 1 至 2)，结果不需要中和来实现溶解。而且进一步，对于待聚合的酸性单体来说，可以是盐形式的，而非游离酸。

[0313]　聚合物 C 的溶解优选地是在进行步骤 b’）的聚合之前实现的，因为这样会产生具有 MFFT 和 Koenig 硬度的改善的平衡的产物。

[0314]　在制备聚合物 D 的聚合过程中存在聚合物 C。可以使用多种方法来形成聚合物 D。这些方法包括乳液聚合、本体聚合和溶液聚合。

[0315]　本发明的这个方面的优选特点是，通常可以消除或大大减小添加表面活性剂作为

制备聚合物D的乳化剂的要求，因为聚合物C本身就能够实现了这个功能（即起到了乳化试剂的作用）。因此，本发明的水性组合物优选地包含非常低水平的这种添加的乳化剂（不包括聚合物C本身），其中基于所使用的添加的单体的总重量，通常小于0.5％（优选地小于0.25％以及通常为零），并且优选地存在的唯一的表面活性剂为聚合物C聚合所剩余的那些（不包括聚合物C本身）。事实上，基于所添加的用于聚合物D的单体的总重量，表面活性剂（不包括聚合物C本身）的总水平为优选地＜1％、更优选地＜0.5％、具体地＜0.35％。

[0316] 可以使用链转移剂进行用于制备聚合物D的聚合，但（不像聚合物C的制备）该聚合通常是在不使用这种材料的情况下进行的，从而确保较高的分子量。

[0317] 聚合物D可以被认为是疏水性聚合物，这种类型的聚合物是本领域技术人员所公知的。一般来说，在本文中其被认为是不溶于水的聚合物，其在整个pH范围内保持水不溶性。聚合物的疏水性质是由于聚合物包含足够浓度的至少一种疏水单体（即以聚合形式）来实现的，这样使得聚合物在整个pH范围内疏水性和水不溶性。

[0318] 聚合物D还可以包含0.5至25重量％、更优选地0.5至20重量％、最优选地1至12重量％、尤其1至8重量％、例如1至5重量％的一种或多种交联多官能（甲基）丙烯酸酯单体。一般来说，可以理解，考虑到聚合物C和D的各自性质，对于给定体系来说，在聚合物C中所使用的多官能（甲基）丙烯酸酯交联单体的量更可能小于在聚合物D中所使用的量。

[0319] 可以理解，聚合物C和可选地聚合物D拥有具有以下性质的官能基团：当与交联剂（如本文其他地方所描述）组合时该官能基团赋予组合物潜在的可交联性能（即，使得交联在涂层形成之后由其进行）。

[0320] 如果存在交联单体，则所采用的交联剂的量优选地使得存在于聚合物C中和聚合物D（如果采用的话）中的交联基团的数目与交联剂中反应性基团（用于交联目的）的数目的比例在10/1至1/3、优选地2/1至1/1.5的范围内。

[0321] 如本文其他地方所描述，本发明的这个方面的聚合物还可以被亚胺化。

[0322] 通常通过在制备聚合物D后（有时正好在使用组合物之前）向水性组合物添加交联剂，来使交联剂与水性组合物结合，尽管原则上也可以在交联剂的存在下进行聚合物D的聚合来结合。原则上，也可以使用两种掺入方式的组合。

[0323] 根据本发明的一个实施方式，提供了水性聚合物涂料组合物，其包含至少：

[0324] α(alpha)）乙烯基聚合物C，其包含：

[0325] i)4至25重量％的酸官能烯属不饱和单体；

[0326] ii)0至15重量％的交联不饱和单体；

[0327] iii)96至60重量％的非酸官能、非交联烯属不饱和单体；所述聚合物C是通过乳液聚合方法获得的并且具有在3000至65000g/mol范围内的分子量、至少50℃的Tg和＞20mgKOH/g的酸值；以及

[0328] β(beta)）乙烯基聚合物D，其在经中和的聚合物C的存在下制得，并且其包含：

[0329] i)0至4重量％、更优选地0重量％的酸官能烯属不饱和单体；

[0330] ii)0至12重量％、更优选地1至8重量％的交联官能烯属不饱和单体；和

[0331] iii)100至84重量％的非酸官能、非交联烯属不饱和单体；

[0332] 其中聚合物D具有至少80000g/mol的分子量和小于50℃的Tg；并且

[0333] 其中基于聚合物C和聚合物D的总重量，聚合物C的重量％为10至60、更优选地20至50重量％；并且

[0334] 其中聚合物C和聚合物D组合包含至少30重量％的式1的衣康酸二酯单体。

[0335] 基于用来形成聚合物C和聚合物D的烯属不饱和单体的总重量，用来形成聚合物C的烯属不饱和单体的重量％在10至60、更优选地20至50重量％的范围内。

[0336] 根据本发明的一个实施方式，提供了用于生产水性聚合物涂料组合物的方法，该方法包括以下步骤：

[0337] 1）第一聚合步骤，以形成聚合物C；

[0338] 2）在来自步骤1）的所获得的聚合物C的存在下的第二聚合步骤，以形成聚合物D；

[0339] 3）在步骤2）之前、之后或者之时的中和步骤，以使聚合物D溶解；

[0340] 4）使用亚烷基亚胺来使（部分）酸基团亚胺化的可选步骤

[0341] 5）在聚合步骤a）和／或步骤2）之后可选地添加交联剂，所述交联剂能够在随后干燥涂料组合物时与聚合物C和／或聚合物D的任何交联官能基团反应，以实现共价键交联。

[0342] 在一个优选的实施方式中，聚合物C中的酸官能单体选自丙烯酸；甲基丙烯酸，巴豆酸，衣康酸酐和衣康酸；在聚合物C和聚合物D二者中使用的交联官能单体为双丙酮丙烯酰胺，并且交联剂是己二酸二酰肼。

[0343] 根据本发明的另一个实施方式，提供了生产水性聚合物涂料组合物的方法，该方法包括以下步骤：

[0344] 1）通过乳液聚合方法制备乙烯基聚合物C，

[0345] 2）随后的中和步骤；以及

[0346] 3）随后，在聚合物C的存在下通过聚合来制备聚合物D；

[0347] 其中，乙烯基聚合物C和乙烯基聚合物D二者均包含至少一种羰基官能烯属不饱和单体；

[0348] 其中乙烯基聚合物C的酸值在30和110mgKOH/g之间，并且乙烯基聚合物D的酸值小于10mgKOH/g、更优选地小于5mgKOH/g；并且其中交联剂是脂族二酰肼。

[0349] 根据本发明的另外一个实施方式，提供了用于生产水性聚合物涂料组合物的方法，其中该方法包括以下步骤：

[0350] 1）通过本体聚合方法、更优选地通过连续的本体聚合方法制备聚合物C，

[0351] 2）将聚合物C分散于水中并且（部分地）中和，优选地使用有机胺或NaOH、KOH或LiOH中和；以及

[0352] 3）随后，在水性介质中在经中和的聚合物C的存在下通过聚合制备聚合物D；

[0353] 其中乙烯基聚合物C的酸值为40至300mgKOH/g的固体聚合物；

[0354] 其中聚合物C具有至少70℃且更优选地至少90℃的Tg；并且

[0355] 其中聚合物C具有2000至25000g/mol的范围内的分子量。

[0356] 根据本发明的另外一个实施方式，提供了用于生产水性聚合物涂料组合物的方法，其中该方法包括以下步骤：

[0357] 1) 通过溶液聚合制备聚合物 C，优选地在选自由丙酮、甲基乙基甲酮、乙醇、异丙醇或其混合物组成的溶液中进行；

[0358] 2) 随后的中和步骤，包括使用碱（优选地有机胺）中和至少部分的酸性基团，添加水并使聚合物 C 乳化；

[0359] 3) 随后，在聚合物 C 的存在下通过乳液聚合制备聚合物 D；

[0360] 4) 通过蒸发去除溶剂；

[0361] 其中聚合物 C 具有至少 50℃的 Tg，

[0362] 其中聚合物 D 不超过 50℃的 Tg，并且

[0363] 其中聚合物 C 和聚合物 D 具有至少 25℃的玻璃化转变温度差值。

[0364] 在另外一个实施方式中，提供了根据本发明的该方面的水性共聚物组合物，其中聚合物 D 包含 0.1 至 1.5 重量％的多不饱和单体、优选地二乙烯基苯。

[0365] 优选的是，存在于组合物中的大多数高级衣康酸酯被用于制备聚合物 D，而非聚合物 C。因此，在另外还有一个实施方式中，提供了根据本发明的该方面的水性共聚物组合物，其中聚合物 D 包含存在于总共聚物组合物中的全部根据式 1 的衣康酸单体的至少 50 重量％、更优选地至少 75 重量％，并且聚合物 C 包含存在于总共聚物组合物中的全部根据式 1 的衣康酸单体的不超过 50 重量％、更优选地不超过 25 重量％的。

[0366] 优选地，本发明的水性组合物的平均颗粒尺寸为 70 至 140nm。

[0367] 本发明的水性组合物的固体含量通常在基于总重量的约 20 至 65 重量％的范围内、更优选地 30 至 50 重量％。如果期望的话，可以通过添加水或去除水（例如通过蒸馏或超滤）来调节固体含量。

[0368] 下面描述本发明的另一个方面，包括设计要解决的具体额外问题和 / 或子问题。

[0369] 本发明涉及乙烯基聚合物珠粒，其包含至少 20 重量％（优选地至少 30 重量％）的式 1 的单体（有用地 DBI），优选地来自生物可再生来源，并且涉及这种乙烯基聚合物珠粒及其制备方法和它们在涂料、墨和粘合剂中的用途。

[0370] 使用乳液聚合技术制备的乙烯基聚合物使得可以良好地控制关键的聚合物参数，诸如分子量、nm（纳米）范围内颗粒尺寸（通常 50-300nm）和残余单体含量。然而，在乳液聚合中获得极少微米级尺寸的颗粒。由于小颗粒尺寸，所以经干燥的乳液乙烯基聚合物具有与经干燥的通过悬浮聚合能够获得的乙烯基聚合物珠粒相比大得多的粉尘化 (dusting) 倾向。另一方面，用来避免粉尘化问题的聚合物乳液本身需要被保存以防止细菌或真菌生长。

[0371] 通过珠型悬浮聚合能够解决干燥乳液聚合物的粉尘化问题，珠型悬浮聚合是一种公知的聚合方法，其中以微米级尺寸的球形珠粒或珠状物的形式来获得所形成的聚合物。即使水溶性副产物可以使用固定的水相在最后的脱水和洗涤循环中去除，水不溶性副产物（诸如具体地未反应的单体）停留在聚合物珠粒中，并导致独特的臭气、玻璃化转变温度 (Tg) 降低以及毒理学问题，尤其是当单体取自乙基酸 / 甲基乙烯基酸及其酯时。

[0372] 本发明的这个方面的一个目的是解决现有技术中存在的（例如本文中所指出的）一些或所有问题或缺点。

[0373] 与本发明有关的术语“聚合物珠粒”表示例如通过过滤或离心简易分离的聚合物颗粒。与本发明有关的聚合物珠粒是微米级尺寸的，例如通常具有至少 50μm（微米）、优选

地至少 150μm（微米）的平均直径。通常，珠粒的平均直径为 50 至 1500μm 之间、更优选地 150 至 600μm（微米）之间。

[0374] 本文中使用时，术语“微米级尺寸的”是指，物体的至少一个线性维度具有约 0.1μm（$1\mu m$ ＝一微米＝ $1x\ 10^{-6}m$）至约 2000μm 的平均尺寸。本文中所描述的微米级尺寸的材料的优选的平均尺寸小于约 1000μm（微米）、更优选地小于约 600μm（微米）、最优选地小于约 500μm（微米）、例如小于约 200μm（微米）。微米级尺寸的材料在三个维度（微型颗粒）、两个维度（具有微尺寸横截面但长度不确定的微管）或者一个维度上（具有微尺寸的厚度但面积不确定的微层）以微米尺寸存在。有益地，本发明的涉及包含微米颗粒的材料。本文中所给出的颗粒尺寸值可以通过 Coulter LS230 颗粒尺寸分析仪（激光衍射）测定并且是体积平均。颗粒尺寸被引述为线性尺寸，其可以是体积与所测量的体积平均值相同的近似球形的直径。

[0375] 这种乙烯基聚合物珠粒广泛用于涂料（例如道路标记、船舶涂层）、粘合剂、着色剂、照相应用、墨、粉末涂料或塑料填料的领域中，如果残余单体含量足够低的话，甚至应用于个人护理产品中。珠粒可用于液体介质中，该液体介质可以是水基的或溶剂基的。优选地，如果使用溶剂，则使用生物可再生溶剂。生物可再生溶剂包括例如生物醇、二甲苯、乙酸丁酯、乙酸乙酯、乳酸乙酯以及可以从 Liberty Chemicals 获得的 VertecBio™ 溶剂。

[0376] 乙烯基聚合物珠粒的制备是公知的，并且描述于例如 EP739359 和 US4463032 中，其中 EP739359 公开了钴螯合物用于 Mw 控制的用途，US4463032 公开了通常通过珠粒（悬浮）聚合方法生产的以珠粒形式的聚合物，使用珠粒（悬浮）聚合方法通过机械作用（搅拌）将单体（分散相）分散于非溶剂（连续相）中并以该形式聚合。

[0377] 因此，本发明的这个方面提供了用于制备乙烯基聚合物珠粒的方法，该乙烯基聚合物珠粒具有在 3000 至 500000g/mol 范围内的分子量和 30℃至 175℃范围内的玻璃化转变温度以及小于 150mgKOH/g、优选地 0 至 100mgKOH/g 的酸值；所述方法包括使用自由基引发剂的烯属不饱和单体的水性悬浮聚合，其中至少 20 重量％的所使用的烯属不饱和单体包含至少一种式 1 的单体（优选地衣康酸二（正丁基）酯 (DBI)）、更优选地衍生自生物可再生来源的式 1 的单体。

[0378] 式 1 的单体对应于本发明方法的组分 (a)，为实现所期望的 AV 而使用的酸官能单体对应于本发明的组分 (b)；并且可以使用的剩余单体适当地对应于本发明方法的可选组分 (c) 和／或 (d)。

[0379] 本发明的这个方面的其他优选特征在下文中给出和／或在权利要求书中给出。

[0380] 在本文中所述的用于制备乙烯基聚合物珠粒的方法中，烯属不饱和单体是生物可再生的并且还包含至少一种选自由生物可再生的（甲基）丙烯酸和／或生物可再生的（甲基）丙烯酸烷基酯组成的组的单体。

[0381] 优选的生物可再生单体选自由以下生物可再生的物质组成的组，所述生物可再生的物质为：α－亚甲基丁内酯、α－亚甲基戊内酯、α－亚甲基 γ-R^1 丁内酯 (R^1 可以是可选地被取代的烷基或可选地被取代的芳基）；衣康酸酯例如衣康酸二烷基酯和衣康酸单烷基酯，衣康酸，衣康酸酐，巴豆酸及其烷基酯，柠康酸及其烷基酯，马来酸酐，亚甲基丙二酸及其单烷基酯和二烷基酯，柠康酸酐，中康酸及其烷基酯。

[0382] 更优选的生物可再生单体选自由以下生物可再生的物质组成的组，所述生

物可再生的物质为：N-R^2，α－亚甲基丁内酰胺（R^2 可以是可选地被取代的烷基或可选地被取代的芳基）；N-R^2，α－亚甲基 γ-R^1 丁内酰胺；N- 烷基衣康酰亚胺；衣康单酰胺（itaconmonoamids）；衣康二酰胺（itacondiamids）；二烷基衣康酰胺（ialkyl itaconamides），单烷基衣康酰胺（mono alkyl itaconamides）；（甲基）丙烯酸糠酯（furfuryl(meth)acrylate）；和脂肪酸官能（甲基）丙烯酸酯。

[0383] 上述方法还可以包括分离珠粒，然后在 40 至 100℃下干燥步骤，可选地进行 3 至 40 小时的时间。

[0384] 通过这种方法获得和／或能够获得的乙烯基聚合物珠粒构成了本发明的另一个方面。

[0385] 本发明的乙烯基聚合物珠粒和／或构成该珠粒的共聚物额外地具有一个或多个下述优选性质：

[0386] 包含至少约 1.5dpm/gC 的碳 -14

[0387] 具有 0 至 20mgKOH/g 的酸值（AV）、更优选地在一个实施方式中具有 45 至 65mg KOH/g 的酸值（AV）或在另外一个实施方式中具有 100 至 150mg KOH/g 的酸值（AV）。

[0388] 本发明的另外一个方面提供了包含本发明的乙烯基聚合物珠粒和载体的组合物。

[0389] 本发明的另一个方面提供了使用包含乙烯珠粒的组合物涂布基材表面的方法，该方法包括将该组合物涂覆到表面上，然后将组合物干燥的步骤。合适的基材可以选自由路面（tarmac）、木材、塑料、金属和纸组成的组。

[0390] 包含本发明的乙烯基聚合物珠粒的组合物可以用作涂料组合物中的生物可再生液体介质。

[0391] 分散相的重量与连续相的重量的相对比例可以为 10/90 至 50/50 且更优选地 30/70 至 45/55。

[0392] 在另一个实施方式中，本发明涉及通过根据本发明这个方面的方法能够获得的乙烯基聚合物珠粒。具体地，根据本发明的乙烯基聚合物珠粒具有小于 2500ppm 和更优选地小于 1000ppm 的残余单体含量。

[0393] 如实施例中所示，根据本发明的乙烯基聚合物珠粒是通过本领域中已知方法的悬浮聚合（由于所获得的聚合物颗粒的形状，其也被称为颗粒聚合、珠粒聚合或珠状聚合）制备的。

[0394] 使单体聚合以提供本发明的乙烯基聚合物珠粒的引发剂是通常适用于丙烯酸酯单体的自由基聚合的那些，并且是油溶性的且在水中具有低溶解度，例如有机过氧化物、有机过氧酯和有机偶氮引发剂。引发剂通常以基于总单体含量的约 0.1 至 2 重量％的量使用。

[0395] 可用的链转移剂包括巯基酸及其烷基酯、四溴化碳、它们的混合物以及钴螯合物。十二烷基硫醇是优选的。巯基链转移剂通常以基于总单体含量的约 0.01 至 3.0 重量％的量、优选地 0.1 至 2 重量％的量使用。所使用的典型钴螯合物水平范围为 1 至 200ppm 且更优选地 10 至 100ppm。

[0396] 可选地，可以添加水溶性抑制剂来抑制水相中的聚合，从而防止在水相中通过乳液聚合和／或溶液聚合而形成过多聚合物，形成过多聚合物会导致珠粒凝聚（agglomeration）或乳液型聚合。合适的抑制剂包括选自硫代硫酸盐／酯、硫氰酸盐／酯、水溶性氢醌和亚硝酸盐的那些。当使用时，水溶性抑制剂通常可以以基于 100 份总单体含

量的约 0.01 至约 1 重量份的量添加。

[0397] 此外，需要水溶性或水可分散性聚合稳定剂来使悬浮液稳定，并获得稳定的珠粒。稳定剂优选地是合成的水溶性或水可分散性聚合物，例如聚乙烯醇、明胶、淀粉、甲基纤维素、羧甲基纤维素、羟乙基纤维素、聚（甲基）乙烯基酸和它们的钠盐以及类似物。稳定剂优选地以基于总单体含量的约 0.001 至 10 重量%、更优选地以约 0.01 至 1 重量%的量使用。

[0398] 可选地使用其他添加剂，例如一价、二价和三价金属盐、硼砂、尿素、乙二醛和脲甲醛树脂。也可以使用生物杀灭剂（包括杀菌剂和杀真菌剂），从而防止在成品中的微生物生长以及其在水基体系中使用时的微生物生长。

[0399] 可以以预定的比例将单体、自由基引发剂和任何可选的材料混合在一起，来形成预混物。可以将稳定剂与水组合，然后再与预混物组合，从而形成水包油型悬浮液。所获得的悬浮液通常包含约 10 至约 50 重量百分比的单体预混物和约 90 至约 50 重量百分比的水相。典型地，按照本发明的珠粒型悬浮聚合是热引发的聚合，并且优选地在搅拌下在约 40℃至 90℃温度下进行约 2 至 16 小时。

[0400] 在根据标准方法（诸如过滤或离心）分离珠粒后，优选地将珠粒进行延长的干燥，优选地在约 40 至 100℃下进行，取决于最终聚合物组合物的实际 Tg。干燥可以通过本领域技术人员所公知的手段进行，例如采用流化床干燥机或传统的烘箱。干燥时间可以容易地被本领域技术人员调节，并且通常进行约 3 至约 40 小时、更通常 8 至 20 小时且具体地 8 至 10 小时的时间段。

[0401] 在一个优选的实施方式中，本发明方法还包括乙烯基聚合物珠粒的分离，然后在 40 至 100℃、更优选地 80 至 100℃下干燥的步骤。

[0402] 除了式 1 的单体（诸如高级衣康酸酯，如 DBI）外，可用于制备本发明的共聚物的其他单体包括：

[0403] 属于普通甲基丙烯酸酯分类的不饱和单体，例如 C_{1-30} 烷基酯，而无论其官能度；

[0404] 属于普通丙烯酸酯分类的不饱和单体，如 C_{1-30} 烷基酯，而无论其官能度；不饱和烃单体，如丁二烯、异戊二烯、苯乙烯、乙烯基甲苯、α-甲基苯乙稀、叔丁基苯乙稀等等；

[0405] 属于卤乙烯、乙烯基酯、乙烯基醚分类的不饱和单体；

[0406] 多烯基不饱和单体，如邻苯二甲酸二烯丙酯、甲基丙烯酸烯丙酯；和/或

[0407] 属于任何前面提到的类型的任意多不饱和单体。

[0408] 优选地，非式 1 的单体也是由生物可再生来源获得的。

[0409] 本发明的珠粒的改善的性质可以包括耐热性、胶体稳定性、颜料相容性、表面活性、耐粘连性和低 MFFT，取决于所使用的单体。

[0410] 除了式 1 的那些单体外，用于制备乙烯基聚合物珠粒的单体体系可以包含适应共聚的烯属不饱和单体（包括本文中所描述的生物可再生单体，当然在下文中也可以是酸官能的、可交联的等等）的任意合适组合。

[0411] 酸官能烯属不饱和单体包括携带酸形成基团的单体，该酸形成基团产生或者随后转化为酸官能基团（诸如酸酐，如甲基丙烯酸酐或马来酸酐）。这种酸官能单体的实例已经在前面作为组分 (b) 给出，并且也可以用于本发明的这个方面中。

[0412] 可以与酸性单体共聚的其他非酸官能、非交联单体包括丙烯酸酯和甲基丙烯酸酯

和苯乙烯；还有二烯诸如1,3-丁二烯和异戊二烯，乙烯基酯诸如乙酸乙烯酯，和烷酸乙烯酯。甲基丙烯酸酯包括C1至C12醇与甲基丙烯酸的正常的或支链的烷基酯，例如甲基丙烯酸甲酯、甲基丙烯酸乙酯和甲基丙烯酸正丁酯；以及甲基丙烯酸（通常C5至C12）环烷基酯，诸如甲基丙烯酸异冰片酯和甲基丙烯酸环己酯。丙烯酸酯包括C1至C12醇与丙烯酸的正常的和支链的烷基酯，例如丙烯酸甲酯、丙烯酸乙酯和丙烯酸正丁酯和丙烯酸2-乙基己酯；以及丙烯酸（通常C5-C12）环烷基酯，诸如丙烯酸异冰片酯和丙烯酸环己酯。苯乙烯包括苯乙烯本身以及各种取代的苯乙烯，例如α-甲基苯乙烯和叔丁基苯乙烯。也可以聚合腈，诸如丙烯腈和甲基丙烯腈，以及烯属不饱和卤化物诸如氯乙烯、偏二氯乙烯和氟乙烯。

[0413] 赋予可交联性能的官能单体（简称交联单体）包括甲基丙烯酸和丙烯酸的环氧基（通常缩水甘油基）酯和羟烷基（通常C1-C12，例如羟乙基）酯；以及酮或醛官能单体，例如丙烯醛、甲基丙烯醛和甲基乙烯基甲酮，丙烯酸和甲基丙烯酸羟烷基（通常C1-C12）酯的乙酰乙酰氧基酯，例如甲基丙烯酸乙酰乙酰氧基乙酯和丙烯酸乙酰乙酰氧基乙酯；以及含酮的酰胺，例如双丙酮丙烯酰胺。使用这种官能单体的目的是在所讨论的获得的聚合物体系中提供随后的可交联性能。（原则上，用于赋予可交联性能的官能单体可以是携带酸的单体，但这并不常见）而且，出于本发明的目的，携带酸的单体不认为是交联单体。

[0414] 在本发明的一个尤其优选的实施方式中，提供了经由悬浮聚合制备的乙烯基共聚物，其包含基于总共聚物组合物的至少10重量％的衣康酸单酯或二酯（除DBI外）。更优选地，衣康酸单酯或二酯的总含量（包括DBI）为至少20重量％、更优选地25重量％、甚至更优选地至少30重量％、最优选地至少40重量％以及尤其优选地至少50重量％。

[0415] 根据本发明所制备的乙烯基聚合物珠粒优选地具有在优选地5000至100000g/mol范围内的分子量。

[0416] 根据本发明所制备的乙烯基聚合物珠粒优选地具有在35℃至150℃范围内且更优选地在50℃至115℃范围内的玻璃化转变温度。

[0417] 根据本发明所制备的乙烯基聚合物珠粒优选地具有约50至500μm（微米）、更优选地200至500μm（微米）的平均颗粒尺寸。

[0418] 在一个实施方式中，根据本发明所制备的乙烯基聚合物珠粒优选地具有0至20mgKOH/g的酸值。

[0419] 本发明的乙烯基聚合物珠粒不仅可以用于涂料组合物，而且可以用于印刷组合物和/或个人护理组合物中。

[0420] 在另一个实施方式中，当用于印刷组合物时，根据本发明所制备的乙烯基聚合物珠粒优选地具有45至65mgKOH/g的酸值。

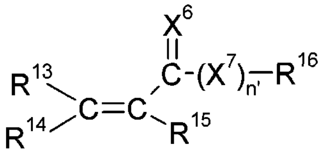
[0421] 在另一个实施方式中，当用于个人护理组合物时，根据本发明所制备的乙烯基聚合物珠粒优选地具有100至150mgKOH/g的酸值。

[0422] 本文中使用时，术语“经活化的不饱和片段”用来表示包含在化学上邻近至少一个活化片段的至少一个不饱和碳-碳双键的物质（species）。优选地，该活化片段包含任何这样的基团，该基团通过稳定的亲电子基团来活化用于在其上加成的烯属不饱和双键。适宜地，活化片段包括氧代、硫代、（任选地有机取代的）氨基、硫代羰基和/或羰基基团（后面的两个基团任选地被硫、氧或（任选地有机取代的）氨基取代）。更适宜的活化片段是（硫代）醚、（硫代）酯和/或（硫代）酰胺片段。最适宜的“经活化的不饱和片段”包含“不

饱和酯片段”,其表示这样的有机物质,这种有机物质包含一个或多个“亚烃烯基(硫代)羰基(硫代)氧基”(hydrocarbylidenyl(thio)carbonyl(thio)oxy)和/或一个或多个“亚烃烯基(硫代)羰基(有机)氨基”(hydrocarbylidenyl(thio)carbonyl(organo)amino)基团和/或类似物和/或衍生的片段,例如包含(甲基)丙烯酸酯官能基团和/或其衍生物的片段。“不饱和酯片段”可以任选地包含可选地被取代的常用 α,β-不饱和酸、酯和/或它们的其他衍生物,包括其硫代衍生物和类似物。

[0423] 优选的经活化的不饱和片段是由式 4 的自由基所表示的那些,以及它们的所有合适的异构体、在相同物质上的它们的所有合适的组合,和/或其混合物,

[0424]



式 4

[0425] 其中 n’是 0 或 1,X^6 是氧或硫;X^7 是氧代、硫代或 NR^{17}(其中 R^{17} 表示 H 或可选地被取代的有机基团),R^{13}、R^{14}、R^{15} 和 R^{16} 每一个都独立地表示到式 1 中的另一个片段的键、H、可选地取代基和/或可选地被取代的有机基团,其中可选地,任意 R^{13}、R^{14}、R^{15} 和 R^{16} 可以连接形成环;其中 R^{13}、R^{14}、R^{15} 和 R^{16} 中至少一个是键。

[0426] 本文中,术语“经活化的不饱和片段”“不饱和酯片段”和/或式 4 表示本文中的化学式的一部分,并且在本文中使用时,这些术语表示自由基片段,根据片段在化学式中的位置该自由基片段可以是单价或多价(例如二价)。

[0427] 更优选的式 4 片段(包括其异构体或混合物)是其中 n’为 1、X^6 是 O、X^7 是 O、S 或 NR^7 的那些。

[0428] R^{13}、R^{14}、R^{15} 和 R^{16} 独立地选自:键、H、可选的取代基和可选地被取代的 C_{1-10} 烃,R^{15} 和 R^{16} 可选地连接形成(与它们相连的片段一起)环;并且其中当前的 R^{17} 选自 H 或可选地被取代的 C_{1-10} 烃。

[0429] 最优选地,n’是 1,X^6 是 O;X^7 是 O 或 S,并且 R^{13}、R^{14}、R^{15} 和 R^{16} 独立地为键、H、羟基和/或可选地被取代的 C_{1-6} 烃基。

[0430] 例如,n’是 1,X^6 和 X^7 均为 O;并且 R^{13}、R^{14}、R^{15} 和 R^{16} 独立地为键、H、OH 和/或 C_{1-4} 烷基;或者,R^{15} 和 R^{16} 可选地连接形成二价 C_{0-4} 亚烷基羰基 C_{0-4} 亚烷基片段,因此式 4 表示环状酸酐(例如当 R^{15} 和 R^{16} 一起为羰基时,式 4 表示马来酸酐或其衍生物)。

[0431] 对于式 4 的片段来说,其中 n’是 1 并且 X^6 和 X^7 均为 O,那么当(R^{13} 和 R^{14})中的一个是 H 并且 R^{15} 是 H 时,式 4 表示丙烯酸酯片段,其包括丙烯酸酯(当 R^{13} 和 R^{14} 均为 H 时)及其衍生物(当 R^{13} 和 R^{14} 中一个不为 H 时)。类似地,当(R^{13} 和 R^{14})中的一个是 H 并且 R^{15} 是 CH_3 时,式 4 表示甲基丙烯酸酯片段,其包括甲基丙烯酸酯(当 R^{13} 和 R^{14} 均为 H 时)及其衍生物(当 R^{13} 和 R^{14} 中一个不为 H 时)。尤其优选的是式 4 的丙烯酸酯和/或甲基丙烯酸酯片段。

[0432] 适宜地,式 4 的片段是具有以下特征的那些:其中 n’为 1;X^6 和 X^7 二者均为 O;R^{13} 和 R^{14} 独立地为键、H、CH_3 或 OH,并且 R^{15} 是 H 或 CH_3;R^{16} 是 H 或者 R^{15} 和 R^{16} 一起都为二价 C=O 基团。

[0433] 更适宜地，式 4 的片段是具有以下特征的那些：其中 n' 为 1；X^6 和 X^7 二者均为 O；R^{13} 是 OH，R^{14} 是 CH_3，并且 R^{15} 是 H，并且 R^{16} 是键，并且／或者是其互变异构体（例如乙酰乙酰氧基官能物质的互变异构体）。

[0434] 最适宜地，不饱和酯片段选自：$-OCO-CH=CH_2$；$-OCO-C(CH_3)=CH_2$；乙酰乙酰氧基，$-OCOCH=C(CH_3)(OH)$ 以及它们的所有合适的互变异构体。

[0435] 可以理解，在本发明的内容中可以使用由式 4 表示的任何合适的片段，例如其他反应性片段。

[0436] 乙烯基聚合物

[0437] 尽管术语"乙烯基聚合物"通常用于指，从含乙烯基团 ($CH_2=CH-$) 的化合物聚合而获得的热塑性聚合物，但本文中使用时，术语"乙烯基聚合物"更广义地指包含一个或多个如下片段（例如作为其中的重复单元）的任何聚合物（无论是否热塑性）和／或由包含一个或多个如下片段的单体和／或聚合物前体获得的任何聚合物（无论是否热塑性），所述片段为：经活化的不饱和片段（例如丙烯酸酯和／或甲基丙烯酸酯）；任何烯属不饱和片段（例如乙烯基片段）；它们的混合物；和／或其在相同片段内的组合。

[0438] 为了改善诸如用在涂料应用中的聚合物的可持续性，对使用生物可再生单体的需求不断增长。考虑到化石燃料资源枯竭以及最近几年造成全球性环境问题的大气中二氧化碳的增加，由生物质来源生产这些聚合物的原料的方法吸引了大量关注。因为这些来源是可再生的因此具有碳平衡生物质 (carbon-neutral biomass)，所以预期这种方法未来尤其重要。因此，本发明以及本文中所描述的各个方面的一个优选特征是其中的单体（尤其是高级衣康酸二酯，例如 DBI) 尽可能是生物可再生的。

[0439] 优选地，至少 30 重量％、更优选地至少 50 重量％以及特别地 70 重量％的用来形成本发明的聚合物的烯属不饱和单体是由至少一种生物可再生烯属不饱和单体获得的。生物可再生单体可以全部或部分地从生物可再生来源获得。因此，优选还测量碳 14 含量来确定生物可再生性。

[0440] 碳 14(C-14) 的含量可以指示生物基材料的年代。本领域已知，C-14 具有约 5700 年的半衰期，其被发现于生物可再生材料中，而尚未在化石燃料中发现。因此，"生物可再生材料"是指其中的碳来自非化石生物来源的有机材料。生物可再生材料的例子包括但不限于糖，淀粉，玉米，天然纤维，甘蔗，甜菜，柑橘类水果，木本植物，纤维素，木质纤维素 (lignocelluosics)，半纤维素，马铃薯，植物油，其他多糖诸如胶质、壳质、果聚糖以及支链淀粉 (pullulan)，以及它们的组合。

[0441] C-14 水平可以通过如下来确定：通过液体闪烁计数法测定其衰变过程（每克碳每分钟的衰变或 dpm/gC)。在本发明的一个实施方式中，当各个聚合物 A、聚合物 B 和／或用于获得聚合物 A 和／或聚合物 B 的一种或多种烯属不饱和单体包含会产生至少约 1.5dpm/gC（每克碳每分钟的衰变）、更优选地至少 2dpm/gC、最优选地至少 2.5dpm/gC 以及尤其至少 4dpm/gC 的衰变的碳 -14 的量时，出于本发明的该实施方式的目的，聚合物 A、聚合物 B 和／或烯属不饱和单体可以被认为是足够生物可再生。

[0442] 优选的是，高级衣康酸二酯诸如 DBI 是生物可再生的，然而本发明中所使用的其他单体也可以是生物可再生的。生物可再生单体的实例包括但不限于生物基丙烯酸类，其例如通过使用生物衍生的醇诸如生物丁醇而获得，并且包括（甲基）丙烯酸和（甲基）丙

烯酸烷基酯，其中烷基优选地选自甲基、乙基、丁基或2-乙基己基。

[0443] 丙烯酸可以由甘油制得（如Arkema所公开），或者由乳酸制得（如US7687661所公开）。甲基丙烯酸可以由乙烯、甲醇和一氧化碳（均是生物可再生的）制备，如Lucite International Ltd所公开。

[0444] 可以额外地有助于改善涂层性质的烯属不饱和生物可再生单体包括α-亚甲基丁内酯、α-亚甲基戊内酯、α-亚甲基γ-R^3丁内酯（R^3可以是可选地被取代的烷基或可选地被取代的芳基）；衣康酸酯例如衣康酸二烷基酯（包括DBI）和衣康酸单烷基酯，衣康酸，衣康酸酐，巴豆酸及其烷基酯，柠康酸及其烷基酯，亚甲基丙二酸及其单烷基酯和二烷基酯，柠康酸酐，中康酸及其烷基酯。

[0445] 其他非酸官能、非交联单体包括衣康酸的二酯。这种单体的优选实例包括衣康酸二甲酯、衣康酸二乙酯、衣康酸二正丙酯、衣康酸二异丙酯、衣康酸二正丁酯、衣康酸二异丁酯和/或衣康酸二2-乙基己酯。

[0446] 另一组可用的生物可再生单体包括N-R^2，α-亚甲基丁内酰胺（R^2可以是可选地被取代的烷基或可选地被取代的芳基）；N-R^2，α-亚甲基γ-R^1丁内酰胺；N-烷基衣康酰亚胺；衣康单酰胺；衣康二酰胺；二烷基衣康酰胺（ialkyl itaconamides），单烷基衣康酰胺；（甲基）丙烯酸糠酯；和脂肪酸官能（甲基）丙烯酸酯，例如从Elementis获得的DAPRO FX-522和从Evonik获得的Visiomer ® MUMA。

[0447] 可以理解的是，为了清楚起见而描述于各自实施方式上下文中的本发明的某些特征也可以在单个实施方式中以组合形式提供。相反地，为了简化起见而在单个实施方式上文中所描述的本发明的各种特征也可以分开提供或者以任意合适的子组合的形式提供。

[0448] 本发明的目的是解决现有技术中的问题或缺点（例如本文中整个申请中所指出的）中的一些或所有问题或缺点。

[0449] 除上下文中另有明确指明外，本文中使用时，本文中的术语的复数表达形式应解释为包括其单数表达形式，反之亦然。

[0450] 本文中使用时，术语“包括”或“包含”应理解为指的是随后的列表并非穷举性的，并且可以包括或者可以不包括其他合适的项目，例如合适地一个或多个其他特征、一种或多种组分、一种或多种成分和/或一个或多个取代基。

[0451] 术语“有效”、“可接受”、“活性”和/或“合适”（本文中适当描述的例如关于任何过程、用途、方法、施用、准备、产品、材料、配制品、化合物、单体、低聚物、聚合物预聚物和/或聚合物）将理解为指的是：发明的那些特性如果以正确的方式使用可以为本文中所描述的它们所添加和/或包含的效用提供所要求的性质。这种效用可以直接是例如材料具有用于前面提到的用途所要求的性质的情形，和/或可以间接是例如材料在制备具有直接效用的其他材料中作为用作合成的中间体和/或诊断工具使用的情形。本文中使用时，这些术语也表示官能基团是与产生有效的、可接受的、活性和/或合适的最终产品相协调的。

[0452] 本发明的优选的效用包括用作涂料组合物。

[0453] 在本发明的讨论中，除相反说明外，公开一个参数的所允许范围的上限和下限的可供选择值再加上指明的所述值中的一个结合比其它值更优选，这应当理解为暗示地记载了，位于所述可供选择值的更优选值和不那么优选值之间的所述参数的每个中间值本身都优于所述不那么优选的值，并且优于每个不那么优选的值和所述中间值。

[0454] 对于本文中给出的任意参数的所有上限和/或下限边界来说，边界值都包含于每个参数的值中。还应当理解的是，在本发明的各种实施方式中本文中所描述的各参数的优选的和/或中间的最小边界值与最大边界值的所有组合也都可以用于定义本发明的各种其他实施方式和/或优选方式中的每个参数的可供选择范围，无论这种值的组合是否已具体地在本文中公开了。

[0455] 因此，例如在本文中描述的以0至“x”的量（例如以质量和/或重量%为单位）的一种物质是指（除非上下文中另有明确说明）包含两种备选方案。首先，较广义的备选方案是该物质可以任选地不存在（当其量为零时）或者仅以低于能够检测量的微量允许量存在。第二个优选的备选方案（在物质量的范围内以0下限量表示））是指该物质存在，零表示下限量是非常小的痕量，例如足以通过合适的常规分析技术检测的任意量，更优选地，零表示物质的用量的下限大于或等于0.001重量%（如本文中计算的）。

[0456] 应当理解的是，本文中以百分数所表示的任何量的总和不能（允许舍入的误差）超过100%。例如，在允许舍入误差的情况下，当以组合物（或其相同的一个或多个部分）的重量（或其他）百分数表示时，本发明的组合物（或其一个或多个部分）包含的所有组分的总和可以总计100%。然而，当一列组分未穷举时，每个这些组分的百分数的总和可以小于100%，以允许一定百分数用于本文中未明确描述的一种或多种任意额外组分的额外量。

[0457] 在本发明中，除另有明确说明外，当以重量百分数表示时，用于描述存在于本发明的组合物中的组分的量是基于组合物中单体的总量（等于100%，因此例如组分(a)+(b)+(c)+(d)总共100%）来计算的。为了方便起见，未落入组分(a)至(d)中任意一项的定义的某些非单体成分（例如链转移剂(CTA)）也可以被计算为基于总单体的重量百分数（即其中总单体的重量单独设定为100%）。由于单体的重量%（例如对于组分(a)至(d)来说）被定义为总共100%，所以可以看出对非单体成分（即在(a)至(d)之外的那些组分）使用基于单体的重量%值会导致总百分数超过100%。因此，以基于单体的重量百分数表示的非单体成分的量可以被看作是提供了，这些成分的重量相对于单体总重量的比例，其仅用作计算用的参考值而不是严格的百分数。当(a)+(b)+(c)+(d)总共100%时，其他成分并非从组合物中排除，并且基于总单体的重量百分数不应与相对于总组合物的重量百分数相混淆。

[0458] 本文中使用时，术语“基本上”可以指，意味着具有较大量或比例的数量或实体(entity)。当在其中使用“基本上”的上下文中相关时，“基本上”可以理解为指的是，该数量或实体定量地（与说明书上下文中涉及的数量或实体相关）包含相关整体的至少80%、优选地至少85%、更优选地至少90%、最优选地至少95%、尤其至少98%、例如约100%的。类似地，术语“基本上不含”可以类似地表示，其所涉及的数量或实体包含不超过相关整体的20%、优选地不超过15%、更优选地不超过10%、甚至更优选地不超过5%、最优选地不超过2%、尤其不超过1.5%、例如约0%（例如完全不存在，或者如果存在的话，仅以不可检测的量存在）。

[0459] 本文中使用的术语“可选的取代基”和/或“可选地被取代”（除非紧跟着一列其他取代基）表示一个或多个如下基团（或被这些基团取代）：羧基、磺基(sulpho)、甲酰基、羟基、氨基、亚氨基、氮基(nitrilo)、巯基、氰基、甲基、甲氧基和/或其组合。这些可选的基

团包括多个（优选地两个）前述基团在相同片段中的所有化学上可行的组合（例如氨基和磺酰基，如果彼此直接相连，则表示氨磺酰基）。优选的可选取代基包括：羧基、磺基、羟基、氨基、巯基、氰基、甲基、卤、三卤甲基和／或甲氧基。

[0460] 本文中使用的同义术语“有机取代基”和“有机基团”（本文中也缩写为“有机”(organo)）表示包含一个或多个碳原子并可选地包含一个或多个其他杂原子的任意单价或多价片段（可选地与一个或多个其他片段相连）。有机基团可以包含有机杂化原子(organoheteryl)基团（也被称为有机元素基团），其包含含碳的单价基团，因而是有机的，但是它们在除碳以外的原子上拥有其自由价（例如有机硫代基团）。或者或另外，有机基团可以包含有机基基团(organyl)，其包括在碳原子上具有一个自由价的任意有机取代基团，不论官能团的类型如何。有机基团还可包括杂环基团，其包括通过从杂环化合物（一种环状化合物，它具有至少两种不同的元素作为环节原子，此时一种原子是碳）的任意环原子上除去一个氢原子而形成的一价基团。优选地，有机基团中的非碳原子可选自：氢、卤、磷、氮、氧、硅和／或硫，更优选地选自：氢、氮、氧、磷和／或硫。

[0461] 最优选的有机基团包括一个或多个如下含碳片段：烷基、烷氧基、烷酰基、羧基、羰基、甲酰基和／或其组合；它们可选地与一个或多个如下含杂原子的片段组合，该含杂原子的片段为：氧基、硫基、亚磺酰基、磺酰基、氨基、亚氨基、次氮基(nitrilo)和／或其组合。有机基团包括多个（优选地两个）前述含碳和／或杂原子片段在相同片段中的所有化学上可行的组合（例如烷氧基和羰基，如果彼此直接相连的话表示烷氧羰基基团）。

[0462] 本文中使用的术语“烃基”是有机基团的子集，其表示由一个或多个氢原子和一个或多个碳原子组成的任何单价或多价片段（可选地与一个或多个其他片段相连），并且可以包含一个或多个饱和的、不饱和的和／或芳族片段。烃基可以包含一个或多个如下基团。烃基包含通过从烃去除一个氢原子而形成的单价基团（例如烷基）。亚烃基(Hydrocarbylene)包含通过从烃去除两个氢原子而形成的二价基团，该基团自由价不形成双键（例如亚烷基）。偏亚烃基(Hydrocarbylidene)包括通过从烃的同一个碳原子上除去两个氢原子而形成的二价基团（其可以表示为″ $R_2C=$”），该基团的自由价形成双键（例如偏亚烷基）。次烃基(hydrocarbylidyne)包括通过从烃的同一碳原子上除去三个氢原子而形成的三价基团（其可以表示为“$RC\equiv$”），该基团的自由化合价形成三键（例如次烷基）。烃基基团还可以包括饱和的碳碳单键（例如在烷基中）；不饱和的碳碳双键和／或三键（例如分别在烯基和炔基中）；芳族基团（例如在芳基中）和／或其在相同片段中的组合，在被指出的情况下，该烃基基团可以被其它官能团取代。

[0463] 本文中使用的术语“烷基”或其等同物（例如烷）在适当的情况下且除非另有声明，可以容易地被包含任何其它烃基团的术语替代，所述其它烃基团诸如为本文所述的那些基团（例如包含双键、三键、芳族片段（诸如分别为烯基、炔基和／或芳基）及／或其组合（例如芳烷基）以及连接两个或更多个片段的任何多价烃基（诸如二价亚烃基，例如亚烷基））。

[0464] 除非另有说明或者上下文中另有指明，本文中提到的任何基团或片段（作为取代基）可以是多价或单价的基团（例如连接两个其他片段的二价亚烃基片段）。然而，在本文指出的情况中，这种单价或多价基团仍可以包含可选的取代基。含有三个或更多个原子形成的链的基团表示这样的基团，该基团中，全部或者部分链可以是直链的、支链的和／或形

成环（包括螺环和／或稠环）。对某些取代基来说，指定了某些原子的总数，例如 C_{1-N} 有机基，表示包含 1 至 N 个碳原子的有机片段。在本文中的任意式中，如果未指明一个或多个取代基与片段中的任何具体原子相连（例如在沿链和／或环的具体位置上），则该取代基可以替代任何 H 和／或可以位于该片段上在化学上适宜和／或有效的任何可用位置上。

[0465]　优选地，本文中所列的任何有机基团包含 1 至 36 个、更优选地 1 至 18 个碳原子。尤其优选的是，有机基团中碳原子的数目为 1 至 12、尤其 1 至 10（包括端点）、例如 1 至 4 个碳原子。

[0466]　本文使用时，含有以括号给出的特征的化学术语（除了明确定义的化合物的 IUAPC 命名之外），例如（烷基）丙烯酸酯、（甲基）丙烯酸酯和／或（共）聚合物，表示括号中的那部分根据上下文的要求是任选的，因此例如术语（甲基）丙烯酸酯代表甲基丙烯酸酯和丙烯酸酯。

[0467]　构成和／或被用在本文所述的本发明的一些或全部的某些片段、物质、基团、重复单元、化合物、低聚物、聚合物、材料、混合物、组合物和／或配制品可以以一种或多种不同的形式存在，例如为如下非穷举性列表中的那些的任意一个：立体异构体（诸如对映异构体（例如 E 和／或 Z 形式）、非对映异构体和／或几何异构体）；互变异构体（例如酮式和／或烯醇式），构象异构体 (conformer)，盐，两性离子，络合物（诸如螯合物、笼合物、冠状化合物、穴状配体／穴状络合物 (cyptands/cryptades)、包合物、嵌入化合物、填隙化合物 (interstitial compound)、配体络合物、有机金属络合物、非化学计量络合物、π－加合物、溶剂化物和／或水合物）；同位素取代的形式、聚合构型［诸如均聚物或共聚物、无规聚合物、接枝聚合物和／或嵌段聚合物、直链和／或支链的聚合物（例如星形和／或侧链的）、交联和／或网状聚合物、可由两价和／或三价重复单元得到的聚合物、树枝状化合物、具有不同立构规整度的聚合物（例如全同立构聚合物、间同立构聚合物或无规立构聚合物）］；多晶形物（诸如间隙形式、结晶形式和／或无定形形式），不同相态，固态溶液；若可行的话，和／或其组合和／或其混合物。本发明包括和／或使用所有这些如本文中定义的有效的形式。

[0468]　本发明的聚合物可以由一个或多个合适的聚合物前体制得，该聚合物前体可以是有机的和／或无机的并且包含任何合适的一个或多个（共聚）单体、一个或多个（共）聚合物［包括一个或多个均聚物］以及其混合物，而且该聚合物前体包含这样的片段，该片段能够与该聚合物前体或每个聚合物前体形成键以扩链，和／或能够经由本文中所指明的直接成键而与该聚合物前体或每个聚合物前体的另一个交联。

[0469]　本发明的聚合物前体可以包含一个或多个单体、低聚物、聚合物；及其组合，它们具有合适的可聚合官能团。应当理解的是，除上下文中另有规定外，本文中使用的术语“单体”涵盖了术语“聚合物前体”，并且不排除本身在性质上 (in character) 可以为聚合的和／或低聚的那些单体。

[0470]　单体是具有低分子量（例如小于一千道尔顿）的基本上单分散的化合物，其能够聚合。

[0471]　聚合物是通过聚合方法制得的具有大分子量（例如数千道尔顿）的大分子的多分散混合物，其中大分子包含多个重复的较小单元（其本身可以是单体、低聚物和／或聚合物），并且其中（除非性质严重依赖于分子结构的精细细节）添加或去除一个或几个单元对

大分子的性质的影响可以忽略。

[0472] 低聚物是具有单体与聚合物之间的中间分子量的分子的多分散混合物，这些分子包含少量单体单元，并且一个或几个单元的去除会显著地改变分子的性质。

[0473] 根据上下文，术语聚合物可以包含低聚物，或者可以不包含低聚物。

[0474] 本发明中的和／或本发明中使用的聚合物前体可以通过直接合成来制备或者（如果聚合前体本身是聚合型的话）通过聚合来制备。如果可聚合的聚合物本身用作本发明中的和／或本发明中使用的聚合物前体，优选的是这种聚合物前体具有低的多分散性、更优选地基本上是单分散的，从而使副反应、副产物的数目和／或由该聚合物前体形成的任意聚合材料中的多分散性降至最小。一种或多种聚合物前体在常温常压下可以是基本上非反应性的。

[0475] 除非本文中指明，本发明中的和／或本发明中使用的聚合物和／或聚合的聚合型聚合物前体可以通过本领域技术人员公知的任何合适的聚合手段来（共）聚合。合适方法的例子包括：热引发；通过添加合适试剂的化学引发；催化；和／或使用任选的引发剂然后辐照的引发，例如在适当波长诸如UV下采用电磁辐射（光化学引发）；和／或采用其他类型的辐射诸如电子束、α 粒子、中子和／或其他粒子。

[0476] 可以选择聚合物和／或低聚物的重复单元上的取代基，来改善具有该聚合物和／或树脂的材料的相容性，其中出于本文中所描述的用途，聚合物和／或树脂可以配制和／或掺入到材料中。因此，可以选择取代基的尺寸和长度以便优化与树脂的物理缠绕或互穿(interlocation)，或者它们可以包含或者可以不含其他反应性实体，这些其他反应性实体在适当情况下能够与这些其他树脂进行化学反应和／或交联。

[0477] 本发明的另一个方面广义地提供了涂料组合物，其包含本发明的和／或本文中所描述的聚合物和／或珠粒。

[0478] 本发明的另外一方面提供了由本发明的涂料组合物获得或者可以获得的涂层。

[0479] 本发明的另外一个方面广义地提供了其上涂布有本发明的（可选地固化的）涂料组合物的基材和／或制品。

[0480] 本发明的另外一个方面广义地提供了使用本发明的和／或本文中所描述的聚合物来制备涂料组合物的方法。

[0481] 本发明的另一个方面提供了用于制备经涂布的基材和／或制品的方法，其包括以下步骤：将本发明的涂料组合物涂覆到基材和／或制品上，并任选地将所述组合物原位固化，来在其上形成经固化的涂层。固化可以是通过任何合适的手段，例如热固化，通过辐射和／或通过使用交联剂。

[0482] 优选的涂料组合物是溶剂涂料组合物或水性涂料组合物，更优选地是水性涂料组合物。

[0483] 可选地，水性涂料组合物还可以包含助溶剂(co-solvent)。本领域已知的助溶剂是在水性组合物中所采用的有机溶剂，其改善该组合物的干燥特性、尤其降低该组合物的最低成膜温度。助溶剂可以是在制备本发明的聚合物时结合或使用的溶剂，或者可以在配制水性组合物时已经添加过。

[0484] 本发明的组合物尤其用作或用于提供涂料配制物（即意图用于涂覆到基材而不需要对其进一步处理或添加的组合物）的主要组分，该涂料配制物诸如为保护性或装饰性

涂料组合物（例如漆料、亮漆或清漆），其中最初制备的组合物可选地可以用水和／或有机溶剂进一步稀释，和／或与其他成分组合，或者可以是更浓缩的形式，该更浓缩的形式通过可选地蒸发最初制备的组合物的液体介质中的水和／或有机组分获得。

[0485] 本发明的组合物可以用于各种应用，并且出于这种目的，其可以任选地与其他添加剂和／或组分组合或配制，所述其他添加剂和／或组分诸如为消泡剂、流变控制剂、增稠剂、分散剂和／或稳定剂（通常为表面活性剂和／或乳化剂）、润湿剂、填料、增量剂(extender)、杀真菌剂、杀菌剂、聚结和润湿溶剂或助溶剂（尽管通常不需要溶剂）、增塑剂、防冻结剂、蜡、着色剂、颜料、染料、热稳定剂、流平剂、抗缩孔剂(anti-cratering agent)、填充剂、沉降抑制剂、UV吸收剂、抗氧化剂、反应性稀释剂、中和剂、粘附促进剂和／或它们的任意合适混合物。

[0486] 前述添加剂和／或组分以及类似物可以在生产过程的任意阶段引入或者随后引入。可以引入阻燃剂（例如氧化锑），来增强阻燃性质。

[0487] 本发明的组合物还可以与其他聚合物共混，诸如乙烯基聚合物、醇酸树脂（饱和的或不饱和的）、聚酯和／或聚氨酯。

[0488] 本发明的涂料组合物可以通过任何常规方法涂覆到各种基材上，该基材包括木材、板、金属、石材、混凝土、玻璃、织物、皮革、纸、塑料、泡沫等等，所述常规方法包括刷涂、浸涂、流涂、喷涂等等。本发明的涂料组合物还可以用于涂布三维制品的内表面和／或外表面。还可以使用本发明的涂料组合物，如果需要的话适当配制，来提供膜、光泽剂、清漆、亮漆、漆料、墨和粘合剂。然而，它们尤其可用于且适用于为基材提供保护性涂层的主要成分，所述基材包括木材（例如木制地板）、塑料、聚合材料、纸和／或金属。

[0489] 一旦本发明的组合物已经被涂覆到基材上了，就可以通过使其在环境温度下自然干燥来将载体介质从本发明的组合物中去除，或者可以通过加热来加速干燥过程。通过在环境温度下长时间静置（几天）或者通过在高温（例如50℃）下加热短得多的时间，可以进行交联。

[0490] 此外，本发明涉及本发明的共聚物在以下任一使用中的用途，该共聚物可选地以有机颗粒／珠粒（可选地纳米和／或微米尺寸的）形式，作为包封着色剂组合物颗粒的颗粒，并且本发明涉及包含本发明的有机纳米颗粒和／或微米颗粒的着色剂组合物。着色剂表示任何带颜色的材料（包括吸收或反射UV或IR辐射而不吸收或反射可见光的材料，或者除了吸收或反射可见光外还吸收或反射UV或IR辐射的材料），并且包括染料和颜料。染料通常可溶于它们要加入的介质中，并且通常(但非穷举性地)是有机液体。颜料通常不溶于它们要加入的介质中，并且通常（但非穷举性地）是无机固体。优选地，着色剂是染料。着色剂组合物颗粒的包封可以如下发生：在乳化之前或乳化时将着色剂组合物的颗粒悬浮于溶液中，以使着色剂组合物颗粒在溶液固化时被包封于纳米颗粒中。或者，着色剂组合物颗粒可以在固化反应后添加，以使包封发生在可选的结块(agglomeration)过程中。

[0491] 本发明的共聚物和／或珠粒的其他最终用途的非限制性列表包括：

[0492] 用于调色剂组合物的粘结剂，并且调色组合物可以包含本发明的颗粒；

[0493] 用作片材模制复合物（本文中也表示为SMC)的添加剂，其中本发明的颗粒（尤其喷雾干燥的颗粒）的存在导致较低密度的产品；

[0494] 用作塑料颜料，尤其用于涂层诸如纸涂层，其中本发明的颗粒的存在可以为产品

提供高光泽度或可调的（tuneable）光泽性质；

[0495] 用作复合材料中、尤其混凝土中的填料，其中例如本发明的颗粒作为微米填料的使用可以提高强度、降低孔隙率、降低密度和/或防止水渗透到结构中；

[0496] 用作涂料的填料，其中例如本发明的颗粒可以向涂层提供抗粘连性质、提高耐划伤性、降低磨损、提高干燥速度、降低溶剂的所需用量并减少收缩；

[0497] 用作蜡的填料，其中例如颗粒可以提供润滑效果、降低重量、降低磨损和/或起到高温填料的作用。

[0498] 本发明的单分散颗粒可以用于间隔物，例如在显示应用中；

[0499] 用作混杂着色剂，其中例如着色剂（优选地颜料）颗粒可以与本发明的颗粒以多种方式相互作用。在一种方式中，可以在树脂和单体固化前将颜料颗粒分散于乳液中。颜料颗粒（通常是疏水的）会倾向于迁移到溶液的疏水性液滴内部。将溶液固化会形成颗粒，在该颗粒中颜料核被包封于固化的聚合物的壳内。在另一种方式中，颜料颗粒可以与纳米颗粒共结块（co-agglomerated），以形成微米颗粒。这两种方法产生的颜料可分散于水中并且可以与周围气氛或其他材料部分地直接接触或者不接触。

[0500] 用于粘合剂中，其中例如本发明的颗粒可以用作填料或收缩减少剂，因为该颗粒在粘合剂固化时是惰性的。由于本发明的颗粒强烈地与粘合剂相连，它们不会对粘合强度产生不利影响。

[0501] 用作活性成分的包封剂，该活性成分可以在固化前被添加到乳液中并在固化后保持在颗粒中。所获得的包含活性成分的颗粒更易于分散，并且该活性成分被保护的了。活性成分的实例为染料和 UV 阻断剂。

[0502] 用作适用于个人护理和/或用作局部药物的组合物中的成分。

[0503] 可以理解的是，上述用途中的一些可以重叠。

[0504] 根据局部药物和/或个人护理组合物的所期望的性质，本发明的颗粒（有机纳米颗粒和/或微型颗粒）可以以总组合物的 0.001 至 99 重量％、优选地 0.1 至 80 重量％、更优选地 0.5 至 50 重量％、最优选地 1 至 20 重量％的量存在。可以使用任何合适的用于这些应用的常规成分，例如这些组合物的熟练配制工所公知的那些。

[0505] 局部药物指的是用于向皮肤或经由皮肤递送治疗性活性试剂而配制的组合物。各种各样的活性试剂可以使用这种配制物递送，包括意图治疗皮肤的试剂诸如抗痤疮剂，以及全身性活性试剂，对全身性活性试剂来说皮肤仅仅是施用的途径而不是作用位点。

[0506] 个人护理组合物的非限制性例子（其可以被局部施用或者可以不被局部施用）包括：化妆品组合物、毛发护理产品、驱虫剂、口部清洁组合物、自晒黑产品（self tanning products）、防晒剂、梳洗（toiletry）组合物及其混合物，和/或在相同组合物中的组合。

[0507] 化妆品组合物指的是，可以用于身体上来修饰其外观的组合物。这种组合物的非限制性例子包括：晒后用组合物、腮红（blushers）、彩妆、眼影、面霜、面膜、粉底、润唇膏（lip balms）、口红（lipsticks）、保湿剂、粉末制剂、临时纹身以及人体艺术（body art）的其他形式；以及爽肤水（toner）洁面乳。化妆品组合物可以作为任何合适的配制物类型来施用，这些类型的非限制性例子包括：乳霜、分散体、乳液（例如油包水（w/o）、水包油（o/w）、水包油包水（w/o/w）、油包水包油（o/w/o）（但连续相为水性的乳液是优选的，例如 o/w 和 w/o/w）、凝胶、洗剂、乳剂（milk）、软膏（ointments）、糊剂、粉剂、滚珠剂（roll on）、油膏

(salves)、精华、溶液、喷雾、棒和悬浮液。

[0508] 毛发护理组合物指的是，可用于动物毛发上、优选地人毛发上、最优选地人头部上的组合物。这种组合物的非限制性例子可以包括合适的：调理剂(conditioner)、乳膏、泡沫、凝胶、染发剂、毛发着色剂、毛发定型产品、热油处理剂(hot oil treatments)、洗剂、睫毛膏、面膜、摩丝、美容泥(mud)、冲洗液、香波、定型喷雾和/或蜡。

[0509] 口部清洁组合物指的是，可以适合用于口腔清洁、牙齿处理和/或以其他方式应用于口腔和/或口部空腔的组合物。这种组合物的非限制性例子可以包括合适的：口香糖、洁齿剂、假牙清洁配方、牙线、玻璃离子黏固剂、含片(lozenges)、口部喷雾、漱口液、牙涂料、牙膏和/或牙粉。

[0510] 防晒剂指的是，可用于身体上来提供对太阳射线或其他UV源的防护作用的组合物。这种组合物的非限制性例子还可以包括：防晒隔离霜(sun blockers)和/或仿晒乳剂。

[0511] 梳洗组合物指的是，用于身体上来清洁、冲洗、洗涤、增香味和/或减少臭味的组合物。这种组合物的非限制性例子可以包括合适的：抗微生物组合物、沐浴产品(例如沐浴泡沫剂和浴盐)、除臭剂、洗涤剂、香水、肥皂和/或沐浴露。清洁组合物(例如配制的家用清洁剂)也可以被看作是梳洗组合物。

[0512] 本发明的许多其他变种实施方式对于本领域技术人员来说是明显的，并且这些变种包含于本发明的宽范围内。

[0513] 本发明的其他方面以及其优选特征在本文中的权利要求书中给出了。

[0514] 测试

[0515] 最低成膜温度

[0516] 本文中所使用的分散体的最低成膜温度(MFFT)是采用DIN 53787且当使用Sheen MFFT bar SS3000涂覆时分散体形成光滑且无裂纹的涂层或膜时的温度。

[0517] 斑点试验(SPOT TESTS)

[0518] 通过本发明的共混物形成的涂料膜可以在公知的常规斑点试验(例如ASTM D1308-02e1)中测试，来确定膜对各种液体试剂诸如水、乙醇、洗涤剂(例如在商标Andy下从Unilever可以购得的)和咖啡的耐性。在一个这样的测试中，可以将标准体积(例如0.5ml)的液体试剂涂覆到膜上，以在其上形成斑点(例如通过移液管)，然后用表面皿覆盖。经过指定的时间(例如在本文的表中的时间)后，可以对膜进行评估并在视觉上在1至5等级上进行评级，如下文所述。

[0519] KOENING硬度

[0520] 本文中使用的Koenig硬度是硬度的一种标准量度，其测定了由分散体形成的膜的粘弹性质怎样将使膜表面变形的摆动运动慢下来，并且是根据DIN 53157 NEN5319测定的。

[0521] 玻璃化转变温度(Tg)

[0522] 本领域公知的是，聚合物玻璃化转变温度是其从玻璃状、易碎状态变为塑性、高弹态时的温度。玻璃化转变温度可以使用差示扫描量热(DSC)来实验测得，取导数曲线的峰作为Tg，或者可以由Fox方程计算得到。因此，具有“n”个共聚了的共聚单体的共聚物的Tg(以开氏度数计)是通过每个共聚单体类型的重量分数W和由每个共聚单体获得的均聚

物的Tg(以开氏度数计)根据如下方程来给出的，该方程为：

[0523] $\underline{1} = \underline{W_1}+\underline{W_2}+\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\underline{W_n}$

[0524] $Tg \quad Tg_1 \quad Tg_2 \qquad\qquad\qquad\qquad Tg_n$

[0525] 计算得到的以开氏度数计的Tg可以容易地转化成℃。

[0526] 固体含量

[0527] 本发明的水性分散体的固体含量通常在基于总重量的约20至65重量%、更常见30至55重量%的范围内。如果需要的话，可以通过添加水或去除水(例如通过蒸馏或超滤)来调节固体含量。

[0528] pH值

[0529] 本发明的分散体的pH值可以为2至10，并且通常6至9.5。

[0530] 粘连(BLOCKING)

[0531] 耐粘连测试[包括粘连和早期粘连]：

[0532] 步骤1：粘连：

[0533] 向本发明的水性乳液添加10%的丁基二甘醇，然后将该水性乳液的100微米湿膜浇铸到纸基材上，并在52℃下干燥16小时。

[0534] 步骤1：早期粘连

[0535] 向本发明的水性乳液添加10%的丁基二甘醇，然后将该水性乳液的250微米湿膜浇铸到纸基材上，并在室温下干燥24小时。

[0536] 步骤2：粘连与早期粘连：

[0537] 冷却至室温后，在1Kg/cm^{2}的载荷下在52℃下，将两片经涂布的膜的经涂布一侧彼此相对放置4小时。在此时间间隔后，去除在样品上的载荷，并使样品冷却至室温(22+2℃)。当两个涂层可以彼此分离且对膜无任何损伤(不粘)时，耐粘连性就非常好而且评价为5。然而当它们完全粘在一起时，耐粘连性非常差并且评价为0。

[0538] 气相色谱质谱(GCMS)

[0539] 为了确认聚合基本上完全，可以通过GCMS测定游离衣康酸酯单体的含量。在顶部空间(head space)装配有CTC combi Pal自动进样器的Trace GC-DSQ MS(Interscience, Breda, the Netherlands)上进行GCMS分析。载气为氦气，并且使用CP Sil5low bleed/MS, 25m x 0.25mm(内径), 1.0μm(CP nr.7862)柱。

[0540] GC-烘箱被如下程序控制：从50℃(5min)开始，随后通过不同的连续温度跃升，以5℃/min的速度升至70℃(0min)、以15℃/min的速度升至220℃(0min)，最后以25℃/min升的速度280℃(10min)。使用1.2ml/min的连续氦气流。在300℃下，在程序升温蒸发器(PTV)中进行热分流进样。进样体积为1μl。MS输送线和离子源均保持为250℃。采用单离子监测(SIM)来测量样品。对于具体的衣康酸二丁酯(DBI)案例，使用127.0和59.0Da的质量(mass)，对于内标(丙烯酸异丁酯)来说使用55.0和73.0的质量。样品溶液为约500mg在3ml内标溶液(在丙酮中的丙烯酸异丁酯)中。用5个从0-500ppm的不同浓度水平进行校准。使用Microsoft Excel用线性校准曲线来进行计算。

[0541] 分子量

[0542] 除上下文中另有明确说明外，本文中使用的聚合物或低聚物的术语分子量表示重均分子量(也表示为M_w)。可以通过任何合适的常规方法，例如通过气相色谱法(GPC，与上

面描述的 GCMS 方法类似地进行）和 / 或通过下述 SEC 方法，来测定 M_w。GPC 方法是优选的。

[0543] 使用 SEC 测定聚合物的分子量

[0544] 还可以使用尺寸排阻色谱法（SEC）采用四氢呋喃作为洗脱剂或采用 1,1,1,3,3,3 六氟异丙醇作为洗脱剂，来测定聚合物的分子量。

[0545] 1) 四氢呋喃

[0546] SEC 分析是在 Alliance Separation Module(Waters 2690) 上进行的，其包含泵、自动进样器、脱气装置和柱温箱。洗脱剂是添加了 1.0 体积％乙酸的四氢呋喃（THF）。进样体积为 150μl。流速定为 1.0ml/min。在 40℃的温度下使用带有保护柱（guard column）的 Three PL MixedB(Polymer Laboratories)(3μm PL)。使用差示折光率检测器（Waters410）来进行检测。制备具有 20mg 固体在 8ml THF(+1 体积％乙酸）中的浓度的样品溶液，并且将样品溶解 24 小时。使用范围在 500 至 4000000g/mol 内的 8 个聚苯乙烯标准品（polymer standard services）来进行校准。使用 Millennium 32 软件（Waters）采用三级校准曲线进行计算。所获得的分子量为聚苯乙烯当量摩尔质量（g/mol）。

[0547] 2)1,1,1,3,3,3 六氟异丙醇

[0548] SEC 分析在 Waters Alliance 2695（泵，脱气装置和自动进样器）上进行，采用 Shodex RI 101 差示折光率检测器和 Shimadzu CTO 20AC 柱温箱。洗脱剂为添加了 0.2M 三氟乙酸钾（KTFA）的 1,1,1,3,3,3 六氟异丙醇（HFIP）。进样体积为 50μl。流速定为 0.8ml/min。在 40℃的温度下使用带有保护柱的两个 PSS PFG Linear XL 柱（Polymer Standards Service)(PFG PSS）。采用差示折光率检测器来进行检测。制备具有 5mg 固体在 2ml HFIP(+0.2M KTFA）中的浓度的样品溶液，并且将样品溶解 24 小时。使用范围在 500 至 2000000g/mol 内的 11 个聚甲基丙烯酸甲酯标准品（polymer standard services）来进行校准。使用 Empower Pro 软件（Waters）采用三级校准曲线进行计算。经由常规校准来获得摩尔质量分布，并且该摩尔质量是聚甲基丙烯酸甲酯当量摩尔质量（g/mol）。

[0549] 标准条件

[0550] 本文中使用时，除上下文另有说明外，标准条件（例如用于干燥膜）指的是相对湿度 50％ 45％、环境温度（本文中表示 23℃ ±2° 的温度）以及空气流速≤（小于或等于）0.1m/s。

[0551] 提供如下实施例来进一步说明本发明的方法和组合物。这些实施例仅仅是示例性的，并且不意图以任何方式限制本发明的范围。除另有指明外，所有份数、百分数和比例均是基于重量的。实例前的前缀 C 表示其为对比例。

[0552] 各种注册的商标、其他名称和 / 或简称在本文中用来表示用来制备本发明的聚合物和组合物的一些成分。下面，通过化学名称和 / 或商品名称和可选地可以购买到这些成分的它们的制造商或供应商来对这些成分进行标识。然而，如果本文中未给出材料的化学名称和 / 或供应商，则可以在本领域技术人员所公知的例如参考文献中找到，例如‘McCutcheon′s Emulsifiers and Detergents’，Rock Road，Glen Rock，N.J.07452 1700，USA，1997 和 / 或 Lewis，Richard J.，Sr. 的 Hawley′s Condensed Chemical Dictionary（第 14 版）；John Wiley&Sons。

[0553] 在实施例中，可以使用如下简称 / 单体：

[0554] BA ＝丙烯酸正丁酯（可以是生物可再生的）

[0555]　BMA ＝甲基丙烯酸正丁酯（可以是使用生物可再生的链烷醇制备的）

[0556]　DBI 表示衣康酸二（正丁基）酯（也称为 2- 偏亚甲基丁二酸二丁酯）（可以是生物可再生的）

[0557]　DDM 表示正十二烷基硫醇

[0558]　DMI ＝衣康酸二甲酯（可以是生物可再生的）

[0559]　DMW 表示去矿物质水

[0560]　EDTA ＝乙二胺四乙酸

[0561]　HFIP 表示六氟异丙醇

[0562]　KTFA 表示三氟乙酸钾

[0563]　MMA ＝甲基丙烯酸甲酯（可以是使用生物可再生的链烷醇制备的）

[0564]　MAA ＝甲基丙烯酸（可以是生物可再生的）

[0565]　NS 表示硫酸钠

[0566]　PAA 表示聚丙烯酸

[0567]　STY 表示苯乙烯；

[0568]　D(iB)I 表示衣康酸二（异丁基）酯（也称为衣康酸二（叔丁基）酯）

[0569]　DPI 表示衣康酸二（戊基）酯

[0570]　DHI 表示衣康酸二（己基）酯

[0571]　DHpI 表示衣康酸二（庚基）酯

[0572]　DOI 表示衣康酸二（正辛基）酯

[0573]　D(EH)I 表示衣康酸二 (2- 乙基己基）酯

[0574]　DDI 表示衣康酸二（癸基）酯

[0575]　DBzI 表示衣康酸二（苄基）酯

[0576]　DPhI 表示衣康酸二（苯基）酯

[0577]　BPI 表示衣康酸丁基戊酯

[0578]　BHI 表示衣康酸丁基己酯

[0579]　HOI 表示衣康酸己基正辛酯

[0580]　IA 表示衣康酸

[0581]　MSA 表示 α - 甲基苯乙烯的磺酸

[0582]　DPrI 表示衣康酸二（丙基）酯

[0583]　CEA 表示 β - 羧乙基丙烯酸酯

[0584]　PA 表示丙烯酸丙酯

[0585]　OA 表示丙烯酸正辛酯

[0586]　MBI 表示衣康酸单酸丁酯（即半酯）

[0587]　IAn 表示衣康酸酐

[0588]　MMalA 表示亚甲基丙二酸，

[0589]　MalAn 表示马来酸酐，

[0590]　PHEMA 表示磷酸化的甲基丙烯酸羟基乙酯

[0591]　AMPS 表示 2- 丙烯酰氨基 -2- 甲基丙烷磺酸

[0592]　URED 表示单体甲基丙烯酸 N-[2-(2- 氧代 -1- 咪唑啉基）乙基] 酯

[0593] MSTY 表示 α-甲基苯乙烯

[0594] 实施例 1 至 3(序列乙烯基聚合物)

[0595] 实施例 1

[0596] 向装配有冷凝器、温度计和机械搅拌器的圆底烧瓶中,添加 84.853 份的水、0.253 份的碳酸氢钠和 1.786 份的 30 重量%的十二烷基硫酸钠在水中的溶液,并将该混合物加热到 50℃。在 50℃温度下,加入 10%的第一单体物料,该第一单体物料由 20.93 份水、4.285 份 30 重量%的十二烷基硫酸钠在水中的溶液、0.726 份碳酸氢钠、0.246 份过硫酸铵、1.340 份甲基丙烯酸、26.811 份的衣康酸二丁酯和 25.456 份甲基丙烯酸甲酯组成,并且将反应器内容物加热到 90℃。达到反应温度后,将反应器内容物搅拌 15 分钟。

[0597] 接下来,在 210 分钟的时间段中,加入第一单体物料的剩余部分。当进料完成后,用 1.885 份水冲洗物料罐。

[0598] 将该批料在 90℃下保持 30 分钟并将其冷却至 70℃。接下来,加入浆料,该浆料包含 0.289 份 70 重量%的叔丁基过氧化氢在水中的溶液和 1.228 份的水,并且将该批料搅拌 5 分钟。接下来,在 240 分钟的时间段中加入第二单体物料,该第二单体物料包含 2.681 份的甲基丙烯酸、4.932 份的甲基丙烯酸甲酯、15.117 份的丙烯酸丁酯和 30.877 份的甲基丙烯酸丁酯。同时,在相同的时间段中加入催化剂物料,该催化剂物料包含 11.943 份的水、0.120 份的异-抗坏血酸和 1.071 份的 30 重量%的十二烷基硫酸钠溶液。在第二单体进料完成后,用 1.885 份水冲洗物料罐。

[0599] 将反应器内容物在 70℃下再搅拌 30 分钟,之后将该批料冷却至 30℃。使用 0.6 份 25%的氨水溶液或者其一部分,将乳液的 pH 调节到 7。同时,加入 0.623 份的水。使用水将乳液的固体含量调节到 45%。

[0600] 所获得的乳液具有 45%的固体含量和 7.0 的 pH。

[0601] 实施例 2

[0602] 向装配有冷凝器、温度计和机械搅拌器的圆底烧瓶中,添加 84.853 份的水、0.253 份的碳酸氢钠和 1.786 份的 30 重量%的十二烷基硫酸钠在水中的溶液,并将该混合物加热到 50℃。在 50℃温度下,加入 10%的第一单体物料,该第一单体物料由 20.93 份水、4.285 份 30 重量%的十二烷基硫酸钠在水中的溶液、0.726 份碳酸氢钠、0.246 份过硫酸铵、1.340 份甲基丙烯酸、14.044 份甲基丙烯酸丁酯、24.123 份的衣康酸二甲酯和 14.100 份甲基丙烯酸甲酯组成,并且将反应器内容物加热到 90℃。达到反应温度后,将反应器内容物搅拌 15 分钟。

[0603] 接下来,在 210 分钟的时间段中,加入第一单体物料的剩余部分。当进料完成后,用 1.885 份水冲洗物料罐。

[0604] 将该批料在 90℃下保持 30 分钟并将其冷却至 70℃。接下来,加入浆料,该浆料包含 0.289 份 70 重量%的叔丁基过氧化氢在水中的溶液和 1.228 份的水,并且将该批料搅拌 5 分钟。接下来,在 240 分钟的时间段中加入第二单体物料,该第二单体物料包含 2.681 份的甲基丙烯酸、4.932 份的甲基丙烯酸甲酯、15.117 份的丙烯酸丁酯、18.762 份的衣康酸二丁酯和 12.115 份的甲基丙烯酸丁酯。同时,在相同的时间段中加入催化剂物料,该催化剂物料包含 11.943 份的水、0.120 份的异-抗坏血酸和 1.071 份 30 重量%的十二烷基硫酸钠溶液。在第二单体进料完成后,用 1.885 份水冲洗物料罐。

[0605] 将反应器内容物在70℃下再搅拌30分钟，之后将该批料冷却至30℃。使用0.6份25％的氨水溶液或者其一部分，将乳液的pH调节到7。同时，加入0.623份的水。使用水将乳液的固体含量调节到45％。

[0606] 所获得的乳液具有45％的固体含量和7.0的pH。

[0607] 实施例3

[0608] 向装配有冷凝器、温度计和机械搅拌器的圆底烧瓶中，添加84.853份的水、0.253份的碳酸氢钠和1.786份的30重量％的十二烷基硫酸钠在水中的溶液，并将该混合物加热到50℃。在50℃温度下，加入10％的第一单体物料，该第一单体物料由20.93份水、4.285份30重量％的十二烷基硫酸钠在水中的溶液、0.726份碳酸氢钠、0.246份过硫酸铵、1.340份甲基丙烯酸、14.044份甲基丙烯酸丁酯和38.223份甲基丙烯酸甲酯组成，并且将反应器内容物加热到90℃。达到反应温度后，将反应器内容物搅拌15分钟。

[0609] 接下来，在210分钟的时间段中，加入第一单体物料的剩余部分。当进料完成后，用1.885份水冲洗物料罐。

[0610] 将该批料在90℃下保持30分钟并将其冷却至70℃。接下来，加入浆料，该浆料包含0.289份70重量％的叔丁基过氧化氢在水中的溶液和1.228份的水，并且将该批料搅拌5分钟。接下来，在240分钟的时间段中加入第二单体物料，该第二单体物料包含2.681份的甲基丙烯酸、4.932份的甲基丙烯酸甲酯、2.673份的双丙酮丙烯酰胺、12.444份的丙烯酸丁酯、26.803份衣康酸二丁酯和4.074份的甲基丙烯酸丁酯。同时，在相同的时间段中加入催化剂物料，该催化剂物料包含11.943份的水、0.120份的异-抗坏血酸和1.071份30重量％的十二烷基硫酸钠溶液。在第二单体进料完成后，用1.885份水冲洗物料罐。

[0611] 将反应器内容物在70℃下再搅拌30分钟，之后将该批料冷却至30℃。使用0.6份25％的氨水溶液或者其一部分，将乳液的pH调节到7。同时，加入0.623份的水。使用水将乳液的固体含量调节到45％。

[0612] 所获得的乳液具有45％的固体含量和7.0的pH。

[0613] 实施例4至7(乙烯基低聚物-聚合物)

[0614] 实施例4

[0615] 低聚物4A

[0616] 向装配有冷凝器、温度计和机械搅拌器的圆底烧瓶中，装入549.0份的水和0.7份Aerosol GPG。将该混合物加热到70℃。在70℃下，加入10％的单体物料，该单体物料由100.8份水、44.1份甲基丙烯酸甲酯、136.2份衣康酸二甲酯、14.6份双丙酮丙烯酰胺、24.3份衣康酸二乙酯、24.3份甲基丙烯酸、2.0份Aerosol GPG和5.8份3-巯基丙酸组成，并且进一步将反应器内容物加热到85℃。在80℃下，加入由0.2份过硫酸铵和11.3份水组成的溶液。

[0617] 在85℃下，在260分钟的时间段中，加入单体物料的剩余部分。在250分钟的时间段中，将催化剂物料进料到反应器中，该催化剂物料包含0.5份过硫酸铵和33.5份水。在单体物料添加结束时，使用5.0份水来冲洗物料罐，并将其加入反应器。将85℃的温度保持20分钟，之后将反应混合物冷却至80℃。在80℃下，使用19.4份25％氨水溶液与21.2份水混合来中和乳液。随后将反应混合物在80℃下再保持20分钟，然后冷却至室温。使用水将乳液的固体含量调节到25％。

[0618] 所获得的乳液具有25.1％的固体含量和8.0的pH。

[0619] 聚合物乳液4B

[0620] 向装配有冷凝器、温度计和机械搅拌器的圆底烧瓶中，添加15.2份的水和498.1份如低聚物4A中所描述而制得的低聚物。将反应器的内容物加热到60℃。

[0621] 加入33％的单体物料，该单体物料由13.9份水、13.9份衣康酸二乙酯、156.0份衣康酸二丁酯、135.9份丙烯酸丁酯和6.2份双丙酮丙烯酰胺组成，然后将乳液搅拌15分钟。接下来，加入0.4份70重量％的叔丁基过氧化氢浆料和1.2份的水，然后加入33％的0.7份异-抗坏血酸在13.8份水中的溶液。

[0622] 温度达到66℃之后，将该批料搅拌10分钟，加入45.5份水，并且将该批料冷却至60℃。接下来，加入50％的剩余单体物料，接着0.4份70重量％的叔丁基过氧化氢浆料、1.2份水和剩余异-抗坏血酸溶液的50％。温度达到62℃之后，将该批料搅拌10分钟，加入56.4份水，并且将该批料冷却至60℃。加入单体物料的剩余部分和5.1份水，然后加入0.4份70重量％的叔丁基过氧化氢浆料、1.8份水和剩余的异-抗坏血酸溶液。温度达到61℃后大约15分钟后，将该批料搅拌额外的10分钟。接下来，加入0.5份70重量％的叔丁基过氧化氢浆料和0.7份水，然后加入0.3份异-抗坏血酸在4.6份水中的溶液。使乳液搅拌30分钟后，将该批料冷却30℃，然后加入6.2份己二酸二酰肼和17.8份水。使用水将乳液的固体含量调整对44％。

[0623] 所获得的乳液具有44.0％的固体含量和7.8的pH。

[0624] 实施例5

[0625] 低聚物5A

[0626] 向装配有冷凝器、温度计和机械搅拌器的圆底烧瓶中，装入1087.6份的水、1.3份的Aerosol GPG。将该混合物加热到70℃。在70℃下，加入10％的单体物料，该单体物料由211.7份水、416.9份甲基丙烯酸甲酯、39.0份双丙酮丙烯酰胺、32.2份甲基丙烯酸、3.9份Aerosol GPG和11.7份月桂基硫醇组成，并且再将反应器内容物加热到85℃。在80℃下，加入由0.4份过硫酸铵和28.8份水组成的溶液。

[0627] 在85℃下，在60分钟的时间段中，加入单体物料的剩余部分。在70分钟的时间中，将催化剂物料进料到反应器中，该催化剂物料包含1.0份过硫酸铵和67.3份水。在单体物料添加结束时，使用31.3份水来冲洗物料罐，并加入反应器。维持85℃的温度20分钟，之后将反应混合物冷却至80℃。在80℃下，使用24.4份25％氨水溶液与41.4份水混合来中和乳液。随后将反应混合物在80℃下再保持20分钟，然后冷却至室温。使用水将乳液的固体含量调节到25％。

[0628] 所获得的乳液具有25.1％的固体含量和8.0的pH。

[0629] 聚合物乳液5B

[0630] 向装配有冷凝器、温度计和机械搅拌器的圆底烧瓶中，添加1.50份的水和49.11份如低聚物5A中所描述而制得的低聚物。将反应器的内容物加热到60℃。

[0631] 加入33％的单体物料，该单体物料由2.77份衣康酸二甲酯、11.08份丙烯酸丁酯和13.84份衣康酸二丁酯组成，然后将乳液搅拌15分钟。接下来，加入0.03份70重量％的叔丁基过氧化氢浆料和0.13份的水，然后加入30％的0.07份异-抗坏血酸在2.73份水中的溶液。温度达到73℃之后，将该批料搅拌10分钟，并冷却至60℃。接下来，加入剩余

单体物料的50%，然后加入4.74份水，并且使乳液搅拌15分钟。加入0.03份70重量%的叔丁基过氧化氢浆料和0.13份水的浆料，然后加入30%的异－抗坏血酸溶液。温度达到69℃后，将混合物再混合10分钟。加入6.71份水，并将该批料冷却至60℃。接下来，加入单体物料的剩余部分，将混合物搅拌15分钟，并加入0.03份70重量%的叔丁基过氧化氢浆料、0.13份水，然后加入30%的异－抗坏血酸溶液。反应混合物达到68℃后，使乳液在该温度下搅拌30分钟，之后将乳液冷却至65℃。

[0632] 加入第二单体物料，该第二单体物料由0.06份双丙酮丙烯酰胺、2.03份丙烯酸丁酯和0.98份甲基丙烯酸甲酯组成。接下来，加入0.01份70重量%的叔丁基过氧化氢浆料和0.04份水，然后加入剩余的异－抗坏血酸溶液。允许温度漂移15分钟，之后再将该批料冷却至65℃。在65℃下，加入0.04份70重量%叔丁基过氧化氢浆料和0.06份水的浆料，然后加入0.03份异－抗坏血酸在1.30份水中的溶液。将该批料冷却至30℃，并加入0.50份水。在30℃下，加入0.61份的己二酸二酰肼和0.90份水。使用水将乳液的固体含量调整到44%。

[0633] 所获得的乳液具有44.0%的固体含量和7.8的pH。

[0634] 实施例6

[0635] 聚合物乳液6B

[0636] 向装配有冷凝器、温度计和机械搅拌器的圆底烧瓶中，添加1.50份的水和49.11份如上面低聚物5A中所描述而制得的低聚物。将反应器的内容物加热到60℃。

[0637] 加入33%的单体物料，该单体物料由2.77份衣康酸单丁酯、11.08份丙烯酸丁酯和6.41份衣康酸二甲酯、7.43份衣康酸二丁酯组成，然后将乳液搅拌15分钟。接下来，加入0.03份70重量%的叔丁基过氧化氢浆料和0.13份的水，然后加入30%的0.07份异－抗坏血酸在2.73份水中的溶液。温度达到73℃之后，将该批料搅拌10分钟，并冷却至60℃。接下来，加入剩余单体物料的50%，然后加入4.74份水，并且使乳液搅拌15分钟。加入0.03份70重量%的叔丁基过氧化氢浆料和0.13份水的浆料，然后加入30%的异－抗坏血酸溶液。温度达到69℃后，将混合物再混合10分钟。加入6.71份水，并将该批料冷却至60℃。接下来，加入单体物料的剩余部分，将混合物搅拌15分钟，并加入0.03份70重量%的叔丁基过氧化氢浆料和0.13份水，然后加入30%的异－抗坏血酸溶液。反应混合物达到68℃后，使乳液在该温度下搅拌30分钟，之后将乳液冷却至65℃。

[0638] 加入第二单体物料，该第二单体物料由0.06份双丙酮丙烯酰胺、2.03份丙烯酸丁酯和0.98份甲基丙烯酸甲酯组成。接下来，加入0.01份70重量%的叔丁基过氧化氢浆料和0.04份水，然后加入剩余的异－抗坏血酸溶液。允许温度漂移15分钟，之后再将该批料冷却至65℃。在65℃下，加入0.04份70重量%叔丁基过氧化氢浆料和0.06份水的浆料，然后加入0.03份异－抗坏血酸在1.30份水中的溶液。将该批料冷却至30℃，并加入0.50份水。在30℃下，加入0.61份的己二酸二酰肼和0.90份水。使用水将乳液的固体含量调整到44%。

[0639] 所获得的乳液具有44.0%的固体含量和7.8的pH。

[0640] 实施例7

[0641] 完全按照上面实施例6中所描述制备乳液，除了在制备聚合物组分（聚合物乳液7B）时单体物料由以下组成：11.08份丙烯酸丁酯、4.86份衣康酸二甲酯和8.98份衣康酸

二丁酯。

[0642] 所获得的乳液具有 44.0％的固体含量和 7.8 的 pH。

[0643] 实施例 8（乙烯基珠粒）

[0644] 实施例 8

[0645] 向装配有冷凝器、温度计、氮气进口和机械搅拌器的圆底烧瓶中，装入 950 份去矿物质水（DMW）、1.6 份硫酸钠（NS）和 7.9 份 20 重量％的聚丙烯酸（PAA）（重均分子量（MW）＝ 100000g/ 摩尔）的溶液。在不断搅拌和氮气吹扫下，加入分散的相，该分散的相由 253 份甲基丙烯酸甲酯（MMA）、190 份衣康酸二丁酯（DBI）、190 份苯乙烯（STY）、9.48 份二月桂基过氧化物（DLP）和 1.58 份十二烷基硫醇（DDM）组成。将反应器内容物加热到 75℃，并允许聚合 5 小时的时间。接下来，将温度提高到 90℃，并允许反应器内容物再搅拌一个小时。接下来，将所获得的聚合混合物冷却到室温。

[0646] 将聚合物珠粒与连续相分离，并用水洗涤，在 40℃下放置干燥。由此获得的聚合物具有 267mm 的颗粒尺寸和用 DSC 测定的 61℃的 Tg。

[0647] 其他实施例

[0648] 实施例 9 至 38

[0649] 各种实施方式的其他实施例可以根据下面的一般方法 E、F 和 G 并参考下表 1-3 来制备。表中的百分数基本上引用为最接近的百分数和 / 或 2 位有效数字（significant figure），因此由于舍入误差而这些百分数可以总和不为 100％。

[0650] 一般方法 E（用于序列乙烯基聚合物）

[0651] 本文中实施例 9 至 18 中使用的单体的总重量可以与制备实施例 1 所使用的总量相同。因此为方便起见，在这些实施例中所使用的单体的量可被表示为在第一单体物料和第二单体物料二者中所使用的总单体的重量百分数。第一单体物料（用于制备聚合物的低 Tg 部分）由与实施例 1（或随后更改的）中所描述的成分相同的成分组成，除了单体可以是：z1％的单体 Z1、y1％的单体 Y1、x1％的单体 X1 和 / 或 w1％的单体 W1。可以在实施例 1 中所描述的条件下向实施例 1 中所描述的设备和其中描述的预进料中添加相同初始量的第一单体物料，然后可以加入第一单体物料的剩余部分，并且反应如实施例 1（或随后更改的）中所描述地进行，直到可以加入第二单体物料。第二单体物料（用于制备聚合物的高 Tg 部分）由与实施例 1（或随后更改的）中所描述的成分相同的成分组成。除了单体可以是：z2％的单体 Z2、y2％的单体 Y2、x2％的单体 X2 和 / 或 w2％的单体 W2。

[0652] 可以参考表 1 如实施例 1 中所描述（或随后更改的）进行该过程的剩余部分，以获得与实施例 1 中所描述的相类似的乙烯基序列聚合物。低 Tg 聚合物 A 的总量与高 Tg 聚合物 B 的总量的相对重量比（R）分别也给出于表 2 中，并且如果需要的话，可以通过调节用于制备聚合物 B 的单体的总重量与用于制备聚合物 A 的总重量之比，来更改实施例 1 中所描述的方法。

[0653] 式 1 单体的总量（作为单体 A+B 的总量的百分数 T 也给出于表 1 中）

[0654] 用于低聚物 / 聚合物的一般方法 F

[0655] 实施例 19 至 28 中使用的单体的总重量可以与制备实施例 4 的每个部分（低聚物实施例 4A 和聚合物实施例 4B）所使用的总量相同。因此为方便起见，在这些实施例中所使用的单体的量可被表示为低聚物（在方法 F1 中）和聚合物（在方法 F2 中）的各个总单体

的重量百分数。

[0656] 低聚物(F1)

[0657] (用于制备低聚物的)单体物料由与实施例4A(或随后更改的)中所描述的成分相同的成分组成,除了单体可以是:z3%的单体Z3、y3%的单体Y3、x3%的单体X3和/或w3%的单体W3。可以在实施例4A中所描述的条件下向实施例4A中所描述的设备添加单体物料,并且可以参考表2如实施例4A(或随后更改的)中所描述继续进行反应,以获得与实施例4A中所描述的相类似的低聚物,该低聚物可以用于下面的步骤F2中。

[0658] 聚合物乳液(F2)

[0659] (用于制备聚合物的)单体物料由与实施例4B(或随后更改的)中所描述的成分相同的成分组成,除了单体可以是:z4%的单体Z4、y4%的单体Y4、x4%的单体X4和/或w4%的单体W4。可以在实施例4B中所描述的条件下向实施例4B中所描述的设备添加单体物料以及来自步骤F1的低聚物,并且可以参考表2如实施例4B(或随后更改的)中所描述继续进行反应,以获得与实施例4中所描述的相类似的低聚物-聚合物。

[0660] 式1单体的总量(作为单体C+D的总量的百分数T'也给出于表2中)

[0661] 一般方法G(用于珠粒)

[0662] 实施例29至38中所使用的单体的总重量可以与用于制备实施例8所使用的总量相同,并因此为方便起见,在这些实施例中所使用的单体的量也可以表示为总单体的重量百分数或绝对质量。

[0663] 可以向实施例8中所描述的设备中添加单体混合物(用于制备聚合物珠粒),该单体混合物由与实施例8(或随后更改的)中所描述的成分相同的成分组成,除了单体可以是:z5%的单体Z5、y5%的单体Y5、x5%的单体X5和/或w5%的单体W5。可以参考表3如实施例8中所描述继续进行该方法的剩余部分,以获得与实施例8中所描述的相类似的聚合珠粒。

[0664]

表 1：实施例 9 至 18 – 序列聚合物（参见方法 E）

Ex	低Tg 聚合物A (A的%)								高Tg 聚合物B (B的%)								R (A与B)	(A+B的) T %
	z1%	Z1	y1%	Y1	x1%	X1	W1%	W1	z2%	Z2	y2 %	Y2	x2%	X2	w2%	W2		
9	10	MAA	40	MMA	50	DPI	-	-	5	MAA	10	MMA	30	DMI	55	BMA	40/60	20
10	0.1	AA	39.9	MA	60	DHI	-	-	10	MAA	10	MMA	20	DEI	60	BMA	45/55	27
11	0.5	MSA	20	EA	65	DOI	14.5	BA	15	MA	5	EMA	50	DPrI	30	OA	50/50	23.5
12	1	CEA	36	PA	30	DBI	33	MA	60	DBzI	30	BA	10	DEI	-	-	55/45	43.5
13	2	MBI	80	MMA	18	EMA	-	-	85	DPhI	10	EMA	5	DMI	-	-	60/40	34
14	4	IA	22	BA	74	DBI	-	-	90	DHI	10	URED	-	-	-	-	65/35	79.6
15	6	IAn	20	MMA	64	DBI	10	EA	5	MAA	10	BA	65	DMI	20	BA	70/30	44.8
16	7.5	MMalA	40	EMA	52.5	BPI	-	-	10	AA	40	EHA	10	DEI	40	BMA	75/25	39.4
17	8	PHEMA	30	MMA	42	BHI	20	EA	1	MMA	49	OA	50	DMI			80/20	33.6
18	3	AMPS	35	PA	62	HOI	-	-	2	MSA	30	DBI	30	DEI	38	EA	90/10	58.8

[0665]

表 2：实施例 19 至 28 – 低聚物-聚合物（参见方法 F1 和 F2）

Ex	低聚物C (C的%)								聚合物D (D的%)								R' (C与D)	(C+ D的)T %
	z3%	Z3	y3%	Y3	x3%	X3	w3%	W3	z4%	Z4	y4%	Y4	x4%	X4	w4%	W4		
19	20	AA	80	EMA	-	-	-	-	80	D(EH)I	20	DEI	-	-	-	-	5:95	76
20	10	AA	10	DBI	70	DMI	10	DAAM	50	DBI	40	BA	10	DAAM	-	-	10:90	46
21	5	MSA	70	MMA	20	DEI	5	DAAM	30	DOI	55	OA	5	DAAM	10	BA	30:70	21
22	20	CEA	50	MA	30	DMI	-	-	40	DHI	60	BMA	-	-	-	-	40:60	24
23	5	MBI	20	EA	70	DPrI	5	DAAM	50	DPI	40	BA	10	DEI	-	-	50:50	25
24	3	IA	10	MMA	80	DBI	7	DAAM	50	DMI	40	EA	10	MA			60:40	48
25	4	IAn	30	MMA	60	DBI	6	DAAM	50	DBI	40	PA	10	MMA			70:30	57
26	5	MMalA	50	MMA	40	DPI	5	DAAM	50	DBI	40	DMI	10	BMA			75:25	42.5
27	2	PHEMA	60	MMA	30	DMI	8	DAAM	50	DBI	20	EA	20	BMA	10	DAAM	50:50	25
28	40	AMPS	20	MMA	40	DBI	-	-	50	DEI	40	MMA	10	BMA			50:50	20

[0666]

表 3：实施例 29 至 38-聚合物珠粒（参见方法 G）

Ex	z3%	Z3	y3%	Y3	x3%	X3	w3%	W3
29	40	MMA	30	DBI	20	STY	10	BA
30	10	AA	50	DHI	20	MSTY	10	OA
31	30	EMA	40	DOI	30	OA	-	-
32	35	MMA	20	DBzI	25	STY	10	DBI
33	10	EA	60	DPhI	30	STY	-	-
34	20	MA	30	DBI	30	STY	10	DMI
35	25	MMA	35	DBI	25	STY	5	DEI
36	40	MMA	30	BPI	20	MSTY	-	-
37	40	EMA	30	BHI	30	MSTY	-	-
38	35	MMA	25	HOI	30	STY	-	-

[0667] 实施例 39 至 43 和对比例 CompI 至 V

[0668] 实施例 39 含湿－粘附促进单体的 DBI 聚合物

[0669] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入 559.2 份去矿物质水、5.5 份碳酸氢钠、29.4 份 30 重量％的十二烷基硫酸钠在水中的溶液和 1.1 份过硫酸钠。将反应器内容物加热至 70℃。在 50℃下，加入 10％的单体物料，该单体物料由 510.3 份去矿物质水、12.5 份 30 重量％的十二烷基硫酸钠在水中的溶液、516.7 份丙烯酸丁酯、33.0 份甲基

丙烯酸、494.7 份衣康酸二丁酯和 110.0 份 50 重量％的 N-(2- 甲基丙烯酰氧乙基）亚乙基脲在水中的溶液（Plex 6852-0，来自 Evonik）组成。由于单体聚合的放热性质，温度升高到 85℃（如果放热不足，则可以对混合物稍微加热来达到 85℃的温度）。在 85℃下，开始添加包含剩余的 90％原始物料的单体物料和引发剂物料，该引发剂物料由 124.5 份去矿物质水、4.4 份过硫酸钠和 2.2 份 30 重量％的十二烷基硫酸钠的水中的溶液组成。两种物料都在 120 分钟的时间段中添加。在单体进料结束时，用 19.7 份去矿物质水冲洗物料罐，并且在 85℃下将该混合物再搅拌 35 分钟。

[0670]　接下来，将乳液冷却至 45℃，并加入 0.7 份异抗坏血酸在 12.5 份去矿物质水中的溶液，然后加入 1.0 份 70 重量％的叔丁基过氧化氢在水中的溶液、1.5 份去矿物质水和 0.3 份 30 重量％的十二烷基硫酸钠的水中的溶液。在 45℃下将整个反应器内容物搅拌 30 分钟。

[0671]　将乳液冷却至室温，并加入 55.0 份 25％氨水溶液与去矿物质水的等量混合物。使用去矿物质水调节乳液的固体含量至 45％。

[0672]　实施例 40 含 DBI 和苯乙烯的聚合物

[0673]　向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入 644.0 份去矿物质水、0.5 份碳酸氢钠、13.3 份 30 重量％的十二烷基硫酸钠在水中的溶液和 0.8 份过硫酸钠。将反应器内容物加热至 80℃，并在 80℃下搅拌 5 分钟。接下来，在由于聚合的放热性质而使温度升高到大约 90℃之后，加入 10％的单体物料，该单体物料由 132.9 份去矿物质水、13.0 份 30 重量％的十二烷基硫酸钠在水中的溶液、23.3 份甲基丙烯酸、280.1 份衣康酸二丁酯和 280.1 份苯乙烯组成。一旦达到 90℃的温度，开始添加剩余单体物料和引发剂物料，该引发剂物料由 58.7 份去矿物质水、2.5 份过硫酸钠和 3.7 份 30 重量％的十二烷基硫酸钠在水中的溶液组成。两种物料都在 2 小时的时间段中添加。在单体进料结束时，用 10.4 份去矿物质水冲洗物料罐。将反应器内容物的温度冷却到 80℃，然后在 30 分钟的时间段中加入 1.8 份异抗坏血酸溶解于 26.5 份去矿物质水中的溶液（使用氨溶液将其调至 pH 8.5），在该时间段中分两次加入 2.8 份叔丁基过氧化氢与 5.6 份去矿物质水的混合物；一次是在异抗坏血酸进料开始时，并且另一次在 15 分钟后。

[0674]　在进料结束时，将混合物在 80℃下搅拌 30 分钟，并使用 25 重量％的氨水溶液使 pH 上升到 7.2。再搅拌 30 分钟后，将该批料冷却到室温。使用去矿物质水将固体含量调节到 40％。

[0675]　对比例 I 含 BA 和苯乙烯的聚合物

[0676]　向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入 639.5 份去矿物质水、0.5 份碳酸氢钠和 13.3 份 30 重量％的十二烷基硫酸钠在水中的溶液。将反应器内容物加热至 80℃，然后加入 0.8 份过硫酸钠在 4.5 份去矿物质水中的溶液，并在 80℃下搅拌 5 分钟。接下来，在由于聚合的放热性质而使温度升高到大约 90℃之后，加入 10％的单体物料，该单体物料由 132.9 份去矿物质水、13.0 份 30 重量％的十二烷基硫酸钠在水中的溶液、23.3 份甲基丙烯酸、280.1 份丙烯酸丁酯和 280.1 份苯乙烯组成。一旦达到 90℃的温度，开始添加剩余单体物料和引发剂物料，该引发剂物料由 58.7 份去矿物质水、2.5 份过硫酸钠和 3.7 份 30 重量％的十二烷基硫酸钠在水中的溶液组成。两种物料都在 2 小时的时间段中添加。在单体进料结束时，用 10.4 份去矿物质水冲洗物料罐。将反应器内容物的温度冷却到 80℃，

然后在 30 分钟的时间段中加入 1.8 份异抗坏血酸溶解于 26.5 份去矿物质水中的溶液（使用氨溶液将其调至 pH 8.5），在该时间段中分两次加入 2.8 份叔丁基过氧化氢与 5.6 份去矿物质水的混合物；一次是在异抗坏血酸进料开始时，并且另一次在 15 分钟后。

[0677] 在进料结束时，将混合物在 80℃下搅拌 30 分钟，并使用 25 重量％的氨水溶液使 pH 上升到 7.2。再搅拌 30 分钟后，将该批料冷却到室温。使用去矿物质水将固体含量调节到 40％。

[0678] 实施例 41 含 DBI 和 MMA 的聚合物

[0679] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入 639.5 份去矿物质水、0.5 份碳酸氢钠和 13.3 份 30 重量％的十二烷基硫酸钠在水中的溶液。将反应器内容物加热至 80℃，然后加入 0.8 份过硫酸钠在 4.5 份去矿物质水中的溶液，并在 80℃下搅拌 5 分钟。接下来，在由于聚合的放热性质而使温度升高到大约 90℃之后，加入 10％的单体物料，该单体物料由 132.9 份去矿物质水、13.0 份 30 重量％的十二烷基硫酸钠在水中的溶液、23.3 份甲基丙烯酸、280.1 份衣康酸二丁酯和 280.1 份甲基丙烯酸甲酯组成。一旦达到 90℃的温度，开始添加剩余单体物料和引发剂物料，该引发剂物料由 58.7 份去矿物质水、2.5 份过硫酸钠和 3.7 份 30 重量％的十二烷基硫酸钠在水中的溶液组成。两种物料都在 2 小时的时间段中添加。在单体进料结束时，用 10.4 份去矿物质水冲洗物料罐。将反应器内容物的温度冷却到 80℃，然后在 30 分钟的时间段中加入 1.8 份异抗坏血酸溶解于 26.5 份去矿物质水中的溶液（使用氨溶液将其调至 pH 8.5），在该时间段中分两次加入 2.8 份叔丁基过氧化氢与 5.6 份去矿物质水的混合物；一次是在异抗坏血酸进料开始时，并且另一次在 15 分钟后。

[0680] 在进料结束时，将混合物在 80℃下搅拌 30 分钟，并使用 25 重量％的氨水溶液使 pH 上升到 7.2。再搅拌 30 分钟后，将该批料冷却到室温。使用去矿物质水将固体含量调节到 40％。

[0681] 对比例 II 含 BA 和 MMA 的聚合物

[0682] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入 639.5 份去矿物质水、0.5 份碳酸氢钠和 13.3 份 30 重量％的十二烷基硫酸钠在水中的溶液。将反应器内容物加热至 80℃，然后加入 0.8 份过硫酸钠在 4.5 份去矿物质水中的溶液，并在 80℃下搅拌 5 分钟。接下来，在由于聚合的放热性质而使温度升高到大约 90℃之后，加入 10％的单体物料，该单体物料由 132.9 份去矿物质水、13.0 份 30 重量％的十二烷基硫酸钠在水中的溶液、23.3 份甲基丙烯酸、280.1 份丙烯酸丁酯和 280.1 份甲基丙烯酸甲酯组成。一旦达到 90℃的温度，开始添加剩余单体物料和引发剂物料，该引发剂物料由 58.7 份去矿物质水、2.5 份过硫酸钠和 3.7 份 30 重量％的十二烷基硫酸钠在水中的溶液组成。两种物料都在 2 小时的时间段中添加。在单体进料结束时，用 10.4 份去矿物质水冲洗物料罐。将反应器内容物的温度冷却到 80℃，然后在 30 分钟的时间段中加入 1.8 份异抗坏血酸溶解于 26.5 份去矿物质水中的溶液（使用氨溶液将其调至 pH 8.5），在该时间段中分两次加入 2.8 份叔丁基过氧化氢与 5.6 份去矿物质水的混合物；一次是在异抗坏血酸进料开始时，并且另一次在 15 分钟后。

[0683] 在进料结束时，将混合物在 80℃下搅拌 30 分钟，并使用 25 重量％的氨水溶液使 pH 上升到 7.2。再搅拌 30 分钟后，将该批料冷却到室温。使用去矿物质水将固体含量调节到 40％。

[0684] 对比例III 含DMI的共聚物

[0685] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入639.5份去矿物质水、0.5份碳酸氢钠和13.3份30重量％的十二烷基硫酸钠在水中的溶液。将反应器内容物加热至80℃，然后加入0.8份过硫酸钠在4.5份去矿物质水中的溶液，并在80℃下搅拌5分钟。接下来，在由于聚合的放热性质而使温度升高到大约90℃之后，加入10％的单体物料，该单体物料由132.9份去矿物质水、13.0份30重量％的十二烷基硫酸钠在水中的溶液、23.3份甲基丙烯酸、414.3份衣康酸二甲酯和145.9份丙烯酸乙酯组成。一旦达到90℃的温度，开始添加剩余单体物料和引发剂物料，该引发剂物料由58.7份去矿物质水、2.5份过硫酸钠和3.7份30重量％的十二烷基硫酸钠在水中的溶液组成。两种物料都在2小时的时间段中添加。

[0686] 单体进料110分钟后，乳液凝胶化，这表明，较之低级衣康酸酯诸如DMI，高级衣康酸酯诸如DBI得到了优异的性质。

[0687] 实施例42 含DBI的h/s序列共聚物

[0688] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入426.6份去矿物质水、0.4份碳酸氢钠、31.3份20重量％的磷酸官能表面活性剂的水溶液(Fosfodet FAZ109V，来自KAO)和0.4份25重量％氨溶液。将反应器内容物加热到80℃，然后加入0.4份的过硫酸钠在7.9份的去矿物质水中的溶液，之后加入10％的第一单体物料，该第一单体物料由115.1份去矿物质水、35.9份20重量％的磷酸官能表面活性剂的水溶液(Fosfodet FAZ109V，来自KAO)、0.6份碳酸氢钠、15.7份丙烯酸、90.1份衣康酸二丁酯和286.0份甲基丙烯酸甲酯组成。由于单体聚合所形成的热量，温度升高至90℃，然后开始添加第一单体物料的剩余部分。在45分钟的时间段中添加第一单体物料。同时，在45分钟的时间段中加入60％的引发剂物料，该引发剂物料由36.3份去矿物质水、0.2份碳酸氢钠和2.0份过硫酸钠组成。在单体进料结束时，使用7.6份去矿物质水冲洗物料罐。

[0689] 接下来，在15分钟的时间段中，加入0.9份25重量％氨溶液与1.2份去矿物质水的混合物。第一单体进料结束后45分钟时，开始添加第二单体物料，该第二单体物料由76.7份去矿物质水、23.9份20重量％的磷酸官能表面活性剂的水溶液(Fosfodet FAZ109V，来自KAO)、0.4份碳酸氢钠、10.5份丙烯酸、198.5份衣康酸二丁酯和52.2份丙烯酸丁酯组成。在30分钟的时间段中加入该物料和同时添加的引发剂物料的剩余部分。第二单体进料完成后，使用15.3份去矿物质水冲洗物料罐，并允许混合物在90℃下再搅拌30分钟。

[0690] 最后，将乳液冷却至室温，使用去矿物质水将固体含量调整到45％，并使用25量％氨溶液将pH调整到7.5。

[0691] 对比例IV 无DBI的h/s序列共聚物

[0692] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入426.6份去矿物质水、0.4份碳酸氢钠、31.3份20重量％的磷酸官能表面活性剂的水溶液(Fosfodet FAZ109V，来自KAO)和0.4份25重量％氨溶液。将反应器内容物加热到80℃，然后加入0.4份的过硫酸钠在7.9份的去矿物质水中的溶液，之后加入10％的第一单体物料，该第一单体物料由115.1份去矿物质水、35.9份20重量％的磷酸官能表面活性剂的水溶液(Fosfodet FAZ109V，来自KAO)、0.6份碳酸氢钠、15.7份丙烯酸、90.1份丙烯酸丁酯和286.0份甲基丙烯酸甲酯组

成。由于单体聚合所形成的热量，温度升高至 90℃，然后开始添加第一单体物料的剩余部分。在 45 分钟的时间段中添加第一单体物料。同时，在 45 分钟的时间段中加入 60％的引发剂物料，该引发剂物料由 36.3 份去矿物质水、0.2 份碳酸氢钠和 2.0 份过硫酸钠组成。在单体进料结束时，使用 7.6 份去矿物质水冲洗物料罐。

[0693] 接下来，在 15 分钟的时间段中，加入 0.9 份 25 重量％氨溶液与 1.2 份去矿物质水的混合物。第一单体进料结束后 45 分钟时，开始添加第二单体物料，该第二单体物料由 76.7 份去矿物质水、23.9 份 20 重量％的磷酸官能表面活性剂的水溶液 (Fosfodet FAZ109V，来自 KAO)、0.4 份碳酸氢钠、10.5 份丙烯酸、250.7 份丙烯酸丁酯组成。在 30 分钟的时间段中加入该物料和同时添加的引发剂物料的剩余部分。第二单体进料完成后，使用 15.3 份去矿物质水冲洗物料罐，并允许混合物在 90℃下再搅拌 30 分钟。

[0694] 最后，将乳液冷却至室温，使用去矿物质水将固体含量调整到 45％，并使用 25 量％氨溶液将 pH 调整到 7.5。

[0695] 实施例 43 含 DBI 的 s/h 序列

[0696] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入 426.6 份去矿物质水、0.4 份碳酸氢钠、31.3 份 20 重量％的磷酸官能表面活性剂的水溶液 (Fosfodet FAZ109V，来自 KAO) 和 0.4 份 25 重量％氨溶液。将反应器内容物加热到 80℃，然后加入 0.4 份的过硫酸钠在 7.9 份的去矿物质水中的溶液，之后加入 10％的第一单体物料，该第一单体物料由 114.3 份去矿物质水、37.9 份 20 重量％的磷酸官能表面活性剂的水溶液 (Fosfodet FAZ109V，来自 KAO)、0.6 份碳酸氢钠、18.3 份丙烯酸、420.6 份衣康酸二丁酯、18.3 份 50 重量％的 N-(2- 甲基丙烯酰氧乙基) 亚乙基脲在水中的溶液 (Plex 6852-0，来自 Evonik) 和 9.1 份甲基丙烯酸甲酯组成。由于单体聚合所形成的热量，温度升高至 90℃，然后开始添加第一单体物料的剩余部分。在 45 分钟的时间段中添加第一单体物料。同时，在 45 分钟的时间段中加入 60％的引发剂物料，该引发剂物料由 36.3 份去矿物质水、0.2 份碳酸氢钠和 2.0 份过硫酸钠组成。在单体进料结束时，使用 7.6 份去矿物质水冲洗物料罐。

[0697] 接下来，在 15 分钟的时间段中，加入 0.9 份 25 重量％氨溶液与 1.2 份去矿物质水的混合物。第一单体进料结束后 45 分钟时，开始添加第二单体物料，该第二单体物料由 77.5 份去矿物质水、21.9 份 20 重量％的磷酸官能表面活性剂的水溶液 (Fosfodet FAZ109V，来自 KAO)、0.4 份碳酸氢钠、7.8 份丙烯酸、45.0 份衣康酸二丁酯和 143.0 份甲基丙烯酸甲酯组成。在 30 分钟的时间段中加入该物料和同时添加的引发剂物料的剩余部分。第二单体进料完成后，使用 15.3 份去矿物质水冲洗物料罐，并允许混合物在 90℃下再搅拌 30 分钟。

[0698] 最后，将乳液冷却至室温，使用去矿物质水将固体含量调整到 45％，并使用 25 量％氨溶液将 pH 调整到 7.5。

[0699] 对比例 V 无 DBI 的 s/h 序列

[0700] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入 426.6 份去矿物质水、0.4 份碳酸氢钠、31.3 份 20 重量％的磷酸官能表面活性剂的水溶液 (Fosfodet FAZ109V，来自 KAO) 和 0.4 份 25 重量％氨溶液。将反应器内容物加热到 80℃，然后加入 0.4 份的过硫酸钠在 7.9 份的去矿物质水中的溶液，之后加入 10％的第一单体物料，该第一单体物料由 114.3 份去矿物质水、37.9 份 20 重量％的磷酸官能表面活性剂的水溶液 (Fosfodet FAZ109V，来

自KAO)、0.6份碳酸氢钠、18.3份丙烯酸、420.6份丙烯酸丁酯、18.3份50重量%的N-(2-甲基丙烯酰氧乙基)亚乙基脲在水中的溶液(Plex 6852-0,来自Evonik)和9.1份甲基丙烯酸甲酯组成。由于单体聚合所形成的热量,温度升高至90℃,然后开始添加第一单体物料的剩余部分。在45分钟的时间段中添加第一单体物料。同时,在45分钟的时间段中加入60%的引发剂物料,该引发剂物料由36.3份去矿物质水、0.2份碳酸氢钠和2.0份过硫酸钠组成。在单体进料结束时,使用7.6份去矿物质水冲洗物料罐。接下来,在15分钟的时间段中,加入0.9份25重量%氨溶液与1.2份去矿物质水的混合物。

[0701] 第一单体进料结束后45分钟时,开始添加第二单体物料,该第二单体物料由77.5份去矿物质水、21.9份20重量%的磷酸官能表面活性剂的水溶液(Fosfodet FAZ109V,来自KAO)、0.4份碳酸氢钠、7.8份丙烯酸、45.0份丙烯酸丁酯和143.0份甲基丙烯酸甲酯组成。在30分钟的时间段中加入该物料和同时添加的引发剂物料的剩余部分。第二单体进料完成后,使用15.3份去矿物质水冲洗物料罐,并允许混合物在90℃下再搅拌30分钟。

[0702] 最后,将乳液冷却至室温,使用去矿物质水将固体含量调整到45%,并使用25量%氨溶液将pH调整到7.5。

[0703] 为了说明本发明,测定膜性质,用来选择上面描述的聚合物乳液。聚合物乳液与8%的丁基二甘醇一起配制,以使它们成膜。将这些膜浇铸并在室温下干燥4小时,并在50℃下再干燥34小时。结果示于下面表4中。

[0704] 表4

[0705] 膜性质:“5”表示优异的耐性,对膜无损伤,”1”表示膜完全损坏

[0706]

	水斑点测试		耐粘连性	耐污性(16小时)*			König硬度(s)
	1小时	16小时		EtOH	Andy	咖啡	
实施例40	5	5	3	5	4	5	201
对比例I	5	4	1	4	2	5	110
实施例41	5	5	5	4	4	5	173
对比例II	5	3	3	3	2	4	115
对比例III	由于处理时不稳定而无法制备						
实施例42	5	5	5	3	4	5	70
对比例IV	5	5	3	3	2	4	60
实施例43	5	5	4	3	3	5	115
对比例V	5	5	0	3	2	4	8

[0707] *如斑点测试中测定。

[0708] 在所有情况下(除对比例III外),水斑点良好。在所有情况下,本发明的聚合物

的耐粘连性和 König 硬度都比它们的最相似的对比例要好。尽管对咖啡和乙醇的耐性在本发明的聚合物和对比例之间类似，但本发明的聚合物对肥皂（Andy）的耐性显然更好。

[0709] 实施例 44 MMA/DMI/AA

[0710] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入 394.0 份 2-丁酮。将反应器内容物加热至 80℃。一旦达到聚合温度，加入 13.3 份偶氮二（2-甲基丁腈），并且开始添加单体物料和催化剂物料。单体物料由 244.4 份甲基丙烯酸甲酯、244.4 份衣康酸二甲酯和 244.4 份丙烯酸组成。催化剂物料由溶解于 125.9 份 2-丁酮的 31.1 份偶氮二（2-甲基丁腈）组成。两种物料都在 180 分钟的时间段中添加。

[0711] 在进料结束时，加入 2.5 份偶氮二（2-甲基丁腈），并且在 80℃下将混合物再搅拌 150 分钟。将混合物冷却至室温。

[0712] 向 615.8 份聚合物溶液中，添加 99.6 份 25 重量％氨水溶液与 1080.5 份水的混合物。接下来，在 50℃下减压下去除 2-丁酮。使用去矿物质水调整固体含量至 22.5％，并且使用 25 重量％氨水溶液将 pH 调整到 8.6-8.8。

[0713] 最终聚合物溶液具有 22.5％的固体含量和 8.7 的 pH。

[0714] 实施例 45 S/DMI/AA

[0715] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入 394.0 份 2-丁酮。将反应器内容物加热至 80℃。一旦达到聚合温度，加入 13.3 份偶氮二（2-甲基丁腈），并且开始添加单体物料和催化剂物料。单体物料由 244.4 份甲基丙烯酸甲酯、244.4 份衣康酸二甲酯和 244.4 份丙烯酸组成。催化剂物料由溶解于 125.9 份 2-丁酮的 31.1 份偶氮二（2-甲基丁腈）组成。两种物料都在 180 分钟的时间段中添加。

[0716] 在进料结束时，加入 2.5 份偶氮二（2-甲基丁腈），并且在 80℃下将混合物再搅拌 150 分钟。将混合物冷却至室温。

[0717] 向 546.1 份聚合物溶液中，添加 105.4 份 25 重量％氨水溶液与 1144.1 份水的混合物。接下来，在 50℃下减压下去除 2-丁酮。使用去矿物质水调整固体含量至 22.5％，并且使用 25 重量％氨水溶液将 pH 调整到 8.6-8.8。

[0718] 最终聚合物溶液具有 22.4％的固体含量和 8.6 的 pH。

[0719] 实施例 46 MMA/DMI/AA

[0720] 向装配有温度计和搅拌器的高压反应器中，装入 500.0 份 2-丁酮。将反应器内容物加热至 140℃。一旦达到聚合温度，加入 2.9 份二叔丁基过氧化物和 40 份 2-丁酮。5 分钟后开始添加单体物料。单体物料由 331.8 份甲基丙烯酸甲酯、331.8 份衣康酸二甲酯、331.8 份丙烯酸、5.7 份二叔丁基过氧化物和 6.6 份过苯甲酸叔丁酯组成，并且单体物料是在 140℃下在 180 分钟的时间段中添加的。

[0721] 在进料结束时，用 90.9 份 2-丁酮冲洗物料罐。单体进料完成后 45 分钟，添加溶解于 40 份 2-丁酮中的 2.5 份过苯甲酸叔丁酯，并且将混合物在 140℃下再搅拌 45 分钟。接下来，加入溶解于 40 份 2-丁酮中的 2.5 份过苯甲酸叔丁酯，并且将混合物在 140℃下再搅拌 135 分钟。

[0722] 将混合物冷却至室温。

[0723] 向 619.3 份聚合物溶液中，添加 99.3 份 25 重量％氨水溶液与 1077.3 份水的混合物。接下来，在 50℃下减压下去除 2-丁酮。使用去矿物质水调整固体含量至 22.5％，并且

使用 25 重量%氨水溶液将 pH 调整到 8.6-8.8。

[0724] 最终聚合物溶液具有 22.5%的固体含量和 8.6 的 pH。

[0725] 实施例 47 S/DMI/AA

[0726] 向装配有温度计和搅拌器的高压反应器中，装入 500.0 份 2- 丁酮。将反应器内容物加热至 140℃。一旦达到聚合温度，加入 4.4 份二叔丁基过氧化物和 40 份 2- 丁酮。5 分钟后开始添加单体物料。单体物料由 331.8 份苯乙烯、331.8 份衣康酸二甲酯、331.8 份丙烯酸、8.6 份二叔丁基过氧化物和 10.0 份过苯甲酸叔丁酯组成，并且单体物料是在 140℃下在 180 分钟的时间段中添加的。

[0727] 在进料结束时，用 90.9 份 2- 丁酮冲洗物料罐。单体进料完成后 45 分钟，添加溶解于 40 份 2- 丁酮中的 2.5 份过苯甲酸叔丁酯，并且将混合物在 140℃下再搅拌 45 分钟。接下来，加入溶解于 40 份 2- 丁酮中的 2.5 份过苯甲酸叔丁酯，并且将混合物在 140℃下再搅拌 135 分钟。

[0728] 将混合物冷却至室温。

[0729] 向 617.8 份聚合物溶液中，添加 99.4 份 25 重量%氨水溶液与 1078.6 份水的混合物。接下来，在 50℃下减压下去除 2- 丁酮。使用去矿物质水调整固体含量至 22.5%，并且使用 25 重量%氨水溶液将 pH 调整到 8.6-8.8。

[0730] 最终聚合物溶液具有 22.5%的固体含量和 8.7 的 pH。

[0731] 实施例 48 使用来自实施例 44 的聚合物的序列聚合

[0732] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中，装入从实施例 44 获得的 128.9 份碱性溶液。将混合物加热到 80℃ ±2℃。

[0733] 一旦达到反应温度，加入 0.2 份过硫酸钠与 0.4 份去矿物质水的混合物。5 分钟后，开始添加单体物料和引发剂物料，该单体物料由 43.8 份甲基丙烯酸甲酯和 43.8 份丙烯酸丁酯组成，该引发剂物料由 10.8 份去矿物质水和 0.4 份过硫酸钠 (使用 25 重量%氨溶液调整到 pH 8)。两种进料应花费 120 分钟。在单体进料结束时，用 1.2 份水冲洗物料罐。两种进料完成后，将该批料在 80℃下再搅拌 30 分钟，之后冷却到 50℃。

[0734] 在 50℃下，加入三分之一的由 0.1 份 70 重量%的叔丁基过氧化氢溶液组成的混合物，然后再加入三分之一的 0.1 份异抗坏血酸在 2.9 份水中的溶液。15 分钟后以及 30 分钟后，加入类似的物料部分，并且将该批料在 50℃下再搅拌 15 分钟。

[0735] 检查 pH，并且如果需要的话使用 25 重量%的氨水溶液调节到 8.4±0.1。将该批料冷却至室温，之后使用去矿物质水将固体含量调节至 48.5% ±1%。

[0736] 实施例 49 使用来自实施例 45 的聚合物的序列聚合

[0737] 采用与实施例 48 中所描述的方法相似的方法来制备实施例 49，其中使用从实施例 45 获得的碱性溶液替换从实施例 44 获得的碱性溶液。所获得的最终乳液是高粘性的，需要稀释剂使固体含量为 35%。

[0738] 实施例 50 使用来自实施例 46 的聚合物的序列聚合

[0739] 采用与实施例 48 中所描述的方法相似的方法来制备实施例 50，其中使用从实施例 46 获得的碱性溶液替换从实施例 44 获得的碱性溶液。

[0740] 实施例 51 使用来自实施例 47 的聚合物的序列聚合

[0741] 采用与实施例 48 中所描述的方法相似的方法来制备实施例 51，其中使用从实施

例 47 获得的碱性溶液替换从实施例 44 获得的碱性溶液。

[0742] 结果（表 5)

[0743]

	SC(%)	粘度 (mPa.s)	pH
实施例 48	47.6	208	8.4
实施例 49	34.8	1006	8.4
实施例 50	48.1	35	8.5
实施例 51	48.1	201	8.4

Abstract

There is described use of a biorenewable copolymers in one or more of: in a topical and/or personal care composition, as a binder for toner, as an encapsulating agent for a colorant, as a hybrid colorant, as additive for sheet moulding compounds, as a plastic pigment, as a filler for composite materials such as concrete, as a filler for coatings and/or waxes; and/or as a spacer in a display; where the biorenewable copolymer comprises (a) at least 8. 5 wt-% preferably >="20" wt-% of a higher itaconate diester (preferably dibutyl itaconate -DBI); (b) less than 23 wt-% acid monomer but also sufficient to have an acid value less than 150 mg KOH/g of polymer, (c) optionally with less than 50 wt-% of other itaconate monomers, and (d) optionally less than 77 wt-%of other monomers not (a) to (c). The DBI may be biorenewable. One embodiment is an aqueous dispersion of vinyl sequential polymer of two phases: A) 40 to 90 wt-% of a vinyl polymer A with Tg from -50 to 30°C; and B) 10 to 60 wt-% of a vinyl polymer B with Tg from 50 to 130°C; where DBI is used to prepare A and/or B and polymer A has from 0.1 to 10 wt-% of at least one acid-functional olefinically unsaturated monomer.