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(54) **POLYMER, PROCESS AND COMPOSITION**

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(57) **ABSTRACT**

There is described a polymer blend of a first and second polymer comprising: a) a first polymer of: vinyl (co)polymer; alkyd; urethane acrylic copolymer; polyurethane and/or polyester; b) a second copolymer from: b1) optionally at least 10 wt-% of one or derivatives of itaconic acid and/or isomers thereof; b2) up to 20 wt-% of one or more acid functional (or potentially acid functional) monomer(s) and b3) vinyl monomer(s) where wt % of each monomer (b1 to b3) is based on total (b) and where at least one of the first and second polymer is obtained from an itacon-functional monomer such as itaconic acid and/or its derivatives.

POLYMER, PROCESS AND COMPOSITION

[0001] The present invention relates to polymers and polymeric materials obtained and/or obtainable from monomers such as 2-methylidenebutanedioates (also referred to herein as itaconates) and/or from monomers related to itaconates; to a process for making such a polymers and their use to prepare for example coatings, inks and/or adhesives.

[0002] Itaconate ester monomers have been described for very many years and can be obtained from biorenewable sources. However they have not been widely used to make commercial vinyl polymers because they are expensive and often difficult to process.

[0003] Copolymers that comprise more than one phase may be usefully prepared for use as binders. For example aqueous emulsions of sequential polymers and copolymers with oligomer and polymer phases may usefully form coating films having improved properties. Generally such multi-phase systems have been prepared by complicated multi-step processes.

[0004] 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. 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.

[0005] WO2012-084974 (DSM) describes sequential vinyl polymers that may be obtained from a bio-based monomer source such as an itaconate.

[0006] WO2012-084973 (DSM) describes vinyl oligomer/polymer compositions that may be obtained from a bio-based monomer source such as an itaconate.

[0007] US2011-237736 (BASF) describes a two phase aqueous binder composition comprising a polymer and up to 10% of an oligomer to form coatings with improved gloss.

[0008] FR2943351 (Arkema) describes a copolymer of a biomass derived C_{1-4}alkyl methacrylate or C_{1-8}alkylacrylate monomer together with a vinyl aromatic monomer.

[0009] Surprisingly the applicant has found that multiphase polymers may be prepared by physically mixing two or more different aqueous polymer emulsion (where at least one polymer of which is obtained from an itacon-functional monomer). Such blended emulsions may also lead to coatings that have improved film forming properties. It has also been found that single phase systems can be prepared by mixing or blending certain of the different polymer systems described herein.

[0010] Therefore broadly in accordance with a first aspect of the invention there is provided a mixture comprising:

- **[0011]** a) a first polymer selected from one or more from the group consisting of: a vinyl (co)polymer; an alkyd polymer; a urethane acrylic copolymer; a polyurethane; a polyester, combinations and/or mixtures thereof;
- **[0012]** b) a second copolymer obtained and/or obtainable from a second monomer composition comprising:
  - **[0013]** b1) optionally at least 10 wt-% of one or more monomer(s) selected from derivatives of mono-unsaturated itaconic acid or itaconic acid isomers;
  - **[0014]** b2) up to 20 wt-% of one or more acid functional (or potentially acid functional) monomer(s)
  - **[0015]** b3) vinyl monomer(s)
  - **[0016]** where the percentages given for each monomer (b1 to b3) in the second monomer composition is calculated based on the total amount of monomer (b1 to b3) being 100%; and
  - **[0017]** where at least one of the first and second polymer comprises a polymer obtained and/or obtainable from an itacon-functional monomer.

[0018] Where (in a preferred embodiment) the second monomer composition comprises no other monomers other than b1 to b3 above then the total amount of monomers b1 to b3 is by definition 100% of the second monomer composition and these percentages are also those of the total second monomer composition. However in another embodiment it is also possible that the second monomer composition comprises additional other monomers which are not any of monomers b1 to b3 in which case the percentages calculated for b1 to b3 will not take into account such other monomers.

[0019] The term itacon-functional monomer as used herein may be acidic or non acidic and comprises for example itaconic acid, mono-unsaturated C_5acid isomers thereof; precursors for these acids (e.g. itaconate anhydride) and/or itaconate derivatives of these acids, (e.g. diesters; mono esters, diamides; ester amides and/or itaconimide and amides thereof). Itacon-functional monomers may thus encompass different species that fall into more than one of the different mutually exclusive components (e.g. (b1) and (b2) above) described and defined herein.

[0020] The term itaconate derivative (for example in relation to component (b1) as used herein denotes all non acidic (or potentially acidic) derivatives of mono-unsaturated C_5acids (e.g. itaconic acid) for example diesters; mono esters, diamides; ester amides and/or itaconimide and amides thereof. Thus itaconate derivatives do not include itaconic acid and its mono-unsaturated C_5acid isomers or precursors for these acids (e.g. itaconate anhydride). Such acids and precursors thereof if present are counted in whole or part of the acid component such as (b2).

[0021] In one preferred embodiment of the invention component (b2) the acid functional (or potentially acid functional) monomer(s) comprises itaconic acid, mono-unsaturated C_5acid isomers thereof and/or precursors for these acids (e.g. itaconate anhydride). As used herein the term “potentially acid” functional denotes any functional group which initially is non-acidic but generates an acid group by reacting under the relevant conditions (for example weak acid groups may only become acidic under certain conditions or precursors for acids such as anhydrides). In the invention herein where acid functional groups or potentially acid functional groups are specified, acid functional groups are preferred to potential acid groups, more preferably carboxylic acids and/or sulfonic acids, most preferably carboxylic acids.

[0022] It will be appreciated that the terms first and second polymer as used herein are for convenience only, as these polymers may be prepared, mixed and/or blended together in any order and for example the first polymer may be added to the second polymer or vice versa or they may be prepared at the same time in the same vessel.

[0023] Advantageously the mixture of the invention is a blended polymer composition (also referred to herein as a ‘polymer blend’) which denotes a macroscopically homogeneous mixture of two or more different polymers, typically homogeneous on scales larger than several times the wavelengths of visible light. The constituents of a polymer blend are separable by physical means. A polymer blend may comprise macromolecules that are miscible (i.e. capability of forming a single phase over certain ranges of temperature, pressure, and composition) or immiscible and thus may contain one or more phase domains. Preferred polymer blends of the invention are multi-phase.

[0024] Usefully the first polymer (a) is vinyl copolymer obtained and/or obtainable from a first monomer composition comprising:

[0025] a1) optionally at least 10 wt-% of one or more monomer(s) selected from derivatives of itaconic acid and/or isomers thereof;

[0026] a2) up to 20 wt-% of one or more acid functional (or potentially acid functional) monomer(s); and

[0027] a3) vinyl monomer(s)

[0028] where the percentages given for each monomer (a1 to a3) in the first monomer composition is calculated based on the total amount of monomer (a1 to a3) being 100% of the first monomer composition.

[0029] However component a1) above is optional as a preferred aspect of the present invention provides a blend of a second polymer (b) comprising one or more itacon-functional polymer(s) with a first polymer (a) substantially free of itacon-functional polymer. For example polymer (a) consists of polymer or polymers other than itacon-functional polymer(s) and the itacon-functional polymer(s) is provided solely by the second polymer (b).

[0030] Broadly in accordance with another aspect of the present invention there is provided: an aqueous polymer composition (optionally suitable for use as a binder), the composition comprising a mixture of:

[0031] A) a first polymer fluid comprising a fluid carrier medium and a first polymer selected from the group consisting of: a vinyl (co)polymer; an alkyd polymer; a urethane acrylic copolymer; a polyurethane; a polyester and/or combinations and/or mixtures thereof;

[0032] B) a second polymer fluid (preferably an emulsion) comprising a second copolymer dispersed in fluid carrier medium (optionally water), where the second copolymer is obtained and/or obtainable from a second monomer composition comprising:

[0033] B1) optionally at least 20 wt-% of one or more monomer(s) selected from derivatives of itaconic acid and/or isomers thereof;

[0034] B2) up to 12.5 wt-% of one or more acid functional (or potentially acid functional) monomer(s)

[0035] B3) other vinyl monomer(s) where the first and second copolymers:

[0036] (i) are different from each other:

[0037] (ii) form morphologically distinct phases (A) and (B) such that the phase ratio of (A) to (B) is from 5:95 and 95:5, more preferably from 10:90 and 75:25, most preferably from 15:85 and 60:40; and

[0038] where the percentages given for each monomer (B1 to B3) in the second monomer composition is calculated based on the total amount of monomer (B1 to B3) being 100% of the second monomer composition;

[0039] where at least one of the first and second polymer comprise a polymer obtained and/or obtainable from an itacon-functional monomer.

[0040] Optionally in the first polymer mixture A) the first polymer is dispersed in the fluid carrier medium to form a sol, emulsion and/or dispersion and/or is dissolved in the fluid carrier medium to form a solution. Preferably the fluid is a liquid medium, more preferably comprises water.

[0041] Preferably the first polymer mixture (A) comprises a first emulsion comprising a first vinyl copolymer dispersed in water, where the first vinyl copolymer is obtained and/or obtainable from a first monomer composition comprising:

[0042] A1) optionally at least 20 wt-% of one or more monomer(s) selected from derivatives of itaconic acid and/or isomers thereof;

[0043] A2) up to 12.5 wt-% of one or more acid functional (or potentially acid functional) monomer(s)

[0044] A3) other vinyl monomer(s)

[0045] where the percentages given for each monomer (A1 to A3) in the first monomer composition is calculated based on the total amount of monomer (A1 to A3) being 100% of the first monomer composition.

[0046] Similar to described for component a1), the component A1) above is optional and it is preferred that (before mixing) the itacon-functional polymer(s) is solely a constituent of the second polymer fluid B).

[0047] Optionally in the present invention the first and second copolymers have respective weight average molecular weights of [(a)/(A) and/or (b)/(B)] at least 50 kg/mole, preferably at least 100 kg/mole, more preferably 200 kg/mole as measured by GPC.

[0048] Broadly in accordance with a further aspect of the invention there is provided an aqueous polymer composition (optionally suitable for use as a binder), the composition comprising a mixture of:

[0049] α) a first polymer fluid comprising a fluid carrier medium and a first polymer selected from the group consisting of: a vinyl (co)polymer; an alkyd polymer; a urethane acrylic copolymer; a polyurethane; a polyester and/or combinations and/or mixtures thereof;

[0050] β) a second polymer fluid (preferably an emulsion) comprising a second copolymer dispersed in fluid carrier medium (optionally water), the second copolymer having a weight average molecular weight of at least 50 kg/mole, more preferred 100 kg/mole as measured by GPC and being obtained and/or obtainable from a second monomer composition comprising:

[0051] β1) optionally at least 20 wt-% of one or more monomer(s) selected from derivatives of itaconic acid and/or isomers thereof;

[0052] β2) up to 12.5 wt-% of one or more acid functional (or potentially acid functional) monomer(s)

[0053] β3) other vinyl monomer(s)

[0054] where the percentages given for each monomer (α1 to α3) in the first monomer composition is calculated based on the total amount of monomer (α1 to α3) being 100% of the first monomer composition; and

[0055] where the percentages given for each monomer (β1 to β3) in the second monomer composition is calculated based on the total amount of monomer (β1 to β3) being 100% of the second monomer composition;

[0056] where at least one of the first and second polymer comprise a polymer obtained and/or obtainable from an itacon-functional monomer.

[0057] Preferably the first fluid (α) is an emulsion comprising a first vinyl copolymer dispersed in water, the first vinyl copolymer having a weight average molecular weight of at least 200 kg/mole (preferably at least 500 kg/mole) as measured by GPC and being obtained and/or obtainable from a first monomer composition comprising:

[0058] α1) optionally at least 20 wt-% of one or more monomer(s) selected from derivatives of itaconic acid and/or isomers thereof;

[0059] α2) up to 12.5 wt-% of one or more acid functional (or potentially acid functional) monomer(s)

[0060] α3) other vinyl monomer(s);

[0061] Similar to described for components α1) and A1, the component α1)) above is optional and it is preferred that (before mixing) the itacon-functional polymer(s) is solely a constituent of the second fluid β).

[0062] More preferred mixtures of this further aspect of the invention are those where at least one of components (α1)) and (β1) are present (i.e. where the mixture is obtained and/or obtainable from itaconic acid, derivatives and/or isomers thereof in the specified amount).

[0063] Conveniently the mixtures independently described in each of aspect of the present invention are each polymer blends.

[0064] Optionally in the further aspect of the present invention the first and second copolymers form morphologically distinct phases (α) and (β) such that the phase ratio measured as dry weight of polymer (α) to dry weight of polymer (β) is from 5:95 and 95:5, more preferably from 10:90 and 75:25, most preferably from 15:85 and 60:40.

[0065] Corresponding preferences for components a1 to a3 and b1 to b3 and for A1 to A3 and B1 to B3 and for α1 to α3 and β1 to β3 for all three aspects of the invention above may (unless the context indicates otherwise) be interchangeable as described herein.

[0066] It will be appreciated that other optional compatible monomers may also be used in addition to the above monomers a1 to a3 and b1 to b3 (and also A1 to A3 and B1 to B3 and α1 to α3 and β1 to β3) to form the first and/or second copolymers. However monomers that fall outside the mutually exclusive definitions for these components above are (unless the context clear indicates otherwise) not considered part of the first or second monomer compositions and the presence of such other monomers are discounted when calculating the percentages of the above monomers given herein.

[0067] It will be understood that the preferred amounts specified herein (a1) to (a3) and (b1) to b3) also correspond to the preferred amounts for the corresponding components (A1) to (A3) and (B1) to (B3) and (α1) to (α3) and (β1) to (β3) calculated on the same corresponding basis. To avoid unnecessary repetition these preferences are not repeated for each aspect of the invention.

[0068] Preferably the amount of the monomer(s) (a1)) comprises at least 30 wt-%, and more preferably of at least 40 wt-% of the first monomer composition.

[0069] Preferably the amount of the monomer(s) (a2) comprises no more than 7 wt-%, and more preferably from 0.5 to 3.5 wt-% of the first monomer composition.

[0070] As indicated the amount of the monomer(s) (a3) is such that total of (a1), (a2) and (a3) is 100% wt-%.

[0071] Preferably where present the amount of the monomer(s) (b1) comprises at least 30 wt-%, and more preferably of at least 40 wt-% of the second monomer composition.

[0072] However in one convenient embodiment of the invention the second monomer composition is substantially free of monomer(s) (b1).

[0073] Preferably the amount of the monomer(s) (b2) comprises no more than 7 wt-%, and more preferably from 0.5 to 3.5 wt-% of the second monomer composition.

[0074] As indicated the amount of the monomer(s) (b3) is such that total of (b1) (where present), (b2) and (b3) is 100% wt-%.

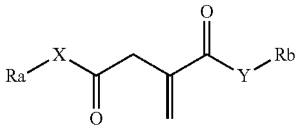
[0075] It will be appreciated that each of the monomer components (a1 to a3) in the first monomer composition are mutually exclusive from each other and thus the itaconic acid derivative (a1)) does not comprise acid functional or potentially acid functional groups (as defined herein).

[0076] It will be appreciated that each of the monomer components (b1 to b3) in the second monomer composition are mutually exclusive from each other, although may be the same as or different to the corresponding component of the first monomer composition, provided that the first and second compositions are different (whether in amounts and/or specific monomers used).

Itacon-Functional Compounds

[0077] Itacon-functional compounds which may be acidic or non acidic and which are suitable for use as monomers in the present invention may be represented generally by Formula 1:

Formula 1



where Ra and Rb independently represent H and/or any optionally substituted hydrocarbo moiety (such as any aliphatic, cycloaliphatic or aromatic moieties); and X and Y independently represent —O— and/or —NRc-, where Rc independently in each case represents H and/or any optionally substituted hydrocarbo moiety (such as any aliphatic, cycloaliphatic or aromatic moieties); or

X and Y may represent the same moiety (either —O— or —NRc-) in which case Ra and Rb are not present and Formula 1 comprises a cyclic moeity.

[0078] Usefully in Formula 1 Rc may represent C_{1-20}alkyl, C_{3-20}aryl or C_{4-20}alkylaryl groups. More usefully Rc does not comprise an aromatic moiety.

[0079] As itacon-functional monomers of Formula 1 may be acidic they may optionally contain acidic groups (such as carboxylic, phosphoric and/or sulphonic acid groups) or any precursor acid groups (i.e. a group which readily generates an acid group under the conditions of polymerisation herein, such as an anhydride group).

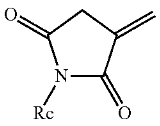
[0080] When X and Y are both O, Formula 1 represents 2-methylidenebutanedioate diesters (also referred to herein as itaconate diesters).

[0081] When X and Y are both NRc, Formula 1 represents itaconate diamides.

[0082] When one or X or Y is O and the other is NRc Formula 1 represents a compound having one ester and one amide group.

[0083] As mentioned above, in one embodiment of the invention Formula 1 may also represent compounds when X and Y are both the same —O— (i:e. itaconic anhydride) or where X and Y are both the same —NRc- moiety i.e. those itaconimides comprising a five membered ring as represented by Formula 1A:

Formula 1A



such as N-ethyl itaconimide when Rc is ethyl.

[0084] Preferred itacon-functional monomers are those of Formula 1 where

[0085] Ra and Rb independently represent:

optionally substituted C_{1-30}hydrocarbyl,

more preferably C_{1-20}alkylene (which may comprise linear, branched and/or cyclic moieties) and/or C_{3-20}arylene;

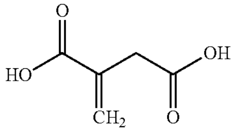
most preferably C_{1-10}alkylene.

[0086] Whilst Ra and Rb may be different, more conveniently they represent identical moieties.

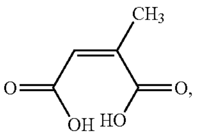
Itaconate Derivatives

[0087] It will be appreciated the (broader) term itacon-functional monomer encompasses the narrower terms 'itaconate derivative' and 'itaconate derived' which as defined herein relates non-acidic (or potentially acidic) itacon-functional compounds.

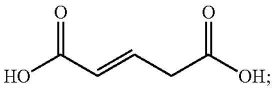
[0088] Thus itaconate derivatives which are suitable for use as monomers in the present invention may comprise itaconate diesters, imides, diamide and/or ester amide monomers. Itaconate derivatives comprise derivates of itaconic acid



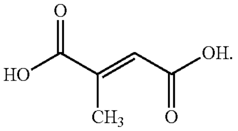
and/or derivatives of isomers of itaconic acid such as derivatives of the isomers: citraconic acid



glutaconic acid

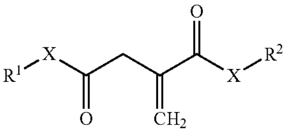


and/or mesaconic acid



[0089] Conveniently the itaconate derived monomer(s) that may comprise components such as optional b1 (and where present optional a1 optionally used to prepare certain polymer a) may independently comprise one or more dialkyl, diaryl, alkyl-aryl diesters and/or diamides of itaconic acid, such as any of those represented by Formula 2

Formula 2



wherein

X can be —O— or —NH—, —NR^3 where R^3 is C_{1-4}alkyl NRc-, where Rc independently in each case represents H and/or any optionally substituted hydrocarbo moiety (such as any aliphatic, cycloaliphatic or aromatic moieties);

R^1 can be an alkyl or aryl group having 1 to 20 carbon atoms, more preferably 1 to 6 carbon atoms, and most preferably 1 to 4 carbon atoms

R^2 can be an alkyl or aryl group having 1 to 20 carbon atoms, more preferably 1 to 6 carbon atoms, and most preferably 1 to 4 carbon atoms

R^1 and R^2 can be different, but preferably are the same.

[0090] As itaconate derivatives are non acidic Formula 2 does not contain acidic groups (such as carboxylic, phosphoric and/or sulphonic acid groups) or any precursor acid groups (i.e. a group which readily generates an acid group under the conditions of polymerisation herein, such as an anhydride group).

[0091] Conveniently Formula 2 may represent dialkyl or aryl esters of itaconic acid, dialkyl or aryl amides of itaconic acid. More conveniently R_1 and R_2 may be independently selected from the group consisting of: methyl, ethyl, i-propyl, n-propyl, n-butyl, i-butyl, t-butyl, hexyl, cyclohexyl, 2-ethylhexyl, decyl, dodecyl, phenyl, 2-phenylethyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, and 4-hydroxybutyl. More conveniently R_1 and R_2 are selected from: methyl, ethyl, n-butyl and 2-ethylhexyl. Most conveniently R_1 and R_2 are selected from methyl and ethyl for example methyl.

[0092] Usefully the total amount of itacon-functional compounds independently and optionally present in each of the monomer compositions (a) and/or (b) may (where present) be present in the various amounts given in the three paragraphs immediately following where the wt-% is based on the total weight of each the respective monomers compositions independently used to prepare each of the respective first polymer (a) and/or second polymer (b) independently being 100%.

[0093] Usefully a minimum amount of at least 25 wt-%, more usefully at least 30 wt-%, even more usefully at least 35 wt-% and most usefully at least 40 wt-%,

[0094] Conveniently a maximum amount of less than 80 wt-%, more conveniently less than 75 wt-%, even more conveniently less than 70 wt-%, most conveniently less than 65 wt-%, and for example less than 60 wt-%.

[0095] Preferably in an amount of from 20 to 80 wt-%, more preferably from 25 to 75 wt-%, even more preferably from 30 to 70 wt-%, most preferably from 35 to 65 wt-%, for example from 40 to 60 wt-%.

[0096] Itaconate monomers such as those represented by Formulae 1 or 2 may also be broadly divided into two types: higher itaconate esters which are generally hydrophobic; and lower itaconate esters which are generally hydrophilic.

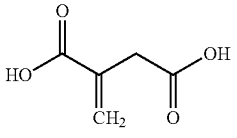
[0097] In one embodiment of the invention the itaconate derived monomer may be an itaconate diester of Formula 2 where R_1 and R_2 are independently optionally substituted C_{1-3}hydrocarbo groups, such as C_{1-3}alkyl, an example of which is dimethyl itaconate (DMI).

[0098] In another embodiment of the invention the itaconate monomer may be an itaconate diester of Formula 2 where R_1 and R_2 are independently optionally substituted C_{4-8}hydrocarbo groups, such as C_{4-6}alkyl, an example of which is dibutyl itaconate (DBI).

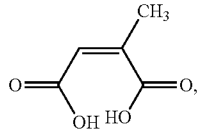
Acid Monomer=(a2 where present) and (b2)

[0099] It will be understood that when referring to acid functional and/or acidic components herein such as acid monomers (a2) and (b2) this refers to both acidic moieties (such as carboxylic, phosphoric and/or sulphonic acid groups) and/or precursor acidic moieties which under the conditions of use or in the processes herein 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 precursors therefor (such as salts, anhydrides and/or acid chlorides). Thus copolymers of the invention comprise acidic functional monomers (a2) and/or (b2) that comprise an acid group and/or a precursor acid group.

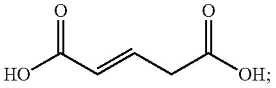
[0100] For convenience itaconic acid and its mono unsaturated pentacarbon isomer acids and precursors therefor (e.g. itaconic anhydride) are not considered to be part of the itaconate derivative monomer components described herein. Thus they are not counted as part of either components (a1) and/or (b1) but instead where present as part of the corresponding acidic components (a2) and/or (b2). Suitable monounstaturated C5diacids comprise: itaconic acid



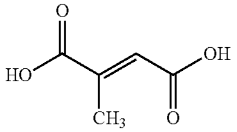
and/or any of its isomers: citraconic acid



glutaconic acid



and/or mesaconic acid



as well as any mixtures of these acids.

[0101] Suitable acid monomers can be monofunctional or difunctional in potential acid functionality. Preferred monomers are acrylic acid, methacrylic acid, alpha-carboxyethyl acrylate, itaconic acid, itaconic anhydride, maleic acid, and maleic anhydride, citraconic acid, citraconic anhydride, glutaconic acid, glutaconic anhydride, mesaconic acid and/or mesaconic anhydride.

[0102] Other preferred acids have one ethylenic group and one or two carboxy groups. Such acid monomers are selected from the group consisting of: acrylic acid (and copolymerisable oligomers thereof), citraconic acid, mesaconic acid, crotonic acid, fumaric acid, itaconic acid, maleic acid, methacrylic acid, methylene malonic acid, anhydrides thereof, salts thereof, acid chlorides thereof, 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, 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). combinations thereof in the same species and/or mixtures thereof.

[0103] More preferred monomers are acrylic acid, methacrylic acid, beta-carboxyethyl acrylate, and itaconic anhydride. The most preferred acid functional monomer is itaconic anhydride.

[0104] Suitable acid functional monomers of component (a2) and/or (b2) are those that are co-polymerisable with the itaconate derivative monomer(s) such as components (a1) and/or (b1). Conveniently at least one monomer of component (a1) and/or (b1) may comprise at least one activated unsaturated moiety as defined herein. Such unsaturated acid functional monomers are not considered to be part of the vinyl monomers (a3) and (b3).

[0105] Usefully the monomer of component (a2) and/or (b2) is an acid functional ethylenically unsaturated monomer for example an acid functional (meth)acrylic monomer.

[0106] Preferred acidic 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.

[0107] 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).

[0108] Useful 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.

[0109] 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.

[0110] Particularly preferred acid monomers are acrylic acid, methacrylic acid, beta carboxy ethyl acrylate, itaconic acid, and/or itaconic anhydride.

[0111] 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.

[0112] Usefully the acidic component (a2) and/or (b2) may be present in the compositions and/or copolymers of the invention in an amount of no more than 20 wt-%, more usefully no more than 15 wt-%, even more usefully more than 10 wt-%, most usefully no more than 7.5 wt-%, based on the total weight of the respective first and/or second monomer compositions being 100%.

[0113] Preferably the acidic component (b) may be present in the compositions and/or copolymers of the invention in an amount of from 0.5 to 7.5 wt-%, more preferably from 1 to 5 wt-%, based on the total weight of the respective first and/or second monomer compositions being 100%.

[0114] Usefully the acid monomer (b) may be present in the compositions and/or copolymers of the invention in an amount sufficient amount to achieve an acid value (AV) of no more than 160 mg KOH/g, more usefully no more than 115 mg KOH/g, most usefully no more than 80 mg KOH/g, for example no more 60 mg KOH/g of solid polymer

[0115] Preferably the acid monomer (b) may be present in the compositions and/or copolymers of the invention in an amount sufficient amount to achieve AV from 3.5 to 60 mg KOH/g, preferably 7.5 to 40 mg KOH/g of solid polymer.

[0116] 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.

[0117] In one embodiment of the invention the acid monomer(s) (a2) and (b2) may be independently selected from the group consisting of: acrylic acid, methacrylic acid, β-carboxy ethylacrylate, crotonic acid, itaconic acid, fumaric acid, maleic acid, itaconic anhydride, maleic anhydride, itaconate C_{1-20}hydrocarbo mono esters, itaconamide C_{1-20}hydrocarbo mono amides, methylidene malonic acid, phosphate or phosphonate functional monomers [such as phosphated hydroxyethyl (meth)acrylate, phosphated hydroxylpropyl (meth) acrylate, and phosphated hydroxybutyl (meth)acrylate], sulfate functional or sulfonate functional monomers [such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and sodium styrene sulfonate]; and/or mixtures thereof.

[0118] In special embodiment the acid monomer(s) (a2) and (b2) are itaconic acid and/or itaconic anhydride.

Vinyl Monomer (a3) and (b3)

[0119] Suitable vinyl monomers that may comprise monomers (a3) and/or (b3) are given below.

[0120] Preferably the vinyl monomers are copolymerisable with monomers in the respective first and/or second monomer compositions using in any suitable technique such as any of those described herein, (for example in a SAD, solution, bulk, and/or an emulsion polymerisation). Emulsion polymerisation and SAD processes are preferred.

[0121] The vinyl monomers may comprise a suitable activated unsaturated moiety (such as ethylenic unsaturation) where the structure(s) does not overlap with any of components (a1), (b1) (a2) or (b2).

[0122] The vinyl monomers are present in an amount of less than 90% and preferably less than 70% based on the total weight of the respective first and/or second monomer compositions being 100%, though are always present in such an amount that that the total of (a1))+(a2)+(a3)=100% and (b1)+(b2)+(b3)=100%

[0123] Vinyl Monomer(s) [(a3) and (b3)] may be independently selected from the group consisting of: C1-20alkyl and/or C3-30aryl esters of (meth)acrylic acid, vinyl aromatics (such as styrene and alpha-methylstyrene), (meth)acrylonitrile, vinyl esters (such as vinyl acetate and VeoVa monomers (VeoVa 9, VeoVa 10, and VeoVa 11)); alkyl and/or aryl (meth) acrylamides and/or mixtures thereof.

[0124] More preferred vinyl monomer(s) may comprise: methacrylic esters, vinyl aromatics, dialkyl methylidene malonates, N-alkyl or N-aryl itaconimides, and alpha-methylene cyclic lactones or lactams.

[0125] The vinyl monomer(s) (a3) and/or (b3) may comprise monomers that can undergo crosslinking (such monomers are referred to as 'cross-linking monomers') 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

[0126] Cross-linking monomers 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). Other examples of crosslinking monomers include hydroxypropyl (meth)acrylate, silane functional monomers, such as 3-methacryloxypropyl trimethoxysilane (Geniosil GF31, ex Wacker).

[0127] Preferably such cross-linking monomers are present in an amount of not more than 15 wt-%, more preferably not more than 10 wt-%, most preferably from 1 to 8 wt-% of their respective first and/or second monomer compositions

[0128] Some other preferred crosslinking monomers are listed below: diacetone acrylamide (in combination with polyhydrazides, polyhydrazines, polysemi-carbazides), acetoacetoxy ethyl methacrylate (in combination with polyamines, or polyhydrazides), glycidyl (meth)acrylates (in combination with polyamines), and hydroxyalkyl (meth) acrylate (such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, or 4-hydroxybutyl (meth)acrylate (in combination with polyisocyanates). fatty acid functional monomers, such as Visiomer MUMA (ex. Evonik) or Dapro Serad 521 and 522 (ex. Elementis)

other oxidatively curing monomers such as esters of geranic acid and hydroxyl functional (meth)acrylates.

silane functional crosslinking monomers such as those having an unsaturated (meth)acrylate or vinyl group and an alkoxy silane group, examples of which are:

3-methacryloxypropyltrimethoxysilane [CAS #: 2530-85-0],

Methacryloxytrimethoxysilane [CAS #: 13688-56-7],

[0129] Methacryloxypropyltris(trimethylsiloxy)silane [CAS #: 17096-07-0], 3-methacryloxypropyltriethoxysilane [CAS #: 21142-29-0], 3-methacryloxypropylmethyldimethoxysilane [CAS #: 14513-34-9], 3-methacryloxypropylmethyldiethoxysilane [CAS #: 65100-04-1],

Methacryloxymethyltrimethoxysilane [CAS #: 54586-78-6],

Methacryloxymethyltriethoxysilane [CAS #: 5577-72-0],

Methacryloxymethyl(methyl)dimethoxysilane [CAS #: 121177-93-3],

Methacryloxymethyl(methyl)diethoxysilane [CAS #: 3978-58-3], 3-Acryloxypropyltrimethoxysilane [CAS #: 4369-14-6].

[0130] The vinyl monomer(s) may comprise monomer(s) with groups that promote adhesion especially to wet surfaces (adhesion promoting monomers).

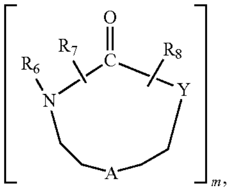
[0131] Preferably such adhesion promoting monomers are present in an amount of not more than 10 wt-%, more preferably not more than 6 wt-%, most preferably from 0.5 to 5 wt-% of the respective first or second monomer compositions.

[0132] Typical adhesion promoting monomers include ureido functional monomers, such as Plex 6852-O (ex. Evonik), i-bornyl (meth)acrylate, polyethylene (meth)acrylate, polypropylene (meth)acrylate and/or HPCA (available from BASF).

[0133] Convenient adhesion promoting monomer comprise olefinically unsaturated monomer with a wet-adhesion promoting functionality group thereon, such as acetoacetoxy groups and optionally substituted amine or urea groups, for example cyclic ureido groups, imidazole groups, pyridine groups, hydrazine or semicarbazide groups.

[0134] Optionally the vinyl monomer (a3) and/or (b3) 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:

[0135] 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

[0136] 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.

[0137] The ring moiet(ies) of Formula 3 are each attached to R$_9$ and in Formula 3 when m is 2, 3 or 4 then R$_9$ 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$_9$ may be attached at any suitable position on the ring.

[0138] 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,

[0139] More preferred monomers of Formula 3 comprise those where: m is 1 or 2

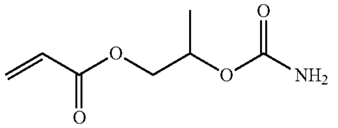
—Y— is —NR$_8$— (i.e. where Formula 2 is attached to R$_9$ via a ring nitrogen), A represents a divalent C$_{1-3}$hydrocarbylene;

R$_6$ is H, R$_7$ is a C$_{1-10}$hydrocarbo; and

R$_9$ comprises a (meth)acryloxyhydrocarbo group or derivative thereof (e.g. maleic anhydride).

[0140] 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.

[0141] Another suitable adhesion promoting monomer is hydroxypropylcarbamatacrylate (HPCA) which for example is available commercially from BASF as a 70% solution in ethanol (HPCA 70% EtOH) HPCA has the structure



and is useful as a (wet) adhesion promoter and/or crosslinker and may be biobased and/or produced by enzymes.

[0142] Some vinyl monomers may perform more than one function (e.g. as a cross-linker and/or adhesion promoter).

[0143] The vinyl monomer(s) may comprise multi-functional monomers (as defined herein). Preferably such multi-functional monomers are present in an amount of not more 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 of the respective first or second monomer compositions.

[0144] It will be appreciated that these weight amounts given above for the cross-linking, adhesion promoting and/or multi-functional monomers may be the same or less than the total amount of vinyl monomer components [(a3) and/or (b3)] present in the respective first and/or second monomer compositions

[0145] Preferred first and/or second copolymers of the invention comprise less than 10 wt-% more preferably from 0.1 to 7.5 wt-%, most preferably between 0.15 and 7.5 wt-% of the weight of the respective first and/or second copolymer of moieties obtained and/or obtainable from cross-linking, adhesion promoting and/or multi-functional monomers.

[0146] Preferably at least 20 parts by weight of the amount vinyl monomer(s) [(a3) and/or (b3)] (calculated with respective to the total amount of the respective vinyl monomer component (a3) or (b3)) for each copolymer being 100 parts by weight) are obtained from biobased sources. Thus for example monomers comprising (meth)acrylate group and/or alcohols may be obtained from biobased resources.

[0147] Other and/or additional component may be used as part of whole of the vinyl monomer (a3) and/or (b3) 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 di-vinyl 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 the respective first and/or second monomer compositions

[0148] Mixtures of the invention and the first and/or second polymers used in the invention may also be obtained and/or obtainable from additional monomers which improve colloidal stability of the mixture such as monomers that comprise polyethlylene glycol (PEG) and/or polypropylene glycol (PPG) moieties and/or moieties derived therefrom. Examples of monomers that may be suitable are polyethlylene glycol methacrylate (PEGMA) and polypropylene glycol methacrylate (PPGMA).

Copolymers

[0149] Preferably at least 20 wt-% of the first and/or the second monomer composition is obtained from a biorenewable resource, more preferably at least 40 wt-%, and most preferably at least 50 wt-%.

[0150] Preferably at least 20 wt-% of the first copolymer comprises components obtained from a biorenewable resource, more preferably at least 40 wt-%, and most preferably at least 50 wt-%.

[0151] Preferably at least 20 wt-% of the second copolymer comprises components obtained from a biorenewable resource, more preferably at least 40 wt-%, and most preferably at least 50 wt-%.

[0152] The first and/or second copolymers described herein may also optionally comprise other additional monomers not being any of a1, a2, a3, b1, b2 and/or b3.

[0153] Preferably the total amount of such other monomers may be present in an amount of no more than 40 parts, more preferably less than 30 parts, even more preferably less than 20 parts, most preferably less than 10 parts, for example less than 5 parts by weight calculated with respect to 100 parts by weight of each of the respective first or second compositions with which they may used.

[0154] Usefully the total amount of such other monomers may be present in an amount of at least 0.1 parts, more usefully more than 0.5 parts, even more usefully more than 1 parts, most usefully more than 2 parts, for example more than 3 parts, by weight calculated with respect to 100 parts by weight of each of the respective first or second compositions with which they may used.

[0155] Conveniently the total amount of such other monomers may be present in an amount of from 0.1 to 40 parts, more usefully from 0.5 to 30 parts, even more usefully from 1 to 20 parts, most usefully from 2 to 10 parts, for example from 3 to 5 parts, by weight calculated with respect to 100 parts by weight of each of the respective first or second compositions with which they may used.

[0156] In one preferred embodiment of the invention the first and/or second copolymer is prepared by an emulsion polymerisation process. Details of these techniques are described later.

[0157] The molecular weight of the first and/or second copolymers may be independently controlled using various conventional techniques. Chain transfer agents (CTA) can be used, such as: mercaptans (thiols). certain halohydrocarbons and/or alpha-methyl styrene. Catalytic chain transfer polymerization (CCTP) can be used with a suitable complex for example conventional cobalt chelate complexes. Alternatively controlled radical polymerization (CRP) processes can be used with appropriate nitroxide or a thiocarbonylthio compounds such as dithioesters, dithiocarbamates, trithiocarbonates, and xanthates to mediate polymerization. Examples of suitable CRP processes are nitrox mediated polymerization (NMP), reversible addition fragmentation chain-transfer process (RAFT) or atom transfer radical polymerization (ATRP).

[0158] Preferably if CTAs (such as mercaptans) are used to prepare the first and/or second copolymer, the CTA is used in an amount of less than 5 parts by weight, more preferably less than 3 parts by weight, and most preferably less than 1.2 parts by weight calculated based on the amount of each of the respective first or second monomer compositions being 100 parts by weight.

[0159] Preferably if a CCTP process is used to prepare the first and/or second copolymer, the complex (e.g. Co chelate complex) is used in a weight amount of less than 200 parts per million (ppm), more preferably less than 100 ppm, and most preferably less than 50 ppm calculated based on the amount of each of the respective first or second monomer compositions being a million parts by weight.

[0160] The molecular weight of a (co)polymer latex can be determined using GPC using THF as solvent and standard styrene-divinylbenzene columns, and calibrated against polystyrene standards as known to those skilled in the art. Preferably the weight average molecular weights as measured by GPC of (co)polymer emulsions a) and b) are higher than 100 kg/mole, more preferably higher than 250 kg/mole, and most preferably higher than 500 kg/mole. Typically, the weight average molecular weights of (co)polymer emulsions a) and b) are higher than 650 kg/mole.

[0161] For polymers of the invention especially those to be used in coating compositions, providing amino functional groups thereon may also be useful. 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 U.S. Pat. No. 7,049,352 the contents of which are hereby incorporated herein by reference. Therefore optionally either (preferably both) of the first and second copolymers as described herein may be iminated. However in one embodiment of the present invention only copolymers that comprise monomers (a1)) and/or (b1) are iminated.

[0162] Conveniently blends of the invention comprise a first copolymer that is iminated and second copolymer that is uniminated. Alternatively blends of the invention comprise a first copolymer that is uniminated and second copolymer that is iminated.

[0163] Preferably sufficient alkylene imine is used in an amount sufficient theoretically to convert between 25 and 90%, more preferably 50 to 75% of the acid groups of the copolymer to be iminated. Most preferably, the alkylene imine used is propylene or ethylene imine.

[0164] The first and second copolymer emulsions of a) and b) may be formed using emulsion polymerization, and/or solution-dispersion polymerization. Such processes are extremely well known and need not be described in great detail.

[0165] 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, or a power feed process, resulting in a gradient particle morphology.

[0166] Copolymer emulsions of the inventions may also be prepared as aqueous crosslinkable polymer compositions obtained from a polymer component and an oligomer component such as the polymer-oligomer compositions described in WO95/29963 (soft polymer/hard oligomer) and/or WO95/29944 (soft oligomer/hard polymer) the contents of both of which are hereby incorporated by reference.

[0167] In the case of a solution polymerization process, 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.

[0168] Solution polymers can be produced via as single feed solution polymerization or by a sequentially fed multiphase polymerization. It is also envisaged that a solution polymer, 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 solution polymerisation process is used as seed in a batch or semi-batch polymerization process.

[0169] Suitable emulsion processes disperse the monomers in an aqueous medium and conduct polymerization using a free-radical initiator (preferably water soluble) appropriate heating (e.g. 30 to 120° C.) and agitation.

[0170] Aqueous emulsion polymerization can be achieved using conventional emulsifying agents (surfactants) such as anionic and/or non-ionic emulsifiers. The amount of emulsifying agent that may be used is low, preferably 0.3 to 2 parts by weight, more preferably 0.3 to 1 parts by weight based on the weight of the respective first or second monomer composition with which they are used being 100 parts by weight.

[0171] The aqueous emulsion polymerization can employ conventional free radical initiators such as peroxides, persulphates and redox systems as are well known in the art. The amount of initiator that may be used is generally 0.05 to 3 parts by weight based on the weight of the respective first or second monomer composition with which they are used being 100 parts by weight.

[0172] The aqueous emulsion polymerization 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 polymerization medium at the start of polymerization) 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 polymerization medium during the polymerization. Although not preferred, fully continuous processes could also be used in principle. Preferably a semi-batch process is employed in the preparation of the (co)polymer emulsion(s) a) and/or b).

[0173] In embodiments of the invention where copolymer a) and/or b) comprises (optionally is) a vinyl copolymer, especially where the copolymer contains itaconate functional monomers, then preferably the monomer feeding time in the preparation of the (co)polymers a) and/or b) is at least 90 minutes, more preferably at least 120 minutes, and most preferably between 120 and 500 minutes.

[0174] When (co)polymer emulsion(s) a) and/or b) are made using solution-dispersion polymerization, the first step includes a solution polymerization step, as known to those skilled in the art. 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 mixture that is regularly used is Solvesso 100. Preferably bio-renewable solvents (for example as available from Liberty Chemicals) are used.

[0175] Often the reaction temperature is around 100° 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.

[0176] 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.

[0177] The glass transition temperature (Tg) of a copolymer can conveniently be calculated using the well known Fox equation.

[0178] Preferably, where the copolymer is a single phase (co)polymers a) and b) have different calculated Tg's.

[0179] In a preferred embodiment of the invention (co) polymer a) has a theoretical Tg of at least 40° C., more preferred of at least 60° C., and most preferred of at least 80° C., while (co)polymer b) has a theoretical Tg of not more than 20° C., more preferred less than 10° C., and most preferably less than 0° C., where the difference in calculated Tg between (co)polymer a) and (co)polymer b) is at least 20° C., more preferred at least 30° C., most preferred at least 40° C., and typically at least 50° C. of even 60° C.

[0180] In another preferred embodiment of the invention (co)polymer a) has a theoretical Tg of not more than 20° C., more preferred less than 10° C., and most preferably less than 0° C., while (co)polymer b) has a theoretical Tg of at least 40° C., more preferred of at least 60° C., and most preferred of at least 80° C., where the difference in calculated Tg between (co)polymer a) and (co)polymer b) is at least 20° C., more preferred at least 30° C., most preferred at least 40° C., and typically at least 50° C. of even 60° C.

[0181] In one preferred embodiment where the copolymer comprises multiple phases there is at least one "hard" phase with a Tg preferably from 10 to 125° C., more preferably from 50 to 125° C., most preferably from 70 to 125° C. and at least one "soft" phase with Tg preferably at least 25° lower (more preferably at least 40° lower) than the Tg of the hard phase. Optionally the hard phase comprises an oligomer and/or the soft phase comprises a hydrophobic polymer. Such multiphase systems are described in WO 95/29963.

[0182] In another useful embodiment where the copolymer comprises multiple phases there is at least one "soft" phase with a Tg usefully below 50° C., more usefully below 20° C. and at least one "hard" phase with Tg usefully at least 25° higher (more usefully at least 40° higher) than the Tg of the soft phase. Optionally the soft phase comprises an oligomer and/or the hard phase comprises a hydrophobic polymer usually having a Tg of from −10 to 120° C., more usually from 20 to 110° C. Such multiphase systems are described in WO 95/29944.

[0183] The preferred average particle sizes of (co)polymer emulsions a) and b) as determined with dynamic light scattering are between 50 and 500 nm, more preferably between 50 and 300 nm, and most preferably between 75 and 200 nm.

[0184] In a preferred embodiment of the invention the average particle size of (co)polymer emulsion a) is higher than 100 nm, more preferably higher than 125 nm, and most preferably higher than 150 nm, while the average particle size of (co)polymer emulsion b) is below 100 nm, more preferred below 80 nm, and most preferably below 60 nm.

[0185] In yet another preferred embodiment of the invention the average particle size of (co)polymer emulsion a) is below 100 nm, more preferred below 80 nm, and most preferably below 60 nm, while the average particle size of (co) polymer emulsion b) is higher than 100 nm, more preferably higher than 125 nm, and most preferably higher than 150 nm.

[0186] In one embodiment the preferred average particle size of the first and/or second (co)polymer emulsion is higher than 100 nm, more preferably higher than 150 nm.

[0187] In another embodiment where a copolymer emulsion comprises from 1 to 8 wt-% of adhesion promoting monomers usefully the average particle size of that copolymer is below 80 nm, more usefully below 60 nm.

[0188] In yet another embodiment where a copolymer is iminated, conveniently the average particle size of copolymer is below 60 nm.

[0189] In a further embodiment of the invention the average particle size of the first copolymer is higher than 100 nm, more preferably higher than 150 nm and the average particle size of the second copolymer is below 80 nm, more preferably below 60 nm and most preferably the second copolymer is iminated.

[0190] Preferably the residual monomer content first and/or second copolymer emulsion is less than 1500 ppm, more preferably less than 1000 ppm, and most preferred less than 600 ppm, for example less than 350 ppm.

[0191] One embodiment of the invention, (co)polymer emulsion a) is prepared using a chaser monomer composition as described in WO2011073417.

[0192] Another embodiment according to the invention provides an aqueous binder composition wherein (co)polymer (a) and/or (b) can independently comprise an oligomer such as the acid functional oligomers described in WO 95/29963 (for example on page 6 line 46 to page 7 line 38 and page 8 lines 5 to page 9 line 27) and/or in WO 95/29944 29963 (for example on page 7 line 13 to page 8 line 8 and page 8 line 21 to page 10 line 5) [all the preceding passages incorporated herein by reference].

[0193] In another special embodiment of the invention is provided an aqueous binder composition wherein (co)polymer (a) and/or (b) can independently comprise an oligomer such as the acid functional oligomers described in WO 95/29963 and/or in WO 95/29944 wherein the (co)polymer (a) and/or (b) is iminated.

[0194] A further embodiment of the invention provides an aqueous binder composition wherein (co)polymer b) is a multi-phase morphology prepared by sequential emulsion polymerization and copolymer (b) is optionally iminated.

[0195] It is envisioned that the emulsion polymers of this invention can be used to prepare an aqueous coating composition which contains one or more inorganic pigments. These pigments are typically materials such as silicates, alumino silicates, alkali earth carbonates such as $CaCO_3$, clays, metal oxides such as Al_2O_3, TiO_2, FeO_xO_y, and ZnO, Phosphates, natural and synthetic zeolites, and organic opacifying materials such as Opaque Polymer (Ropaque™ Ultra). The PVC of the aqueous coating composition is defined as the fractional volume of pigment including opaque polymer based on the total volume of pigment and polymer in the coating composition. Preferred aqueous coating composition prepared using the emulsion polymer blends of this invention may have a PVC of less than 90%. For interior and exterior decorative paints the PVC is more preferably less than 60%, and most preferably less than 50%. For paints with 60 degree gloss values above 10 the PVC is preferably less than 40% and more preferably less than 30%. Barrier types of primers, direct to metal coatings, and decorative top coats preferably have a PVC of less than 30%. In certain embodiments the coatings may have a 60 degree gloss value less than 10, and be transparent. In these cases PVC levels below 5% are preferred.

[0196] In a preferred embodiment of the invention is provided a coating composition comprising an aqueous binder composition according to the invention.

[0197] In a preferred embodiment of the invention is provided a coating composition comprising an aqueous binder composition according to the invention having a PVC of less than 50%, more preferably of less than 25%. Preferably, stains would have a PVC of less than 10%, top coats would have a PVC of between 15 and 25%, and primer would have a PVC of between 25 and 50%.

[0198] In a preferred embodiment of the invention is provided a coating composition comprising an aqueous binder according to the invention, where the coating composition comprises hollow sphere pigment particles, such as for instance ROPAQUE™ DUAL, ROPAQUE™ ULTRA, ROPAQUE™ ULTRA E, and ROPAQUE™ Ultra EF (ex. DOW).

[0199] The aqueous compositions of the invention may be used in various applications and for such purposes may be optionally further combined or formulated with other additives or components, such as defoamers, rheology control agents, thickeners, dispersing and stabilizing agents (usually surfactants), wetting agents, fillers, extenders, fungicides, bacteriocides, coalescing and wetting solvents (although solvents may not normally be required), plasticisers, anti-freeze agents, waxes and pigments.

[0200] The aqueous compositions may e.g. 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 interior and exterior decorative coatings for wood, metal, plastic, masonry, concrete, and wood composites including plastic wood and cement wood composite materials, clear and semi-transparent stains and top coats for wood and wood composites including plastic wood and cement wood composite materials, clear and pigmented primers and top coats for wood furniture and flooring, road marking paints, coatings to protect and preserve structural metal against corrosion, such as bridges, water towers and tank farms, coatings for flooring including wood, wood composite and concrete flooring, barrier primers for wall board, wood and masonry to block migration of water soluble materials such as nicotine, inorganic salts, and tannins, coatings for paper, primers, coloured base coats and clear top coats for automotive parts including plastics and metals, temporary coatings designed to temporarily protect a substrate, and then be easily removed at a later time, temporary coatings designed to be thermally decomposed after manufacture such as those used in the manufacture of cathode ray tubes or fluorescent lights, sound deadening coatings such as those used on the underside of a car, inks, and overprint varnishes, and adhesive primers and structural adhesives.

[0201] Preferred application areas for compositions and/or coatings or the invention include wood coatings, such as joinery, industrial wood, parquet, and decorative applications, adhesive and graphic arts applications, such as inks, adhesives, overprint varnishes, film coatings, coatings for application on various plastics, such as polystyrene, polyester, PVC, polypropylene, polyethylene, or application to glass or metal.

[0202] The compositions once applied as a coating may be allowed to dry naturally at ambient temperature, or the drying process may be accelerated by heat. Crosslinking can be developed by allowing the coating 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.

[0203] Mixtures and/or polymer blends of the invention may be mixed with a variety of other further polymer emulsions in addition to the first and second copolymer emulsions.

[0204] Examples of such further polymer emulsions can be polyurethane emulsions, polyurethane-poly(meth)acrylate emulsions, alkyd emulsions, polyester emulsions and/or polyvinyl emulsions (which may comprise oligomer-polymer emulsions, gradient morphology emulsions, sequentially polymerized emulsions, or single phase copolymer emulsions).

[0205] If itaconic anhydride is used to prepare the first and/or second copolymers these copolymers can be post modified using chemicals having anhydride reactive groups. This can be used to introduce additional functionalities, such as crosslinking or adhesion promoting groups, while maintaining an acid group that can be used for colloidal stabilization.

[0206] 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.

[0207] 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.

[0208] If it is desired to crosslink polymers (for example in a polymer dispersion), the relevant copolymers 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.

[0209] 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.

[0210] 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 a 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.

[0211] Preferably at least 20 wt-%, more preferably at least 30 wt-%, and especially 40 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. In a preferred embodiment methacrylate monomers are used as monomer (c) where the alcohol is made from biorenewable sources. In yet another preferred embodiment both the (meth)acrylate unit and the possible alcohol are made from biorenewable sources. Thus it is preferred to also measure the carbon-14 content to determine the biorenewability.

[0212] 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 biorenewable 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 biorenewable 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.

[0213] 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 and or polymer B comprise at least about 1.5 dpm/gC (disintegrations per minute per gram carbon) of carbon-14, more preferably at least 2 dpm/gC, most preferably at least 2.5 dpm/gC, and especially at least 4 dpm/gC.

[0214] Acrylic acid can be made from glycerol, as is disclosed by Arkema, or from lactic acid as described by U.S. Pat. No. 7,687,661. Methacrylic acid can be prepared from ethene, methanol and carbon monoxide (all bio-renewable), as disclosed by Lucite International Ltd.

[0215] 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.

[0216] 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; furfuryl (meth)acrylate; fatty acid functional (meth)acrylates such as DAPRO FX-522 from Elementis and Visiomer® MUMA from Evonik.

[0217] 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.

[0218] 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.

[0219] 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.

[0220] 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.

[0221] 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.

[0222] Preferred utility of the present invention comprises as component of a coating composition.

[0223] 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.

[0224] 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.

[0225] 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 such a small amount that this is below which would be detected by any conventional routine analytical method. 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).

[0226] 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.

[0227] 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.

[0228] 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%, most preferably no more than 5%, especially no more than 2%, for example about 0% of the relevant whole.

[0229] 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.

[0230] The synonymous terms "organic substituent", "moiety", 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.

[0231] 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).

[0232] The term 'hydrocarbo group' as used herein is a sub-set of an 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

[0233] 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).

[0234] 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-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.

[0235] 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.

[0236] 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.

[0237] 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, Tr-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.

[0238] 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.

[0239] 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.

[0240] A monomer is a substantially monodisperse compound of a low molecular weight (for example less than one thousand g/mole) which is capable of being polymerised.

[0241] A polymer is a polydisperse mixture of macromolecules of large molecular weight (for example many thousands of g/mole) 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.

[0242] 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.

[0243] Depending on the context the term polymer may or may not encompass oligomer.

[0244] 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.

[0245] 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.

[0246] 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.

[0247] 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.

[0248] A further aspect of the invention provides a coating obtained or obtainable from a coating composition of the present invention.

[0249] 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.

[0250] 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.

[0251] 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.

[0252] Preferred coating compositions are solvent coating compositions or aqueous coating compositions, more preferably are aqueous coating compositions.

[0253] 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.

[0254] 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.

[0255] 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.

[0256] 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.

[0257] The compositions of the invention may also be blended with other polymers such as vinyl polymers, alkyds (saturated or unsaturated), polyesters and or polyurethanes.

[0258] 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.

[0259] 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.

[0260] A still further aspect of the present invention comprises paints obtained, obtainable and/or comprising polymer compositions of the invention, especially where polymers compositions of the invention are emulsion polymers. Thus for example paint made from the emulsion polymer compositions of this invention may contain pigment at pigment volume concentrations in the range of 0 to 85%, preferably in the range of 0 to 55%. The pigment volume concentration of a species of pigment particles is the percentage of the volume occupied by that species of pigment particles, based on the total volume of the dried coating prepared from the emulsion polymer compositions. Suitable pigments include inorganic pigments, such as titanium dioxide, iron oxide, zinc oxide, magnesium silicate, calcium carbonate, organic and inorganic coloured pigments, aluminosilicates, silica, and various clays. Titanium dioxide is a preferred for its ability to provide opacity. Suitable organic pigments also include plastic pigments such as solid bead pigments and microsphere pigments containing voids or vesicles. Examples of solid bead pigments include polystyrene and polyvinyl chloride beads. Examples of microsphere pigments, which include polymer particles containing one or more voids and vesiculated polymer particles, are disclosed in U.S. Pat. No. 4,427,836, U.S. Pat. No. 4,920,160, U.S. Pat. No. 4,594,363, U.S. Pat. No. 4,469,825, U.S. Pat. No. 4,468,498, U.S. Pat. No. 4,880,842, U.S. Pat. No. 4,985,064, U.S. Pat. No. 5,157,084, U.S. Pat. No. 5,041,464, U.S. Pat. No. 5,036,109, U.S. Pat. No. 5,409,776 and U.S. Pat. No. 5,510,422. Other suitable pigments include, for example, Expancel™ 551 DE20 acrylonitrile/vinyl chloride expanded particles (Expancel Inc. Duluth Ga.); Sil-Cell™ 35/34 sodium potassium aluminum silicate particles (Silbrico Corporation, Hodgkins Ill.); Dualite™ 27 polyvinylidene chloride copolymer coated with $CaCO_3$ (Pierce and Stevens Corporation, Buffalo N.Y.); Fillitte™ 150 ceramic spherical particles (Trelleborg Fillite Inc. Norcross Ga.); Microbeads™ 4A soda lime particles (Cataphote Inc.); Sphericell™ hollow glass particles (Potter Industries Inc. Valley Forge Pa.); Eccosphere™ hollow glass spheres (New Metals & Chemicals Ltd.; Essex England); Z-Light™ Zeeospheres W-410 and W-610 ceramic hollow spheres (3M St. Paul Minn.); Scotchlite™ K46 glass bubbles (3M St. Paul Minn.); Vistamer™ UH 1500 polyethylene particles; and Vistamer™ HD 1800 polyethylene particles (Fluoro-Seal Inc., Houston Tex.). Ropaque™ Polymer is a preferred component in the coatings. Z-Light™ Zeeospheres W-410 and W-610 ceramic hollow spheres are also preferred components. Combinations of the above ingredients are frequently preferred.

[0261] Paints prepared from the emulsion polymer compositions of this invention may be thickened with various aqueous thickening agents. These include but not are limited to Hydrophobically Modified Alkali swellable emulsion such Acrysol™ TT-935, Acrysol™ TT-615, Acrysol™ RM-6, Polyphobe™ TR-116. Alkali swellable emulsions such as Acrysol™ ASE-60 may also be used. Hydrophobically modified water soluble polymers may also be used such as Acrysol™ RM-2020, Acrysol™ RM-8, Aquaflow™ XLS-500, Aquaflow™ NHS-310, Rheolate™ CVS-11, and hydrophobically modified HEC such as Natrosol™ Plus 330. Hydroxyethyl cellulose may also be used such as Natrosol™ HBR, or Cellosize™ QP-3000. Clays such as Attagel™ 50 or Bentone™ DE may also be used for sagging and settling control.

[0262] Paints prepared from the emulsion polymer compositions of this invention may utilize dispersants to help stabilize the pigments in the paint. Polyacid dispersants such as Hydropalat™ 44, or hydrophobic copolymer dispersants such as Tamol™ 681, Tamol™ 165, and Tamol™ 731 may be used. Styrene Maleic anhydride copolymers may also be used. Small molecule dispersants such as polyphosphates and citric acid may also be used. Examples of polyphosphates include tetra-potassium pyrophosphate, potassium tripolyphosphate, sodium hexameta phosphate, and higher phosphates sold under the trade name Calgon™. The latter phosphates are used in conjunction with ZnO pigments to help provide stability.

[0263] Paints prepared from the emulsion polymer compositions of this invention may utilize coalescing aids to aid in the film formation of the latex emulsion polymers. These coalescing aids can be volatile such as ethoxy and propoxy ethers of common alcohols. Examples include ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, propylene glycol monobutyl, and dipropylene glycol monobutyl ether. A common and preferred coalescing agent is Texanol™. Paints prepared from the emulsion polymer compositions of this invention may also utilize non volatile coalescing agents which do not contribute to VOC's. These coalescing agents would include materials like Optifilm™ 400, Dioctyl maleate, triethyl citrate, or tributyl phosphate. In some instances oxidatively curing reactive plasticizers such as Oxi-Cure™ 100 may be used. In addition the paint may also contain a humectant material such as ethylene glycol or propylene glycol. Open time additives such as Rhodaline™ OTE, or Optifilm™ OT1200 may also be used. It is preferred that the paint made from the emulsion polymer compositions contain less than 5% VOC by weight based on total weight of the composition. More preferred are paint compositions containing less than 2% VOC by weight, and most preferred are paint compositions containing less than 0.05% VOC by weight.

[0264] Paints prepared from the emulsion polymer compositions of this invention will also contain added surfactants. These surfactants are used to improve substrate wetting, insure pigment and colorant compatibility, and improve stability. Nonionic surfactants such as ethoxylated alcohols are frequently added to improve free/thaw stability and colorant compatibility. These would include low HLB nonionics such as Igepal™ CO-430, Igepal™ CO-630 and higher HLB nonionics such as Triton X-405. For these surfactants it is also desirable to use analogs based on alkyl alcohols such as tridecyl alcohol, or branched secondary alcohols such as Tergitol™ TMN-10. Triton™ CF-10 is also quite commonly used to aid in pigment wetting. Dioctyl sulfosuccinates are frequently used to enhance substrate wetting such as Aerosol™ OT-100. Acetylenic diols such as Surfynol™ 104 can also be used and are sometimes desired due to their low dynamic surface tension. Phosphate based surfactants can also be employed particularly to improve TiO_2 compatibility and stability. These would include surfactants from the Strodex™ line such as PK-90 or PK-0VOC.

[0265] Paints prepared from the emulsion polymer compositions of this invention may also contain additives which can alter the surface blocking characteristics. Such additives would include fluorocarbon surfactants such as Capstone™ FS-61.

[0266] Paints prepared from the emulsion polymer compositions of this invention may also contain multivalent metal ions to provide for post film formation crosslinking. These multivalent metal ions will improve the hardness, and scratch resistance of the final paint as well as to improve the chemical resistance. In particular it is seen that this will improve resistance to organic solvents. Examples of multivalent metal ions include Zn, Mg, Zr, and Ca. These are frequently added in the form of water soluble salts such as acetates or carbonates. Zinc Ammonium Carbonate is frequently used to great advantage; however $Mg(OH)_2$ is also effective and sometimes desired.

[0267] Paints prepared from the emulsion polymer compositions of this invention may contain phosphate or borosilicate based corrosion inhibiting pigments such as Heucophos™ ZPO, Halox™ SPZ-391, Halox™ SZP-391 JM, Halox™ 430, or Halox™ CW-291. The paints prepared from the emulsion polymer compositions of this invention may contain organic corrosion inhibitors such as Halox™ 510, Halox™ 520 or Halox™ 570. The paints prepared from the emulsion polymer compositions of this invention may contain flash rust inhibitors such as nitrite salts, phosphate salts, benzoic acid salts, or Halox™ Flash-X 330. These ingredients are typically added to a direct to metal coating to reduce flash rusting and long term corrosion.

[0268] Paints prepared from the emulsion polymer compositions of this invention may contain tannin stain blocking additives to block the migration of tannins through the coating. These additives are typically based on multivalent cations such as Zr^{2+} and Zn^{2+} or solid inorganic materials capable of binding negatively charged tannins. The additives would include Stainban™ 185, Stainban™ 186, Stainban™ 187, Halox™ BW-100, Halox™ L-44, and Halox™ 1-66. In addition ZnO is frequently added to these paints to improve tannin stain blocking. In many instances it is particularly desired to prepare paints which contain inorganic pigments with high aspect ratios. An example would be a platy talc such as Vertal™ 7. This is known to improve the tannin blocking character of the paint.

[0269] Paints prepared from the emulsion polymer compositions of this invention may contain UV absorbers and free radical scavengers. These are used to improve the long term exterior durability of a coating, or to protect the underlying substrate from UV degradation. This is particularly useful when formulating clear to semi-transparent wood stains. The UV blockers can be organic materials such as benzotriazoles, or can be inorganic UV blockers such as sub 100 nm metal oxides. The free radical scavengers are based on hindered amine light stabilizers. Examples of UV blockers include Tinuvin 1130, trans iron oxides such as Tint-ayd CW5499 or Tint-ayd CW5600, nano zinc oxide, and nano titanium oxide. Combinations of Tinuvin 1130 with Tint-ayd CW5499 are particularly useful for semi-transparent wood stains.

[0270] Paints prepared from the emulsion polymer compositions of this invention may contain waxes or surface modification additives such as silicone slip aids. Waxes may be used to reduce the gloss of the paint and maintain a high level of coffee, wine, or tea stain resistance. These waxes also can improve the burnish resistance of the coating. Examples of such waxes include Ceraflour™ 916, Ceraflour™ 920, and Ceraflour™ 962. Waxes may also be used to improve the mar and scratch resistance of the paint. An example would be Michem Emulsion™ 39235. Silicone slip aids may also be used to improve mar and scratch. An example would be Tego Glide™ 410.

[0271] Paints prepared from the emulsion polymer compositions of this invention may contain reactive silanes which contain an epoxy group or an amine group. The silane can be a trialkoxy, a dialkoxy, or a mono alkoxy. The alkoxy groups are typically methoxy, ethoxy, or propoxy. In the case of the dialkoxy, or a mono alkoxy materials the silicon atom is bonded to a methyl group. For example, monomethyldimethoxy silane would be common siloxane group. Trialkoxy, and dialkoxy silanes based on methoxy or ethoxy are preferred. The emulsion polymer may also contain reactive groups such as epoxy or acetoacetoxy which can react with the amine functional portion of the amino silane. An example of a useful amino silane would be Silquest A-1100 which is alpha-amino propyl-triethoxysilane. Alpha-amino propylmethyldimethoxysilane is a useful coupling agent for adhesion to metal oxides such as aluminum oxide. An example of useful epoxy silanes are Silquest A-186 and Silquest A-187. The silanes are typically used at around 1% and provide for adhesion to metals and metal oxide surfaces. They can also be used to crosslink the paint.

[0272] 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.

[0273] Further aspects of the invention and preferred features thereof are given in the claims herein.

Tests

Minimum Film Forming Temperature

[0274] 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

[0275] 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.

Assessment of Coating Film

[0276] Where indicated in some of the tests herein, the performance of a coating film can be assessed by assessing the damage to the coating. Damage is preferably assessed either by measuring the weight percentage of the coating left on the substrate after the test but the coating can also be evaluated visually using the rating scale below where 5 is the best and 1 is the worse:

5=very good: no visible damage or degradation/discoloration;
4=only slight visible damage or haze/blooming;
3=clear damage or haze/blooming;
2=coating partially dissolved/damaged;
1=very poor; coating is completely dissolved/damaged.

Koenig Hardness

[0277] 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)

[0278] 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:

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

[0279] The calculated Tg in degrees Kelvin may be readily converted to ° C.

Solids Content

[0280] 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

[0281] 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:

[0282] 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:

[0283] 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:

[0284] 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)

[0285] 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×0.25 mm i.d., 1.0 μm (CP nr. 7862) column has been used.

[0286] 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 1 μl. 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

[0287] 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

[0288] 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

[0289] 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 150 μl. The flow was established at 1.0 ml/min. Three PL MixedB (Polymer Laboratories) with a guard column (3 μm 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 (+1 vol % 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

[0290] 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 50 µl. 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

[0291] 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) 0.1 m/s.

[0292] 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.

[0293] 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.

[0294] In the examples the following abbreviations/monomers may be used:

DBI denotes dibutyl itaconate (may be (partly) bio-renewable)

DEI denotes diethyl itaconate (may be (partly) bio-renewable)

DMI denotes dimethyl itaconate (may be (partly) bio-renewable)

MFA denotes the (totally fluorinated) perfluoroalkoxy (methyl vinyl ether) polymer (available commercially from Fluorotherm under the trade name Hyflon);

MMA denotes methyl methacrylate (may be (partly) bio-renewable)

BA denotes butyl acrylate (may be (partly) bio-renewable)

STY denotes styrene

IA denotes itaconic acid (may be bio-renewable)

IANH denotes itaconic anhydride (may be bio-renewable)

AA denotes acrylic acid (may be bio-renewable)

MAA denotes methacrylic acid (may be bio-renewable)

AIBN denotes azobisisobutyronitrile

DTPO denotes di-tertiary butyl peroxide

PEG350 denotes the methoxy polyethylene glycol methacrylate available commercially from Cognis (part of BASF) under the trade mark Bisomer® mPEG350MA.

Components A1 to A8 are known polymer emulsions used to prepare blends of the invention together with other components as described below.

[0295] Emulsion A1 High Tg poly(meth)acrylate emulsion (available commercially from DSM under the registered trademark NeoCryl XK-26®)

[0296] Emulsion A2 High oil length alkyd emulsion (available commercially from DSM under the registered trademark Uradil AZ-515 Z-60®

[0297] Emulsion A3 Multi-phase poly(meth)acrylate emulsion with improved adhesion (available commercially from DSM under the registered trademark NeoCryl XK-90®)

[0298] Emulsion A4 polyurethane-poly(meth)acrylate copolymer emulsion (available commercially from DSM under the registered trademark NeoPac E-129®)

[0299] Emulsion A5 Multi-phase self-crosslinkable poly (meth)acrylate emulsion (available commercially from DSM under the registered trademark NeoCryl XK-98®)

[0300] Emulsion A6 Poly(meth)acrylate emulsion with improved adhesion (available commercially from DSM under the registered trademark NeoCryl XK-75®)

[0301] Emulsion A7 Self-crosslinking poly(meth)acrylate emulsion (available commercially from DSM under the registered trademark NeoCryl XK-12®)

[0302] Emulsion A8 Polyurethane emulsion (available commercially from DSM under the registered trademark NeoRez R-974®)

Components B1 to B7 are Also Used to Prepare Blends of the Present Invention

[0303] The itaconate copolymer Examples B1 to B7 herein that form a component of the blends of the present invention are also described in the applicant's application EP12153842.5 filed 3 Feb. 2012 (as respective Examples 1 to 7) from which this application claims priority.

EXAMPLES B1 TO B3

Sequential Vinyl Polymers

Example B1

[0304] 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.

[0305] 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.

[0306] 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.

[0307] 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.

[0308] The resulting emulsion has a solids content of 45%, and a pH of 7.0.

Example B2

[0309] 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.

[0310] 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.

[0311] 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.

[0312] 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.

[0313] The resulting emulsion has a solids content of 45%, and a pH of 7.0.

Example B3

[0314] 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.

[0315] 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.

[0316] 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.

[0317] 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.

[0318] The resulting emulsion has a solids content of 45%, and a pH of 7.0.

EXAMPLES B4 TO B7

Vinyl Oligomer-Polymers

Example B4

Oligomer B4A

[0319] 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.

[0320] 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.

[0321] The resulting emulsion had a solids content of 25.1% and a pH of 8.0.

Polymer Emulsion B4B

[0322] 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.

[0323] 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.

[0324] 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.

[0325] The resulting emulsion had a solids content of 44.0% and a pH of 7.8.

Example B5

Oligomer B5A

[0326] 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.

[0327] 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.

[0328] The resulting emulsion had a solids content of 25.1% and a pH of 8.0.

Polymer Emulsion B5B

[0329] 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.

[0330] 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.

[0331] 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.

[0332] The resulting emulsion had a solids content of 44.0% and a pH of 7.8.

Example B6

Polymer Emulsion B6B

[0333] 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.

[0334] 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.

[0335] 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.

[0336] The resulting emulsion had a solids content of 44.0% and a pH of 7.8.

Example B7

[0337] An emulsion was prepared exactly as described in Example B6 above except in preparing the polymer component (Polymer Emulsion B7B) the monomer feed consisted of: 11.08 parts of butyl acrylate, 4.86 parts of dimethyl itaconate, and 8.98 parts of dibutyl itaconate.

[0338] The resulting emulsion had a solids content of 44.0% and a pH of 7.8.

EXAMPLES OF ITACONATE-CONTAINING POLYMERS

B8 to B14

Example B8

Oligomer-Polymer PP

[0339] 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, 205.0 parts of methyl methacrylate, 39.0 parts of diacetone acrylamide, 48.8 parts of methacrylic acid, 195.2 parts of dimethyl itaconate, 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 part 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 neutralised using 37.0 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 resulting emulsion had a solids content of 25.3% and a pH of 7.9.

Example B9

Oligomer-Polymer

[0340] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer 43.7 parts of water, 3.6 parts of a 30 wt-% solution of sodium lauryl sulphate in water, and 859.5 parts of the oligomer from Example B8 were added. The contents of the reactor were heated to 30° C. Then 50% of a monomer feed consisting of 24.0 parts of water, 219.8 parts of dibutyl itaconate, 318.9 parts of butyl acrylate, and 10.8 parts of diacetone acrylamide was added after which the emulsion was stirred for 5 minutes. Next, 0.3 parts of a 70 wt-% slurry of t-butyl hydroperoxide, 4.0 parts of water and 0.1 parts of a 1 wt-% solution of FeEDTA were added, followed by 40% of a solution of 0.9 parts of i-ascorbic acid in 26.2 parts of water. After the temperature had reached 74° C., the batch was stirred for 10 minutes and cooled to 45° C. Next, the remainder of the monomer feed was added, followed by 195.5 parts of water, and the emulsion was allowed to stir for 15 minutes. A slurry of 0.3 parts of a 70 wt-% slurry of t-butyl hydroperoxide, 4.0 parts of water was added followed by the remainder of the i-ascorbic acid solution. The temperature reached 66° C. after which the mixture was mixed for another 10 minutes. The batch was cooled to 60° C. and a slurry of 0.8 parts of a 70 wt-% slurry of t-butyl hydroperoxide and 1.1 parts of water was added followed by a solution of 0.5 parts of i-ascorbic acid in 7.9 parts of water. The mixture was stirred for 15 minutes. The batch was cooled to 30° C. and 10.7 parts of adipic dihydrazide and 2.8 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 7.4.

Example B10

Sequential/Multiphase Polymer Emulsion

[0341] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer 70.1 parts of demineralised water were charged and heated to 80° C. At 80° C. 0.06 parts of sodium bicarbonate and 5.138 of Fosfodet FAZ109V (ex. KAO) were charged to the reactor, followed by 0.07 parts of a 25% ammonia solution in water. A solution of 0.06 parts of ammonium persulphate dissolved in 1.3 parts of demineralised water was added to the reactor. Immediately thereafter 10% of an emulsified monomer feed, comprising 1.50 parts of acrylic acid, 11.27 parts of dimethyl itaconate, 26.29 parts of dibutyl itaconate, 36.06 parts of butyl acrylate, 0.09 parts of sodium bicarbonate, 6.23 parts of Fosfodet FAZ109V (ex. KAO) and 20.28 parts of demineralised water, was added. The temperature will rise to 90° C. At 90° C., 67% of an initiator feed, comprising 0.32 parts of ammonium persulphate, 0.04 parts of sodium bicarbonate, and 5.96 parts of demineralised water, was started together with the remainder of the monomer feed. The monomer feed should be completed in 50 minutes, the initiator feed in 75 minutes. At the end of the monomer feed the feed tank is rinsed with 1.25 parts of demineralised water. At the end of the monomer feed a mixture of 0.15 parts of a 25% ammonia solution in water and 0.19 parts of demineralised water are feed to the reactor in 15 minutes. At the end of the initiator feed 2.52 parts of demineralised water was added to the initiator feed. Then 45 minutes after completion of the monomer feed a second monomer feed, comprising 1.61 parts of methacrylic acid, 11.27 parts of dimethyl itaconate, 19.31 parts of methyl methacrylate, 0.06 parts of sodium bicarbonate, 3.59 parts of Fosfodet FAZ109V (ex. KAO), and 12.73 parts of demineralised water, was started together with the remainder of the initiator feed. Both feeds took about 25 minutes. At the end of the monomer feed the feed tank was rinsed with 1.25 parts of demineralised water. Finally, the solids content of the emulsion was adjusted to 45% using demineralised water and the pH is adjusted to 7.5 using a 25% ammonia solution in water.

Example B11

High Tg Polymer Emulsion

[0342] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer 124.15 parts of demineralised water, 0.21 parts of potassium persulphate, 0.54 parts of sodium bicarbonate, and 8.94 parts of a 30 wt-% solution of sodium lauryl sulphate were charged and heated to 50° C. At 50° C. 10% of a monomer feed consisting of 42.89 parts of dimethyl itaconate, 61.12 parts of styrene, and 3.22 parts of acrylic acid was charged to the reactor and the batch was further heated to 90° C. As soon as the reaction temperature is reached, the remainder of the monomer feed was added over a period of 70 minutes. When the feed was completed the feed tank was rinsed with 1.26 parts of demineralised water, which was then added to the reactor. The reactor contents were stirred at reaction temperature for another 30 minutes, after which the batch was cooled back to room temperature. The pH was adjusted to between 7.0 and 7.5 using a 25% ammonia solution. The solids content was adjusted to 45% using demineralised water.

Example B12

Low Tg Polymer Emulsion

[0343] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer 124.15 parts of demineralised water, 0.21 parts of potassium persulphate, 0.54 parts of sodium bicarbonate, and 8.94 parts of a 30 wt-% solution of sodium lauryl sulphate were charged and heated to 50° C. At 50° C. 10% of a monomer feed consisting of 48.25 parts of dibutyl itaconate, 53.62 parts of butyl acrylate, and 5.36 parts of methacrylic acid was charged to the reactor and the batch was further heated to 90° C. As soon as the reaction temperature was reached, the remainder of the monomer feed was added over a period of 70 minutes. When the feed was completed the feed tank was rinsed with 1.26 parts of demineralised water, which was then added to the reactor. The reactor contents were stirred at reaction temperature for another 30 minutes, after which the batch was cooled back to room temperature. The pH was adjusted to between 7.0 and 7.5 using a 25% ammonia solution. The solids content was adjusted to 42.5% using demineralised water.

Example B13

Crosslinkable Emulsion

[0344] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer were charged 40.38 parts of demineralised water, 0.40 parts of sodium bicarbonate, 2.12 parts of a 30 wt-% solution of sodium lauryl sulphate in demineralised water, and 0.08 parts of sodium persulphate and the mixture was heated to 50° C. At 50° C., 10% of a monomer feed comprising 36.85 parts of demineralised water, 27.78 parts of dimethyl itaconate, 6.35 parts of diacetone acrylamide, 43.66 parts of butyl acrylate, 1.59 parts of acrylic acid, and 0.90 parts of a 30 wt-% solution of sodium lauryl sulphate in demineralised water, was added to the reactor, and its contents were further heated to 70° C. Due to the exothermic character of the reaction the temperature will rise to 85° C., if necessary the batch will be heated to 85° C. At 85° C. an initiator feed consisting of 0.32 parts of sodium persulphate, 8.99 parts of demineralised water, and 0.16 parts of a 30 wt-% solution of sodium lauryl sulphate in demineralised water, was started and should take 135 minutes. 5 minutes after the start of the initiator feed addition of the remainder of the monomer feed was started. The monomer feed took 120 minutes. When the monomer feed was completed, the feed tank was rinsed with 1.42 parts of demineralised water. At the end of the initiator feed, the batch was stirred at reaction temperature for 20 minutes, after which it was cooled to 48° C. At 48° C., a solution consisting of 0.05 parts of iso-ascorbic acid in 0.90 parts of demineralised water (of which the pH is adjusted to 4.5±0.5) was charged to the reactor, followed by a mixture of 0.02 parts of a 30 wt-% solution of sodium lauryl sulphate in demineralised water, 0.07 parts of a 70 wt-% solution of t-butyl hydroperoxide in water, and 0.11 parts of demineralised water. The batch was stirred at 48° C. for 30 minutes and next cooled to 35° C. At 35° C. sufficient amount of a 25% solution of ammonia in water (up to 2.0 parts) was added to raise the pH of the reactor contents to 7.8±0.2. Next, 2.94 parts of adipic acid dihydrazide was added, after which the solids content of the polymer emulsion was adjusted to 45.0% using sufficient demineralised water (up to 4.0 parts).

Example B14

Polymer Emulsion Having Adhesion Promoting Groups

[0345] To a round-bottomed flask equipped with a condenser, thermometer and mechanical stirrer were charged 40.38 parts of demineralised water, 0.40 parts of sodium bicarbonate, 2.12 parts of a 30 wt-% solution of sodium lauryl sulphate in demineralised water, and 0.08 parts of sodium persulphate and the mixture was heated to 50° C. At 50° C., 10% of a monomer feed comprising 36.85 parts of demineralised water, 35.72 parts of dibutyl itaconate, 7.94 parts of N-(2-methacryloyloxyethyl) ethylene urea (50% in water, ex. Evonik), 37.31 parts of butyl acrylate, 2.38 parts of methacrylic acid, and 0.90 parts of a 30 wt-% solution of sodium lauryl sulphate in demineralised water, was added to the reactor, and its contents are further heated to 70° C. Due to the exothermic character of the reaction the temperature rose to 85° C., (though if necessary the batch can be heated to 85° C.) and at 85° C., an initiator feed consisting of 0.32 parts of sodium persulphate, 8.99 parts of demineralised water, and 0.16 parts of a 30 wt-% solution of sodium lauryl sulphate in demineralised water was fed to the reactor over 135 minutes. Then 5 minutes after the initiator feed began the remainder of the monomer was fed to the reactor over 120 minutes. When the monomer feed was completed, the feed tank was rinsed with 1.42 parts of demineralised water. At the end of the initiator feed, the batch was stirred at reaction temperature for 20 minutes, after which it was cooled to 48° C. and then a solution consisting of 0.05 parts of iso-ascorbic acid in 0.90 parts of demineralised water (of which the pH is adjusted to 4.5±0.5) was charged to the reactor, followed by a mixture of 0.02 parts of a 30 wt-% solution of sodium lauryl sulphate in demineralised water, 0.07 parts of a 70 wt-% solution of t-butyl hydroperoxide in water, and 0.11 parts of demineralised water. The batch was stirred at 48° C. for 30 minutes and next cooled to 35° C. when sufficient of a 25% solution of ammonia in water (up to 2.0 parts) was added to raise the pH of the reactor contents to 7.8±0.2. Next, the solids content of the polymer emulsion was adjusted to 45.0% using sufficient demineralised water (up to 4.0 parts).

Examples 1 to 40

Blends

[0346] Blends of the invention may be prepared by mixing the emulsions described above in the weight proportions given in the tables below (using any suitable mixing means in a suitable vessel) to obtain as blends Examples 1 to 40 of the present invention.

TABLE 1

	Blend Ex (#)		
	Ex 1	Ex 2	Ex 3
Example B4	36.38	27.60	39.46
Emulsion A2	63.62		
Emulsion A8		72.40	
Emulsion A5			60.54

TABLE 2

	Blend Ex (#)	
	Ex 4	Ex 5
Example B5	84.11	61.36
Emulsion A1	15.89	
Emulsion A7		38.64

TABLE 3

	Blend Ex (#)	
	Ex 6	Ex 7
Example B6	49.44	70.00
Emulsion A1	50.56	
Emulsion A7		30.00

TABLE 4

	Blend Ex (#)		
	Ex 8	Ex 9	Ex 10
Example B7	83.33	70.00	80.00
Emulsion A1	16.67		
Emulsion A6		30.00	
Emulsion A7			20.00

TABLE 5

	Blend Ex (#)		
	Ex 11	Ex 12	Ex 13
Example B2	76.09	50.00	78.43
Emulsion A1	23.91		
Emulsion A6		50.00	
Emulsion A7			21.57

TABLE 6

	Blend Ex (#)			
	Ex 14	Ex 15	Ex 16	Ex 17
Example B3	83.33	75.67	70.00	78.05
Emulsion A1	16.67			
Emulsion A2		24.33		
Emulsion A6			30.00	
Emulsion A8				21.95

TABLE 7

	Blend Ex (#)		
	Ex 18	Ex 19	Ex 20
Example B2	90.09	83.83	
Example B3			57.83
Example B4			9.64
MFA*	9.91	16.17	
Emulsion A8			32.53

*fluorinated polymer described previously.

TABLE 8

	Blend Ex (#)		
	Ex 21	Ex 22	Ex 23
Example B11	36.38	27.60	39.46
Emulsion A2	63.62		
Emulsion A8		72.40	
Emulsion A5			60.54

TABLE 9

	Blend Ex (#)	
	Ex 24	Ex 25
Example B12	84.11	61.36
Emulsion A1	15.89	
Emulsion A7		38.64

TABLE 10

	Blend Ex (#)	
	Ex 26	Ex 27
Example B13	49.44	70.00
Emulsion A1	50.56	
Emulsion A7		30.00

TABLE 11

	Blend Ex (#)		
	Ex 28	Ex 29	Ex 30
Example B14	83.33	70.00	80.00
Emulsion A1	16.67		
Emulsion A6		30.00	
Emulsion A7			20.00

TABLE 12

	Blend Ex (#)		
	Ex 31	Ex 32	Ex 33
Example B9	76.09	50.00	78.43
Emulsion A1	23.91		
Emulsion A6		50.00	
Emulsion A7			21.57

TABLE 13

	Blend Ex (#)			
	Ex 34	Ex 35	Ex 36	Ex 37
Example B10	83.33	75.67	70.00	78.05
Emulsion A1	16.67			
Emulsion A2		24.33		
Emulsion A6			30.00	
Emulsion A8				21.95

TABLE 14

	Blend Ex (#)		
	Ex 38	Ex 39	Ex 40
Example B9	90.09	83.83	
Example B10			57.83
Example B11			9.64
MFA*	9.91	16.17	
Emulsion A8			32.53

*fluorinated polymer described previously.

Film Properties

[0347] For a selection of the blends described above, their film properties were assessed and set out in the following tables. More detail about each test is described previously. For this purpose, emulsions were formulated with 2 wt-% of butyl di-glycol. Film were cast, dried for 4 hours under ambient conditions and, next, dried at 50° C. for 24 hours.

TABLE 15

Test	Example B11	Blend Ex 23
Water spot (16 hrs)	5	5
Ethanol spot (16 hrs)	3	5
Andy** spot (16 hrs)	2	5
Coffee spot (16 hrs)	2	4
König hardness (s)	72	106
Blocking resistance	3	5

**"Andy" denotes the liquid detergent available commercially from Unilever under the trade mark "Handy Andy".

TABLE 16

Test	Example B12	Blend Ex 25
Water spot (16 hrs)	1	3
Ethanol spot (16 hrs)	1	3
Andy spot (16 hrs)	2	2
Coffee spot (16 hrs)	1	4
König hardness (s)	<10	25
Blocking resistance	1	4

TABLE 17

Test	Example B13	Blend Ex 26
Water spot (16 hrs)	3	4
Ethanol spot (16 hrs)	4	5
Andy spot (16 hrs)	4	4
Coffee spot (16 hrs)	3	3
König hardness (s)	46	104
Blocking resistance	4	4

TABLE 18

Test	Example B7	Blend Ex 29
Water spot (16 hrs)	2	2
Ethanol spot (16 hrs)	2	3
Andy spot (16 hrs)	3	3
Coffee spot (16 hrs)	3	3
König hardness (s)	12	32
Blocking resistance	1	2

TABLE 19

Test	Example B3	Blend Ex 38
Water spot (16 hrs)	4	4
Ethanol spot (16 hrs)	1	1
Andy spot (16 hrs)	1	1
Coffee spot (16 hrs)	3	4
König hardness (s)	28	55
Blocking resistance	2	4

[0348] A clear improvement is observed upon blending the itaconate functional binders (B10 to B14) with another emulsion to form blends (Ex 23, 25, 26, 29 & 38). In all cases the König hardness improved, in most cases blocking resistance improved, while resistance to chemicals such as ethanol, water, detergent and coffee was equal or better for the blends compared to the pure binders.

1. A mixture comprising:

a) a first polymer selected from one or more from the group consisting of: a vinyl (co)polymer; an alkyd polymer; a urethane acrylic copolymer; a polyurethane; a polyester, combinations and/or mixtures thereof;

b) a second copolymer obtained and/or obtainable from a second monomer composition comprising:

b1) optionally at least 10 wt-% of one or more monomer(s) selected from derivatives of itaconic acid and/or isomers thereof;

b2) up to 20 wt-% of one or more acid functional (or potentially acid functional) monomer(s)

b3) vinyl monomer(s)

where the percentages given for each monomer (b1 to b3) in the second monomer composition is calculated based on the total amount of monomer (b1 to b3) being 100%;

where at least one of the first and second polymer comprise a polymer obtained and/or obtainable from an itacon-functional monomer.

2. A mixture as claimed in claim **1** comprising an aqueous composition comprising:

a) a first emulsion comprising a first copolymer dispersed in water, where the first copolymer is obtained and/or obtainable from a first monomer composition comprising:

a1) optionally at least 20 wt-% of one or more monomer(s) selected from derivatives of itaconic acid and/or isomers thereof;

a2) up to 12.5 wt-% of one or more acid functional (or potentially acid functional) monomer(s)

a3) other vinyl monomer(s)

b) a second emulsion comprising a second copolymer dispersed in water, where the second copolymer is obtained and/or obtainable from a second monomer composition comprising:

b1) at least 20 wt-% of one or more monomer(s) selected from derivatives of itaconic acid and/or isomers thereof;

b2) up to 12.5 wt-% of one or more acid functional (or potentially acid functional) monomer(s)

b3) other vinyl monomer(s)

where the first and second copolymers:

(i) are different from each other:

(ii) form morphologically distinct phases (a) and (b) such that the phase ratio of (a) to (b) is from 5:95 and 95:5; and

where the percentages given for each monomer (a1 to a3) in the first monomer composition is calculated based on the total amount of monomer (a1 to a3) being 100% of the first monomer composition; and

where the percentages given for each monomer (b1 to b3) in the second monomer composition is calculated based on the total amount of monomer (b1 to b3) being 100% of the second monomer composition.

3. A mixture as claimed in claim **1** comprising an aqueous composition comprising:

a) a first emulsion comprising a first copolymer dispersed in water, the first copolymer having a weight average molecular weight of at least 200 kg/mole as measured by GPC and being obtained and/or obtainable from a first monomer composition comprising:

a2) up to 12.5 wt-% of one or more acid functional (or potentially acid functional) monomer(s)

a3) other vinyl monomer(s)

b) a second emulsion comprising a second copolymer dispersed in water, the second copolymer having a weight average molecular weight of no more than 50 kg/mole as measured by GPC and being obtained and/or obtainable from a second monomer composition comprising:

b1) at least 20 wt-% of one or more monomer(s) selected from derivatives of itaconic acid and/or isomers thereof;

b2) up to 12.5 wt-% of one or more acid functional (or potentially acid functional) monomer(s)

b3) other vinyl monomer(s)

where the percentages given for each monomer (a2 to a3) in the first monomer composition is calculated based on the total amount of monomer (a2 to a3) being 100% of the first monomer composition; and

where the percentages given for each monomer (b1 to b3) in the second monomer composition is calculated based on the total amount of monomer (b1 to b3) being 100% of the second monomer composition.

4. A polymer composition as claimed in claim **2**, in which the first and second copolymers form morphologically distinct phases (a) and (b) such that the phase ratio of (a) to (b) is from 5:95 and 95:5

5. A polymer composition as claimed in claim **1**, in which at least one of (a1) where present and/or (b1) comprises a C1-10alkyl itaconate diester.

6. A process for preparing an aqueous polymer composition as claimed in claim **1** comprising the steps of:

(i) polymerising suitable monomers to obtain a first polymer (a) selected from the group consisting of: a vinyl (co)polymer; an alkyd polymer; a urethane acrylic copolymer; a polyurethane; a polyester, combinations and/or mixtures thereof;

(ii) polymerising the monomer components (b2), (b3) and optionally (b1) as described in any preceding claim, in an emulsion polymerisation in the presence of water (and optionally a surfactant) to obtain an emulsion of a second copolymer;

(iii) mixing the first and second copolymers from steps (i) and (ii) to form a blended polymer.

7. A process for preparing an aqueous polymer composition as claimed in **6** comprising the steps of:

polymerising monomer components (a2) and (a3) and optionally (a1) in an emulsion polymerisation in the presence of water (and optionally a surfactant) to obtain an emulsion of the first copolymer (a), where the first polymer comprises a vinyl (co)polymer;

(ii) polymerising monomer components (b2), (b3) and optionally (b1) in an emulsion polymerisation in the presence of water (and optionally a surfactant) to obtain an emulsion of a second copolymer;

(iii) mixing the first and second copolymers from steps (i) and (ii) to form an aqueous composition of blended polymer.

8. A polymer mixture obtained and/or obtainable by a process as claimed in claim **6**.

9. A coating composition comprising a polymer mixture as claimed in claim **1**.

10. A substrate and/or article having coated thereon an (optionally cured) coating composition of claim **9**.

11. A method of using a mixture as claimed in claim **1** to prepare a coating composition.

12. A method for preparing a coated substrate and/or article comprising the steps of applying a coating composition of claim **9** to the substrate and/or article and optionally curing said composition in situ to form a cured coating thereon

13. Use as a binder for a coating composition of a polymer mixture as claimed in claim **1**.

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