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

(57) **Abstract:** There is described a low number average molecular weight ($M_N < 10$ kD) and high glass transition temperature (> 75 °C) copolymer (optionally a solid grade oligomer (SGO)) that comprises (a) at least 20 wt-% of itaconate functional monomer(s), (b) not more than 40 % of a hydrophilic monomer, preferably an acid functional monomer(s) in an amount sufficient to achieve an acid value from 65 to 325 mg KOH per g of solid polymer; (c) optionally not more than 70 % of other monomers not being either (a) or (b), having a max content of vinyl aromatic monomer(s) of 40 wt-% and/or max content of methacrylate(s) of 40 wt-%; where the weight percentages of monomers (a), (b) and (c) are calculated as a proportion of the total amount of monomers in the copolymer being 100 %.



POLYMER, PROCESS AND COMPOSITION

This invention relates to polymers made from itaconate and similar monomers; to a process for making these polymers and to their use in coatings, inks and adhesives.

Itaconate esters, also known as 2 methylenedibutanedioate esters, are monomers that can be obtained from biorenewable sources. Yet despite been well known for many years, they have not been widely used to make commercial polymers because they often are expensive and difficult to process.

Polymers with a low molecular weight (low M_n) and a high glass transition temperature (high T_g) are desirable for several reasons. They can form useful coatings, may be used as stabilizers (e.g. in emulsion polymerization). They may produce films with improved hardness and blocking resistance. Examples of such low M_n , high T_g polymers are solid grade oligomers (also referred to as SGO).

The applicant has found that itaconate esters can be used to prepare improved polymers such as low M_w / high T_g solid grade oligomers. Surprisingly the various difficulties of using itaconate ester monomers can be overcome and they may be incorporated into polymers having some or all of the advantages described herein. Itaconate polymers of the invention may also form films at room temperature which are highly flexible (elastic) and are less prone to blocking.

As used herein the term solid grade oligomer (SGO) preferably denotes an oligomer composition comprising an oligomer (preferably the oligomer having a weight average molecular weight as measured by GPC of no more than 100,000 g/mol) the composition substantially comprising solid material (preferably solid in an amount greater than or equal to 95% by weight of oligomer composition, more preferably consists of solid material) under standard conditions. The terms "oligomer", "substantially comprises" and "standard conditions" are defined later in this document,

Polymers prepared by bulk polymerisation of methacrylate monomers are generally poorly converted or require undesirable process conditions. In a further problem addressed by this invention the applicant has also found that these methacrylate monomers can be wholly or partially replaced by itaconate or similar monomers. This can reduce the concentration of initiators and/or lower the polymerisation temperatures required to produce polymers. The resultant polymers are

prepared at a high conversion rate of monomer and have similar properties to those made from the methacrylate monomers .

The further optional problem is addressed by the invention. It has also been found that omitting styrene monomers results in several undesirable changes to the polymerization process especially when producing low molecular weight polymers. For example initiator concentration is increased, chain transfer agent (CTA) is used and/or polymerization temperature is increased. Vinyl aromatic monomers such as styrene are also undesirable for other reasons as they are possible carcinogens and have other potentially chronic adverse health effects. It would be preferable to use as little vinyl aromatic monomer as possible and preferably omit these monomers entirely. Styrene monomers have previously been replaced with methacrylate monomers (for example as described in EP156170). However as described above there are problems with using methacrylate monomers as a direct styrene replacement. The applicant has unexpectedly found that itaconate functional monomers can be used to replace vinyl aromatic monomers such as styrene (in whole or in part) to achieve similar properties to those imparted by such monomers in the resultant polymer. As used herein unless the context dictates otherwise 'styrene' (e.g. styrene-free) may also refer to any similar vinyl aromatic monomers.

Thus to summarise one aspect of the invention the applicant has now surprisingly found that itaconate ester monomers can be used to replace or reduce the amount of styrene and/or methacrylate (MA) monomers added to a polymer whilst addressing some or all of the consequent problems with low-styrene, low-MA, styrene-free and/or MA-free polymers. Thus (in one aspect of the invention) low M_w / high T_g polymers can be prepared with low water sensitivity at a much reduced (or even zero) styrene and/or MA content at a reasonable monomer conversion using lower amounts of chain transfer agent (CTA), lower initiator concentrations and/or lower temperatures than before.

For example one preferred object of the present invention is to provide polymers having a number average molecular weight of less than 15 kg/mole and T_g greater than 75°C that are substantially free of vinyl aromatic monomers. Such polymers may be prepared using no more than 1 weight part (per 100 monomer) of CTA, less than 1 mole parts (per 100 monomer) of initiator and/or from a polymerisation at a temperature of no more than 275°C.

Further problems that may also be addressed by the present invention are described herein and it is an object of the present invention to solve some or all of the problems identified herein.

Some of the prior art documents are discussed below.

5 WO82/02387 (SCJ) describes a bulk polymerization process for preparing low molecular weight vinyl polymers having a dispersion index less than 2 and a number average molecular weight from 1000 to 6000. The polymers are prepared by continuously charging a mixture of at least one mono alkenyl aromatic monomer and at least one acrylic monomer into a reactor containing a molten resin
10 mixture of unreacted monomers and the vinyl polymers at a temperature from 235°C to 310°C, whilst maintaining a flow rate so the residence time of the monomer in the reactor is 2 minutes and the reaction mix is kept at a predetermined level.

EP156170 (SCJ) describes a similar bulk polymerization process to that described above for preparing enhanced yields of high solids, low molecular
15 weight acrylic polymers having a narrow molecular weight distribution and a low chromophore content. The process involves continuously charging mixture of a polymerization initiator and at least one acrylic monomer (in respective molar ratio of 0.0005:1 to 0.06:1) and a reaction solvent (in amount of 0 to 25 % by weight % of the acrylic monomer) into a reactor containing a molten mixture of unreacted acrylic
20 monomers and the acrylic polymer whilst maintaining a flow rate so the residence time of the monomer in the reactor is ≥ 1 minute, the reaction mix is kept at a predetermined level and the molten resin mixture is kept at an elevated reaction temperature sufficient to provide accelerated conversion to a readily processable, uniform, concentrated polymer product.

25 EP554783 (BASF) describes a process for the continuous polymerization of vinyl monomers to form vinyl polymers by free radical initiated or thermally initiated polymerization within an annular gap reactor comprising an outer tube and a cylindrical rotor inserted therein so the annular gap is 0.5 to 10 mm wide, giving a residence period of from 1 to 10 minutes. The outer tube is temperature
30 controlled so the polymerization is performed at 150 to 270°C providing a vinyl polymer having a molecular weight M_n of from 1000 to 20,000 and a polydispersity (M_w/M_n) < 3.5 .

US6346590 describes a continuous polymerization and condensation process of continuously charging into a primary reactor a mixture of: at least one
35 radically-polymerisable monomer with a radically polymerisable group and also a

condensation reactive functionality (CRF); at least one modifying agent (not a monohydroxy alcohol) having a group that reacts with the CRF; where the temperature in the primary reactor is kept at a level to polymerize the monomer effectively and to allow at least a portion of the CRF to react with the modifying agent to produce a gel-free first polymer incorporating at least some of the modifying agent. The radically-polymerisable monomer is being added to primary reactor as the first polymer is being simultaneously removed. The first polymer is added to a secondary reactor maintained at an effective temperature to form a second polymer.

WO2005/097854 (DSM) describes an aqueous composition comprising: i) at least a cross-linkable vinyl oligomer A with a weight average molecular weight in the range of from 1000 to 80,000 g/mole obtained by bulk polymerisation of: (a) 5 to 45 wt% of vinyl monomers bearing ionic or potentially ionic water-dispersing groups; (b) 0 to 30 wt% of vinyl monomers bearing non-ionic water-dispersing groups; (c) 2 to 25 wt% of vinyl monomers bearing cross-linkable groups; (d) 0 to 40 wt% of *o*-methyl styrene; (e) 10 to 93 wt% of vinyl monomers not in (a), (b), (c) or (d); where (a) + (b) + (c) + (d) + (e) = 100%; and ii) at least a vinyl polymer B with a weight average molecular weight > 5000 g/mole, obtained by polymerisation in the presence of vinyl oligomer A of: (f) 0 to 5 wt% of vinyl monomers bearing ionic or potentially ionic water-dispersing groups; (g) 0 to 20 wt% of vinyl monomers bearing non-ionic water-dispersing groups; (h) 0 to 15 wt% of vinyl monomers bearing cross-linkable groups; (i) 60 to 100 wt% of vinyl monomers not in (f), (g) or (h); where (f) + (g) + (h) + (i) = 100%; where the ratio of vinyl oligomer A to vinyl polymer B is in the range of from 5: 95 to 95:5; where polymer B is more hydrophobic than vinyl oligomer A; where the weight average molecular weight of vinyl polymer B is more than the weight average molecular weight of vinyl oligomer A; iii) 0 to 20 wt% of co-solvent; and iv) 30 to 90 wt% of water; where i) + ii) + iii) + iv) = 100%.

Further prior art documents describe the use of itaconate esters in general terms.

US4206292 (Kureha Kagaku Kogyo Kabushiki Kaisha) describes a vinyl chloride resin composition having surface smoothness comprises: (1) 100 parts of vinyl chloride polymer; and (2) 0.1 to 30 parts of a polymer processing aid comprising: (A) 10 to 100 parts of a copolymer comprising 20 to 99% of an alkyl methacrylate, 1 to 70% of a dialkyl itaconate, and 0 to 60% of a copolymerisable monomer; and (B) 0 to 90 parts of a copolymer comprising 80 to 100% of an alkyl methacrylate, and 0 to 20% of a copolymerisable monomer. This vinyl chloride resin composition is not very

relevant for coating compositions to be prepared from bio-based or other environmentally benign sources.

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

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

US6951909 (3M) describes a polymerisable system comprises an organoborane, at least one polymerisable monomer, and a work-life extending agent.

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 itaconate esters are difficult to process (see page 2, lines 23 to 25) which combined with the teaching of the examples demotivates a reader to incorporate 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.

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

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

Therefore broadly in accordance with the present invention there is provided a copolymer having a low molecular weight (Low MW) and high glass transition temperature (High TG) the copolymer comprising (preferably consisting essentially of) moieties obtained and/or obtainable from the following components:

- (a) at least 20 wt-% of one or more itaconate functional monomer(s) not containing acidic groups or precursor acid groups (also referred to herein as 'Itaconate Monomer'),
- (b) not more than 40 wt-% of an acid functional monomer(s) in an amount sufficient to achieve an acid value from 65 to 325 mg KOH per g of solid polymer (also referred to herein as 'Acidic Monomer')

- (c) optionally not more than 72 wt-% of other monomers not being either (a) or (b) (also referred to herein as 'Other Monomer');

where the weight percentages of monomers (a), (b) and (c) total 100% and are calculated as a proportion of the total amount of monomers in the copolymer being 100%; and with the provisos:

- (I) the copolymer has a number average molecular weight (M_n) of no more than 15 kilograms / mole (also referred to herein as 'Low MW'); and
(II) the copolymer has a glass transition temperature of at least 75 °C (also referred to herein as 'High TG'),

and where optionally either or both of provisos (III) and/or (IV) apply:

- (III) the copolymer contains less than 40 wt-% vinyl aromatic monomer(s) (also referred to herein as 'Low Vinyl Aromatic' or Low-Styrene'); and/or
(IV) the copolymer contains less than 40 wt-% methacrylate monomer(s) (also referred to herein as 'Low-MA').

Optionally the copolymers of the invention are solid grade oligomers (SGO).

It is preferred that polymers of the invention, and/or the itaconate monomers are obtained from bio-renewable sources.

A further aspect of the present invention comprises a coating composition comprising from 5 to 80 wt-% of the total composition of a Low MW and High TG copolymer of the invention as described herein.

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

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

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

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

- (VIII) the copolymer is substantially free of styrene (preferably styrene free), more preferably component (d) if present is other than styrene or a mixture

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

- (IX) is prepared by other than an emulsion polymerisation method in which a
5 chaser monomer is used; and
- (X) the copolymer is prepared by other than an emulsion polymerisation method in which a chaser monomer is used optionally this proviso applying only when component (a) consists of DBI preferably in an amount of from 8.5 to 15% by weight of the total monomers (a) + (b) + (c) + (d).
- 10 (XI) when component (a) consists of DBI then component (a) is present in an amount other than 8.5 wt-%, 21.8 wt-%, 22.5 wt-% or 22.7 wt % of the total monomer composition, preferably other than from 8 wt-% to 23 wt%,
- (XII) when component (a) consists of DBI then component (a) is present in an
15 amount other than 4.7 wt-%, 5.0 wt-%, 8.5 wt-%, 21.8 wt-%, 22.5 wt-%, 22.7 wt %, 25.0 wt-%, 28.7 wt-%, 30,0 wt-% or 41,2 wt-% of the total monomer composition, preferably other than from 4 wt-% to 42 wt%,
- (XIII) the copolymer is obtained other than from a polymerisation of a dimethyl itaconate (DMI) and dibutyl itaconate (DBI) in the respective weight ratio of 15 to 85 in the presence of poly diethyl itaconate seed polymer; more preferably
20 the copolymer is obtained other than from polymerisation of dialkyl itaconate(s) in the presence of a poly diethyl itaconate seed polymer; most preferably the copolymer is obtained other than from polymerisation in the presence of a poly dialkyl itaconate seed polymer; and/or
- (XIV) if polymerisation of the copolymer occurs in the presence of an initiator system
25 comprising organoborane amine complex and an activator then component (a) is present in an amount greater than 20 wt-%, preferably at least 24 wt-% of total monomers (a) + (b) + (c) + (d).

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

Provisos

(I) Low MW

Copolymers of the invention preferably have a number average molecular weight (M_n) of no more than 15 kilograms / mole (defined herein as Low MW), conveniently less than 10 kilograms / mole. Preferred copolymers of the invention have a number average molecular weight from 500 to 10000 g/mole, more preferably from 500 to 7000 g/mole, most preferably from 500 to 5000 g/mole, for example from 700 to 3000 g/mole.

10 (II) High TG

Copolymers of the invention have a high glass transition temperature of at least 75 °C (defined herein as High TG) as calculated using the Fox equation. Preferred High TG copolymers of the invention have a glass transition temperature of at least 80°C, more preferably at least 85 °C, most preferably at least 90°C for example at least 100 °C.

(III) Low Vinyl Aromatic

The copolymer according to the invention may contain less than 40 wt-% of vinyl aromatic monomer(s), more preferably less than 20 wt-%, most preferably less than 10 wt-%, and even most preferably less than 5 wt-%, for example is substantially free of, (such as 0 wt-%) of vinyl aromatic monomer(s) by weight of the total monomers being 100%. The limits to what is meant herein by 'substantially free' are also as defined later. It is optionally desired to limit the amount of vinyl aromatic monomer in the compositions and copolymers of the invention as their presence may result in yellowing, reduced outdoor durability, and may have potential adverse environmental and/or health impacts.

It is preferably desirable that copolymers and compositions of the invention comprise low amounts of vinyl aromatic monomer(s) such as styrene and/or other arylalkylene monomer(s). As used herein the term vinyl aromatic monomer(s) denotes monomers such as styrene, alpha-methyl styrene, vinyl toluene, vinyl anthracene, p-methyl styrene, and chloromethyl styrene. The term arylalkylene is also defined below. It is more preferred that monomers such as styrene and α -methyl styrene are present in low amounts (or absent) from compositions of the invention. Most preferred compositions of the invention are those that are substantially free of

vinyl aromatics. If a vinyl aromatic monomer is used in the invention, is conventionally styrene.

However as described in the section on acidic monomers by using low molecular weight polymers of high AV it can be possible to use higher amounts of vinyl aromatic monomers (up to 40% by weight of monomers). Nevertheless in a convenient embodiment of the invention the copolymers comprise only a small amount of vinyl aromatic monomers (<20% by weight of monomers) and conveniently copolymers of the invention are substantially free of any vinyl aromatic monomers.

Surprisingly the applicant has discovered that embodiments of the invention in which the copolymer contains none or low amounts of vinyl aromatic monomers, the copolymer may be also be prepared by an improved polymerisation process that exhibits preferably at least one, more preferably two, most preferably three of the following features (I) to (III):

- (I) uses no more than 1 weight parts, preferably no more than 0.5, more preferably no more than 0.2, even more preferably no more than 0.1 parts by weight, most preferably no chain transfer agent; relative to the total monomer composition (i.e. (a) + (b) + (c)) being 100 parts by weight (also denoted herein as wt parts per 100 monomer)
- (II) uses no more than 1 mole parts of initiator, preferably no more than 0.5, more preferably no more than 0.2, even more preferably no more than 0.1 parts by mole relative to the total monomer composition (i.e. (a) + (b) + (c)) being 100 mole parts; (also denoted herein as mole parts per 100 monomer) and/or
- (III) has a maximum polymerisation temperature of no more than 275 °C, preferably no more than 225 °C, more preferably no more than 200°C.

(IV) Low Methacrylate (Low-MA)

The copolymer according to the invention may contain less than 40 wt-% of methacrylate monomer(s), more preferably less than 20 wt-%, most preferably less than 10 wt-%, and even most preferably less than 5 wt-%, for example is substantially free of, such as 0 wt-% of MA monomer(s) by weight of the total monomers being 100%.. The limits to what is meant herein by 'substantially free' are also as defined later. It is desired to limit the amount of MA monomer in the compositions and copolymers of the invention for the reasons already given.

(III) and (IV) Low-Styrene and Low-MA

The copolymers and compositions of the invention may also comprise low amounts of both vinyl aromatic monomer(s) and MA, usefully the total amount of vinyl aromatic monomer(s) and MA monomer(s) is less than 40 wt-%, more usefully less than 20 wt-%, most usefully less than 10 wt-%, and even most usefully less than 5 wt-%, for example is substantially free of (such as 0 wt-%) of such monomer(s) by weight of the total monomers being 100%. The limits to what is meant herein by 'substantially free' are also as defined later.

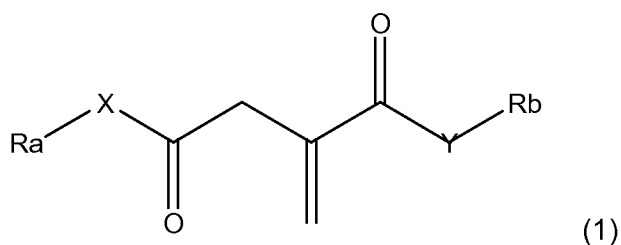
Component Monomers

Components (a), (b) and (c) are mutually exclusive. Thus it will be appreciated that acid functional monomers that may also be derived from itaconates, such as itaconic acid, itaconic anhydride, half itaconate esters, acid derivatives thereof, combinations and/or mixtures thereof are considered part of the acid component (b) and are not part of the itaconate functional component (a)

In one preferred embodiment of the invention components (a) and (b) are each derived from itaconates and/or derivatives thereof, more preferably from a biorenewable source. Thus for example component (a) may be a di(C₁₋₆dialkyl)itaconate, (e.g. DBI and/or DMI) and component (b) may be itaconic anhydride and/or C₁₋₄alkyl monoester thereof (e.g. itaconic acid). In such an embodiment optionally there is no component (c) so the copolymer may advantageously be obtained from monomers from the same itaconate source.

Component (a) ITACONATE MONOMER

Itaconate functional monomers that are suitable for use as component (a) in the present invention may be represented generally by Formula 1:



where Ra and Rb independently represent any optionally substituted hydrocarbon 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);

with the proviso that Formula 1 does not contain:

- 5 any acidic groups (such as carboxylic, phosphoric and/or sulphonic acid groups) or any precursor acid groups, that is a group which readily generates an acid group under the conditions of polymerisation herein (such as an anhydride group).

When X and Y are both O, Formula 1 represents

2-methylidenebutanedioate diesters (also referred to herein as itaconate diesters).

- 10 X and Y are both NRc, Formula 1 represents itaconate diamides.

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

- 15 It will be appreciated that the term itaconate functional monomer(s) as used herein denotes any itaconate diester and/or diamide monomers of Formula 1 (as defined herein), other itaconate esters, itaconate amides,

Preferred itaconate functional monomers are those of Formula 1

where Ra and Rb independently represent:

- optionally substituted C₁₋₃₀hydrocarbyl,
- more preferably C₁₋₂₀alkylene (which may comprise linear, branched and/or cyclic
- 20 moieties) and/or C₃₋₂₀arylne;
- most preferably C₁₋₁₀alkylene.

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

- 25 Conveniently Formula 1 may represent dialkyl or aryl esters of itaconic acid, dialkyl or aryl amides of itaconic acid. More conveniently Ra and Rb may be independently selected from the group consisting of: methyl, ethyl, n-propyl, i-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 Ra and Rb are selected from: methyl, ethyl, n-butyl and 2-ethylhexyl. Most conveniently Ra and Rb are selected from methyl and ethyl for
- 30 example methyl.

The itaconate functional component (a) is present in the compositions and/or copolymers of the invention in an amount of at least 20 wt-%, usefully at least 25 wt-%, more usefully at least 30 wt-%, even more usefully at least 35 wt-% and most

usefully at least 40 wt-%, based on the total weight of monomers (a), (b) and (c) used to prepare the copolymer being 100%..

Conveniently the itaconate functional component (a) may be present in the compositions and/or copolymers of the invention in an amount of less than 80 wt-%, more conveniently less than 75 wt-%, even more conveniently less than 70 wt-%, most conveniently less than 65 wt-%, and for example less than 60 wt-%; based on the total weight of monomers (a), (b) and (c) used to prepare the copolymer being 100%.

Preferably the itaconate functional component (a) may be present in the compositions and/or copolymers of the invention in an amount of from 20 to 80 wt-%, more preferably from 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-% based on the total weight of monomers (a), (b) and (c) used to prepare the copolymer being 100%.

Itaconate functional monomers such as those represented by Formula 1 may also be broadly divided into two types higher itaconate esters which are generally hydrophobic and lower itaconate esters which are generally hydrophilic

In one embodiment of the invention the itaconate functional monomer may be an itaconate diester of Formula 1 where Ra and Rb are independently optionally substituted C₁₋₃hydrocarbo groups, such as C₁₋₃alkyl, an example of which is dimethyl itaconate (DMI).

In another embodiment of the invention the itaconate functional monomer may be an itaconate diester of Formula 1 where Ra and Rb are independently optionally substituted C₄₋₈hydrocarbo groups, such as C₄₋₆alkyl, an example of which is dibutyl itaconate (DBI).

The itaconate functional monomers (a) may be selected from those itaconate monomers that form homopolymers having a Tg of preferably more than 40 °C, more preferred more than 60 °C, and most preferred more than 80 °C.

Component (b) ACIDIC MONOMER (also referred to as 'acidic component')

It will be understood that when referring to acid functional and/or acidic components herein 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 may form acidic groups (e.g. anhydrides). An acid bearing monomer could be polymerised as the free acid or as a salt, e.g. the ammonium and/or alkali metal salt thereof. References herein to acids should therefore also be understood to

include suitable salts and/or derivatives thereof (such as anhydrides and/or acid chlorides thereof).

Thus copolymers of the invention comprise acidic functional monomers (component (b)) that comprise an acid group and/or a precursor acid group.

5 Suitable acid monomers can be monofunctional or difunctional in potential acid functionality. Preferred monomers are acrylic acid, methacrylic acid, β -carboxyethyl acrylate, itaconic acid, itaconic anhydride, maleic acid, and maleic anhydride.

Other preferred acids have one ethylenic group and one or two
10 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
15 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
20 R_a or R_b is H). combinations thereof in the same species and/or mixtures thereof.

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

Suitable acid functional monomers of Component (b) are those that
25 are co-polymerisable with the itaconate functional monomer(s) of component (a). Conveniently at least one monomer of component (b) may comprise at least one activated unsaturated moiety as defined herein.

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

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.

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).

5 Useful arylalkylene sulphonic acids are those where the arylalkylene moiety comprises optionally hydrocarbo substituted styrene, conveniently optionally C₁₋₁₀hydrocarbyl substituted styrene more conveniently optionally C₁₋₄alkyl substituted styrene. Useful acids are sulphonic acid substituted derivatives of styrenic compounds selected from the group consisting of styrene, α -methyl styrene, vinyl toluene, t-butyl
10 styrene, di-methyl styrene and/or mixtures thereof. Especially preferred is styrene p-sulphonic acid and its corresponding acid chloride styrene p-sulphonyl chloride. However it is a preferred object of the invention to reduce (in one embodiment preferably eliminate) the amount of vinyl aromatic moieties (such as styrene and the like) in the copolymers of the invention. Therefore arylalkylene sulphonic acids are not
15 preferred for use as the acidic monomer (b) or if present are in such amounts to satisfy proviso (III) that the copolymer of the invention comprises less than 40% of vinyl aromatic monomer.

Preferred phosphated organo acids comprise phosphated (meth) acrylates optionally substituted for example with one or more hydroxyl groups, for
20 example phosphated hydroxy(meth)acrylates and C₁₋₄alkyl esters thereof.

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

It is known that certain acidic components which may or may not themselves polymerise directly to form copolymers of the invention may also act as
25 precursors for other monomers that undergo polymerisation to form a copolymer of the invention. For example at sufficiently high temperatures in one embodiment of the invention itaconic acid will dehydrate to form itaconic anhydride in situ which may be then react as a monomer in a copolymerisation to form a copolymer of the invention.

For emulsion polymerization acidic monomers such as acrylic acid,
30 methacrylic acid, beta carboxy ethyl acrylate, and/or itaconic acid may be convenient. For a Solvent Assisted Dispersion (SAD) copolymerization acidic monomers such as acrylic acid, methacrylic acid, and/or itaconic anhydride are preferred.

Usefully the acidic component (b) may be present in the compositions and/or copolymers of the invention in an amount of at least 10 wt-%, more usefully at
35 least 15 wt-%, even more usefully at least 20 wt-%, most usefully at least 25 wt-%,

based on the total weight of monomers (a), (b) and (c) used to prepare the copolymer being 100%..

The Acidic Monomer (b) is present in the compositions and/or copolymers of the invention in an amount not more than 40 wt-%, conveniently less than 35 wt-%, more conveniently less than 30 wt-%; based on the total weight of monomers (a), (b) and (c) used to prepare the copolymer being 100%.

Preferably (and subject to the caveats relating to AV values below) the acidic component (b) may be present in the compositions and/or copolymers of the invention in an amount of from 10 to 40 wt-%, more preferably from 15 to 40 wt-%, even more preferably from 20 to 40 wt-%, most preferably from 25 to 40 wt-%, for example from 25 to 35 wt-% based on the total weight of monomers (a), (b) and (c) used to prepare the copolymer being 100%.

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 at least 80 mg KOH / g, more usefully at least 120 mg KOH / g, most usefully at least 160 mg KOH / g, for example at least 195 mg KOH / g of solid polymer

Conveniently the acid monomer (b) may be present in the compositions and/or copolymers of the invention in an amount sufficient amount to achieve AV of no more than 325 mg KOH / g, more conveniently no more than 290 mg KOH / g, most conveniently no more than 260 mg KOH / g, for example no more than 200 mg KOH / g of solid polymer.

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 65 to 325 mg KOH / g. of solid polymer.

It is an optional object of the invention to limit the amount of vinyl aromatic monomer as far as possible for the various reasons described herein. However the applicant has surprisingly discovered that the processing difficulties with use of higher amounts (up to 40% by weight) of vinyl aromatic monomer can be compensated to some extent by increasing AV number. Therefore in various alternative embodiments of the present invention the acid monomer may be present in the compositions and/or copolymers of the invention in various amounts sufficient to achieve certain acid values (in KOH / g per g of solid polymer) when the copolymer contains certain corresponding total amounts of vinyl aromatic monomer (in % by weight of total monomers of the copolymer):

Acid Value (AV)	Vinyl Aromatic Monomer
-----------------	------------------------

from 200 to 325 mg KOH / g with	from 30 up to 40 weight%;	or
from 160 to 290 mg KOH / g with,	from 20 up to 30 weight %;	or
from 120 to 260 mg KOH / g with	from 10 up to 20 weight %;	or
from 80 to 195 mg KOH / g with	from 0 up to 10 weight %.	

5 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

10 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.

 The acidic functional monomers (b) may be selected from those acidic monomers (or precursors therefore) that form homopolymers having a Tg of

15 preferably more than 40 °C, more preferred more than 60 °C, and most preferred more than 80 °C.

Component (c) - OTHER MONOMERS

 The copolymers of the invention comprise no more than 72 wt-%,

20 preferably no more than 70 wt-%, preferably no more than 60 wt-%, more preferably no more than 40 wt-% of other monomers (component (c)) that are neither itaconate functional monomers (a) nor acid functional monomers (b). Component (c) may also satisfy proviso (III) and/or (IV) that the copolymer of the invention comprises less than 40% of vinyl aromatic monomer and/or less than 40% of methacrylate monomers.

25 Therefore monomers such as arylalkylene and/or methacrylate monomers described herein are preferred as component (c) only to the limited extent described herein and optionally are substantially absent from the compositions of the invention.

 Conveniently the other monomers of component (c) may be present in the compositions and/or copolymers of the invention in an amount of less than 30 wt-

30 %, more conveniently less than 20 wt-%, even more conveniently less than 10 wt-% and most conveniently less than 5 wt-%, based on the total weight of monomers (a), (b) and (c) used to prepare the copolymer being 100%.

 Usefully where present the other monomers of component (c) are present in the compositions and/or copolymers of the invention in an amount of at least

35 0.1 wt-%, more usefully at least 0.5 wt-%, even more usefully at least 5 wt-%, , based

on the total weight of monomers (a), (b) and (c) used to prepare the copolymer being 100%..

Preferably the other monomers of component (c) may be present in the compositions and/or copolymers of the invention in an amount of from 0.1 to 40 wt-%, more preferably from 0.5 to 40 wt-%,, even more preferably from 5 to 40 wt-%, most preferably from 5 to 30 wt-%, for example from 5 to 20 wt-% based on the total weight of monomers (a), (b) and (c) used to prepare the copolymer being 100%.

Suitable non-itaconate functional non acid functional monomers are given below. Preferably component (c) comprises low amounts of (more preferably is other than) vinyl aromatic monomers and/or arylalkylene monomers.

The non-itaconate functional monomers can comprise any acrylic or methacrylic acid ester or amide having a homopolymer Tg of preferably more than 40 °C, more preferred more than 60 °C, and most preferred more than 80 °C.

Preferred examples of such monomers are methyl methacrylate, ethyl methacrylate, diacetone acrylamide, acrylonitrile, hydroxyethyl methacrylate, cyclohexyl methacrylate, isobornyl (meth)acrylate, polyethylene (meth)acrylate, polypropylene (meth)acrylate, acryl amide and methacryl amide. Specifically preferred crosslinking monomers that can be used to prepare the low molecular weight copolymer of the invention are described in WO2005/097854 (DSM).

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

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

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

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

Component (c) may also comprise crosslinking monomers that can induce crosslinking of the copolymer composition. Crosslinking can occur at ambient temperatures (using for instance diacetone acryl amide combined with adipic

dihydrazide), at elevated temperatures (stoving conditions in which for instance copolymerized hydroxyethyl (meth)acrylate reacts with hexamethoxy methyl melamines), or as 2C composition (copolymerized hydroxyethyl (meth)acrylate reacting with polyisocyanates, such as Bayhydur 3100). Other examples of crosslinking monomers include hydroxypropyl (meth)acrylate, silane functional monomers, such as 3-methacryloxypropyl trimethoxysilane (Geniosil GF31, ex Wacker). When the intention is to use the coating composition as a UV coating the aqueous composition comprising the low molecular weight polymer according to the invention, may be admixed with polymers or oligomers having multiple unsaturated groups are admixed.

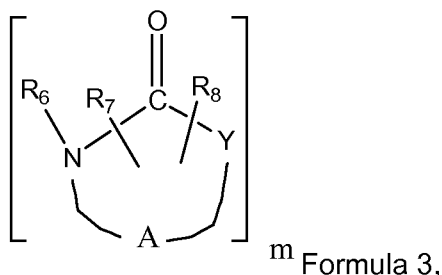
Typical examples include di- or tri-functional multifunctional acrylates such as trimethylol propane triacrylate or ethoxylated or propoxylated versions thereof).

Preferably, the crosslinking monomer(s) is used in concentrations of less than 15 wt-%, more preferably less than 10 wt-%, and most preferably between 0 and 10 wt-%.

Component (c) may also comprise monomers that improve (wet) adhesion properties. Typical monomers include ureido functional monomers, such as Plex 6852-O (ex. Evonik), *i*-bornyl (meth)acrylate, polyethylene (meth)acrylate, polypropylene (meth)acrylate.

Preferably, the adhesion promoting monomer(s) is used in concentrations of less than 15 wt-%, more preferably less than 10 wt-%, and most preferably between 0 and 10 wt-%.

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



where Y denotes an electronegative group,

R₆ is H, OH or an optionally hydroxy substituted C₁₋₁₀hydrocarbo

R₇ is H or a C₁₋₁₀hydrocarbo;

R₈ is a C₁₋₁₀hydrocarbo group substituted by at least one activated unsaturated moiety; and; either:

A represents a divalent organo moiety attached to both the –HN- and –Y- moieties so

the -A-, -NH-, -C(=O)- and -Y- moieties together represent a ring of 4 to 8 ring atoms, and R₇ and R₈ are attached to any suitable point on the ring; or

A is not present (and Formula 3 represents a linear and/or branched moiety that does not comprise a heterocyclic ring) in which case R₇ and R₈ are attached to R₆; and

5 m is an integer from 1 to 4.

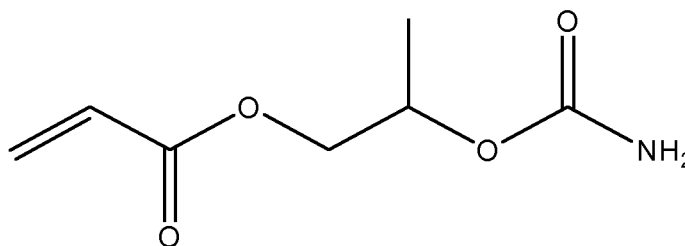
The ring moiety(ies) of Formula 3 are each attached to R₈ and in Formula 3 when m is 2, 3 or 4 then R₈ is multi-valent (depending on the value of m). If m is not 1 R₇ and -Y- may respectively denote the same or different moieties in each ring, preferably the same respective moieties in each ring. R₇ and R₈ may be attached
10 at any suitable position on the ring.

Preferred monomers of Formula 3 comprise, conveniently consist essentially of, those where: A represents an optional substituted divalent C₁₋₅hydrocarbylene; and -Y- is divalent -NR₉- (where R₉ is H, OH, optionally hydroxy substituted C₁₋₁₀hydrocarbo or R₈) or divalent O,
15

More preferred monomers of Formula 3 comprise those where: m is 1 or 2 -Y- is -NR₈- (i.e. where Formula 2 is attached to R₈ via a ring nitrogen), A represents a divalent C₁₋₃hydrocarbylene; R₆ is H, R₇ is a C₁₋₁₀hydrocarbo; and
20 R₈ comprises a (meth)acryloxyhydrocarbo group or derivative thereof (e.g. maleic anhydride).

Monomers represented by Formula 3 include some monomers informally referred to as ureido monomers. Further suitable ureido monomers of Formula 3 are described in "Novel wet adhesion monomers for use in latex paints" Singh et al, Progress in Organic Coatings, 34 (1998), 214-219, (see especially sections 2.2 & 2.3) and EP 0629672 (National Starch) both of which are hereby incorporated by reference. Conveniently the monomers of Formula 3 may be used as a substantially pure compound (or mixture of compounds) or may be dissolved in a suitable solvent such as a suitable (meth)acrylate or acrylic derivative for example methyl methacrylate.
25

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)
30



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

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

OTHER ASPECTS OF THE INVENTION PROCESSES

The present invention relates to the selection of the monomers and properties of the resultant copolymer. The polymerisation process by which copolymers of the invention may be prepared is not especially important as any suitable conventional polymerisation process may be used.

In one preferred embodiment of the invention the copolymer is prepared by a bulk polymerisation process. In another preferred embodiment of the invention the copolymer is prepared by a solution polymerisation process. In still other preferred embodiment of the invention the copolymer is prepared by a suspension polymerisation process. In a yet other preferred embodiment of the invention the copolymer is prepared by an emulsion polymerisation process. Details of these techniques are described later.

CHAIN TRANSFER AGENT (CTA)

In one preference in any embodiment of the invention which uses a polymerisation process where a chain transfer agent may usually have been required (such as but not limited to a radical polymerisation, such as an emulsion polymerisation for example using the low styrene embodiment described herein) the process of the

invention uses chain transfer agent in the following total amounts relative to the total monomer composition (i.e. (a) + (b) + (c)) being 100%:

No more than 1 wt-%, preferably no more than 0.5%, more preferably no more than 0.2%, even more preferably no more than 0.1%, most preferably less than 50 ppm, for example no chain transfer agent.

Typical chain transfer agents that have been used in the prior art include mercapto-acids and alkyl esters thereof, carbon tetrabromide, mixtures thereof and cobalt chelate, dodecylmercaptane (DDM) being one of the most commonly used. Mercapto chain transfer agent have been generally used in amounts of less than 1 wt-% based on the total monomer content. Typically cobalt chelate CTAs are used in amounts of less than 50 ppm of Co on total weight of copolymer.

INITIATOR

In one preference in any embodiment of the invention which uses a polymerisation process where an initiator may usually have been required the process of the invention uses initiator in the following total amounts relative to the total monomer composition (i.e. (a) + (b) + (c)) being 100%:

For a bulk or solution polymerisation process, no more than 1 mole-%, preferably no more than 0.5 mole-%, more preferably no more than 0.2 mole-%, even more preferably no more than 0.1 mole-%.

For an emulsion polymerisation process, no more than 1.5 mole-%, preferably no more than 1 mole-%, more preferably no more than 0.75 mole-%, even more preferably no more than 0.5 mole-%.

Initiators for radical polymerization of monomers to make vinyl polymers are well known and are any which are normally suitable for free-radical polymerisation of acrylate monomers. They may be oil-soluble and have low solubility in water such as organic peroxides, organic peroxyesters and organic azo initiators and are generally used in an amount of about 0.1 to 2 wt-% based on the total monomer content.

The applicant has found that in general especially for the embodiment of the invention that has lower amounts of vinyl aromatic monomer then lower amounts of initiator can be used to prepare the itaconate functional polymers of the invention than would be used to prepare polymers where a methacrylate monomer is used (in whole or in part) rather the itaconate functional monomer (component (a)).

Subject to the optional limitations on initiator described herein, initiators that can be used to produce the low molecular weight polymer via solution or bulk polymerization can be any organic peroxide, including hydroperoxides, dialkyl peroxides, and/or alkyl peroxyalkanoates.

5 Examples of suitable initiators may also comprise any of the following and/or suitable mixtures thereof (as well as chemically similar and/or analogous initiators - for example of the same structural type - as any of those listed below):

 All those available commercially from Akzo-Nobel under the Laurox®, Perkadox® and/or Trigonox® trademarks and/or trade designations such as given in
10 parentheses below:
diisobutyryl peroxide (Trigonox® 187-C30 and/or 187-W40);
cumyl peroxyneodecanoate (Trigonox® 99-C75 and/or 99-W50);
di(3-methoxybutyl) peroxydicarbonate (Trigonox® 181);
1,1,3,3-tetramethylbutyl peroxyneodecanoate (Trigonox® 423-C70 and/or 423-W50);
15 cumyl peroxyneohexanoate (Trigonox® 197-C75);
tert-amyl peroxyneodecanoate (Trigonox® 123-C75);
the mixtures of peroxydicarbonates available under the trademarks Trigonox® ADC and/or Trigonox® ADC-NS60;
di-sec-butyl peroxydicarbonate (Trigonox® SBP, SBP-C60, SBPS and/or SBPS-C60);
20 diisopropyl peroxydicarbonate (Perkadox® IPP-NA30 and/or IPP-NA27);
di(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox® 16S, 16, 16-W75 and/or 16-W40);
di(2-ethylhexyl) peroxydicarbonate (Trigonox® EHP-C75, EHP-W60, EHP-W50, EHP-W40S, EHPS and/or EHPS-C75);
25 tert-butyl peroxyneodecanoate (Trigonox® 23, 23-C75, 23-C30 and/or 23-W50);
dibutyl peroxydicarbonate (Trigonox® NBP-C50);
dicetyl peroxydicarbonate (Perkadox® 24-FL, 24L and/or 24-W35);
dimyristyl peroxydicarbonate (Perkadox® 26);
1,1,3-tetramethylbutyl peroxyneodecanoate (Trigonox® 425-C75);
30 tert-butyl peroxyneohexanoate (Trigonox® 257-C75);
tert-amyl peroxyneodecanoate (Trigonox® 125-C75);
tert-butyl peroxyneodecanoate (Trigonox® 25-C75, 25-C40 and/or 25-C25);
di(3,3,5-trimethylhexanoyl) peroxide (Trigonox® 36-C75, 36-C40, 36-C37.5 and/or 36-W50);
35 dilauroyl peroxide (Laurox®, Laurox® S and/or Laurox® W-40);

- didecanoyl peroxide (Perkadox® SE-10);
2,2-azodi(isobutyronitrile) (Perkadox® AIBN);
2,2-azodi(2-methylbutyronitrile) (Perkadox® AMBN and/or AMBN-GR);
2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane (Trigonox® 141);
5 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate (Trigonox® 421);
tert-amyl peroxy-2-ethylhexanoate (Trigonox® 121 and/or 121-C75);
dibenzoyl peroxide (Perkadox® L-W75, L-W75 SF, L-W40, CH-50, API and/or L-DFG)
tert-butyl peroxy-2-ethylhexanoate (Trigonox® 21S, 21-C70, 21-C50 and/or 21-C30);
tert-butyl peroxydiethylacetate (Trigonox® 27);
10 tert-butyl peroxyisobutyrate (Trigonox® 41-C50);
1,1'-azodi(hexahydrobenzonitrile) (Perkadox® ACCN);
1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane (Trigonox® 29, 29-B90 and/or 29-C75);
1,1-di(tert-amylperoxy)cyclohexane (Trigonox® 122-C80);
15 1,1-di(tert-butylperoxy)cyclohexane (Trigonox® 22-B50, 22-E50 and/or 22-C80);
tert-amylperoxy 2-ethylhexyl carbonate (Trigonox® 131);
tert-amylperoxy acetate (Trigonox® 133-CK60);
tert-butyl peroxy-3,3,5-trimethylhexanoate (Trigonox® 42S, 42-C60 and/or 42-C30);
2,2-di(tert-butylperoxy)butane (Trigonox® D-C50 and/or D-E50);
20 tert-butylperoxy isopropyl carbonate (Trigonox® BPIC-C75);
tert-butylperoxy 2-ethylhexyl carbonate (Trigonox® 117);
tert-amyl peroxybenzoate (Trigonox® 127);
tert-butyl peroxyacetate (Trigonox® F-C50);
butyl 4,4-di(tert-butylperoxy)valerate (Trigonox® 17);
25 tert-butyl peroxybenzoate (Trigonox® C and/or C-C75);
dicumyl peroxide (Perkadox® BC-FF);
di(tert-butylperoxyisopropyl)benzene(s) (Perkadox® 14S and/or 14S-FL);
2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (Trigonox® 101, 101-50D-PD, 101-20PP,
101-7.5PP-PD and/or 101-E50);
30 tert-butyl cumyl peroxide (Trigonox® T);
2,5-dimethyl-2,5-di(tert-butylperoxy)hexyne-3 (Trigonox® 145-E85);
di-tert-butyl peroxide (Trigonox® B, B-C75, B-C50 and/or B-C30);
3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxonane (Trigonox® 301 and/or 301-20PP);
isopropylcumyl peroxide (Trigonox® M-55);
35 1,1,3,3-tetramethylbutyl hydroperoxide (Trigonox® TMBH-L);

- 3,3,5,7,7-pentamethyl-1,2,4-trioxepane (Trigonox® 311);
cumyl hydroperoxide (Trigonox® K-90);
tert-butyl hydroperoxide (Trigonox® A-80 and/or A-W70);
tert-amyl hydroperoxide (Trigonox® TAHP-W85); and/or
5 2,3-dimethyl-2,3-diphenylbutane (Perkadox® 30).

TEMPERATURE.

In one preference in any embodiment of the process of the invention (for example low styrene embodiment of the process of the invention) the maximum
10 polymerisation temperature exhibited is as follows:

For a bulk polymerisation process, no more than 275 °C, preferably no more than 225 °C, more preferably no more than 200 °C, .

For a solution polymerisation process, no more than 180 °C, more preferably no more than 160 °C, and most preferably no more than 150 °C.

15 For an emulsion or dispersion polymerisation process, no more than 130 °C, more preferably no more than 120 °C, and typically no more than 100 °C.

It is appreciated that in those cases where the polymerisation temperature is higher than the boiling point of the solvent (or water in the case of emulsion or dispersion polymerisation), this implicates that the polymerisation is
20 performed at a pressure of higher than 1 bar.

Optionally certain copolymers of the invention may also be limited by the following optional provisos:

- (I) when component (a) consists of DBI in an amount of less than 30% by weight of the total monomers then the copolymer is substantially free of any
25 chloro group; and
(II) when component (a) consists of DBI in an amount of from 8.5 to 15% by weight of the total monomers the copolymer is prepared by other than an emulsion polymerisation method in which a chaser monomer is used.

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

A further aspect of the invention provides a coating composition comprising between 5 and 80 wt-% of a low molecular weight polymer(s) characterized
35 by that the low molecular weight (Low MW) polymer comprises at least 20 wt-% of

itaconate functional monomer(s), and has a number average molecular weight of from 500 to 10000 g/mole.

The polymer of the invention has a low number average molecular weight (Low MW polymer) and can be made via emulsion polymerization, dispersion
5 polymerization, (continuous) bulk polymerization or via solution polymerization. The preferred polymerization processes are bulk polymerization and solution polymerization. Where Low MW polymers of the invention are prepared via emulsion, dispersion and/or solution polymerization, the monomer composition can be added in different sequential phases.

10 The Low MW polymer of the invention is preferably used as colloidal stabilizer in a second stage emulsion polymerization. For this purpose, the acid groups of the low molecular weight polymer are (partially) neutralized and the low molecular weight polymer is (partially) dissolved prior to starting the emulsion polymerization stage. The low MW polymer can, however, also be advantageously used as additive to
15 a second polymer emulsion. In these cases an alkaline solution of the low MW polymer is admixed after the polymerisation process of the second polymer emulsion is completed.

Preferred copolymers of the invention have a polydispersity of from 2 to 2.5, more preferably about 2.5. Therefore suitable desired corresponding values for
20 weight average molecular weight of the copolymers of the invention can be calculated by multiplying each of the values given for number average molecular weight herein by 2.5. Such calculated weight average molecular weight values and ranges are disclosed herein without being recited explicitly.

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

Preferably the polymerisation method is selected from bulk, solution,
30 suspension and/or emulsion polymerisation, more preferably bulk polymerisation.

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

In a yet another embodiment of the invention the copolymer may be prepared by a continuous bulk polymerization for example using a method analogous
35 to that described in WO82/02387 or EP554783. Thus for example the Low MW

polymer may be prepared using (continuous) bulk polymerization, preferably using a solvent concentration of less than 40 wt-% (based on solid polymer being 100%), more preferably using less than 20 wt-% of solvent. Examples of suitable solvents and suitable initiators (subject to the optional limitations described herein) can also be
5 found in WO82/02387 or EP554783 the contents of both of which are hereby incorporated by reference.

In the case that the low molecular weight polymer is prepared using solution polymerization, the preferred solvents are those having a boiling point of not more than 130 °C, more preferred not more than 100 °C, and most preferred not more
10 than 90 °C.

Preferred solvents are acetone, methylethyl ketone, methanol, ethanol, i-propanol, ethyl acetate, butyl acetate and/or toluene. Other suitable solvents will be well known to those skilled in the art. In those cases where the polymerization temperature exceeds that of the boiling points of solvent and/or monomer, the
15 polymerization will be performed under increased pressure.

Preferably, the solids content of the solution polymer is at least 40 wt-%, more preferred between 50 and 90 wt-%, most preferred between 60 and 85 wt-%. Usefully the solid polymer of the invention is obtained by removal of substantially all of the solvent used during the solution polymerisation step and the solid polymer so
20 isolated has a solid content of at least 95%, more preferably at least 98%, most preferably at least 99%. Conveniently the solid polymer of the invention obtained by solution polymerisation is isolated in amorphous form (e.g. as flakes or pellets) or in crystalline form (e.g. as needle like crystals).

The low molecular weight polymer prepared via solution
25 polymerization can be dissolved by increasing pH and next be used as is. It is, however, preferred when the solvent used in the polymerization step is removed after the low molecular weight polymer is dissolved is water using a base. Removal of the solvent can be done by increasing temperature or reducing pressure. It is preferred to combine these. Solvent can be removed after dissolving the low molecular weight
30 polymer prior to further use. It can, however, be envisaged that solvent can also be removed after the low molecular weight polymer is used in the subsequent steps that are elaborated below.

Although less preferred the low molecular weight polymer can also be prepared via emulsion polymerization or dispersion polymerization by techniques well
35 known to those skilled in the art.

In a special embodiment where itaconic anhydride or maleic anhydride are used as acid functional monomers, they may be modified after completion of the polymerization. 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 remaining acid group can subsequently be used for dissolving the low molecular weight polymer.

10 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.

20 The preferred (poly)amines, (poly)hydrazines, or (poly)hydrazides are well known to those skilled in the art and include those described herein.

When the low molecular weight polymer comprises itaconic anhydride or maleic anhydride that is to be used in a modification step, it is strongly preferred that the anhydride is not hydrolysed prior to the reaction with hydroxyl or amine functional moieties. Hence, in those cases the preferred polymerization methods are bulk polymerization and/or solution polymerization, where the solvent is non-protic.

25 The low molecular weight polymer of the invention can be dissolved in water according to various procedures especially where it comprises acid functional groups (e.g. introduced by an acid monomer). For example the low molecular weight polymer can be added to water, followed by neutralizing the acid groups to a sufficiently high level, the acid groups of the low molecular weight polymer can be neutralized prior to addition to water, or the water used to dissolve the low MW polymer is neutralised prior to addition of the low MW polymer. Each of these steps can be performed at ambient or at elevated temperatures (i.e. higher than ambient).

A further aspect of the invention provides for a coating composition comprising a low molecular weight polymer as described herein. The low molecular weight polymer can be introduced to the coating composition in different ways, non-limiting examples of which are described below:

5 The low molecular weight polymer can be blended or admixed for example with a preformed latex. This can be done by dissolving the low molecular weight polymer first and next admixing it with a second emulsion(s) or the low molecular weight polymer can be dissolved in second emulsion(s). The second emulsion(s) can be any type of polymer emulsion, including polyvinyl compositions, comprising sequential, oligomer supported, gradient morphology emulsions, polyurethane emulsions, urethane-acrylate emulsions, alkyd emulsions, and/or polyester emulsions.

10 The low molecular weight polymer, which is dissolved in water, can be used as a surfactant and/or stabilizer for the emulsion polymerization step. An example of such a process can be found in Comparative example 1 in WO2005/097854.

20 The low molecular weight polymer can be used as a pigment dispersant for example by added to a coating composition by first mixing it in a pigment dispersion. In this case the low molecular weight polymer is added to a pigment dispersion comprising inorganic pigment particles and the mixture grinded until a stable pigment dispersion is obtained. Next, the pigment dispersion is added to a polymer emulsion(s) to form a pigmented coating.

25 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.

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

35 In one embodiment the copolymers of the invention may be made using a bulk polymerisation process. Bulk polymerisation of olefinically unsaturated monomers is described in detail in EP 0156170, WO82/02387, and US4414370 the

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

10 In another embodiment emulsion polymerisation may be used to form copolymers of the invention. A conventional emulsion process involves dispersing the monomers in an aqueous medium and conducting polymerisation using a free-radical initiator (normally water soluble) and appropriate heating (e.g. 30 to 120 C°) and agitation.

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

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

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

The polymerisation technique employed may be such that a low molecular weight polymer is formed, e.g. by employing a chain transfer agent such as one selected from mercaptans (thiols), certain halohydrocarbons and alpha-methyl styrene; or catalytic chain transfer polymerisation using for example cobalt chelate
35 complexes as is quite conventional. Alternatively a controlled radical polymerisation

process can be used, for instance by making use of an appropriate nitroxide or a thiocarbonylthio compounds such as dithioesters, dithiocarbamates, trithiocarbonates, and xanthates in order to mediate the polymerization via for example a nitrox mediated polymerisation (NMP), a reversible addition fragmentation chain-transfer process

5 (RAFT) or atom transfer radical polymerization (ATRP).

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

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

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

20 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.

Solution polymers can be produced via as single feed solution polymerization or by a sequentially fed multi-phase 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.

30 The preferred polymerization process is a bulk of solution polymerisation.

Surfactants are used in emulsion polymerization as known to those skilled in the art. Typical surfactants have been extensively described in all kinds of patent applications. The choice and concentration of surfactants are not deemed to be critical for this invention. The aqueous emulsion polymerisation can be effected with

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

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

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

If it is desired to crosslink polymers (for example in a polymer dispersion), the relevant low MW copolymers can carry functional groups such as hydroxyl groups and the dispersion subsequently formulated with a crosslinking agent
15 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
20 that such crosslinking agents will effect crosslinking by virtue of forming covalent bonds.

Whilst the term vinyl polymer is commonly used to refer to thermoplastic polymers derived by polymerization from compounds containing the vinyl group ($\text{CH}_2=\text{CH}-$), the term "vinyl polymer" is used herein more broadly to denote any
25 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.

30 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
35 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.

5 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
10 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.

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

 C-14 levels can be determined by measuring its decay process (disintegrations per minute per gram carbon or dpm/gC) through liquid scintillation counting. In one embodiment of the present invention, polymer A and or polymer B
25 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.

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

 Olefinically unsaturated bio-renewable monomers which may additionally provide a contribution to improved coating properties include α -methylene butyrolactone, α -methylene valerolactone, α -methylene γ -R³ butyrolactone (R³ can be
35 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.

5 Another useful set of useful bio-renewable monomers include N-R², α-methylene butyrolactam (R² can be an optionally substituted alkyl or optionally substituted aryl); N-R², α-methylene γ-R¹ butyrolactam; N-alkyl itaconimids; furfuryl (meth)acrylate; fatty acid functional (meth)acrylates such as DAPRO FX-522 from Elementis and Visiomer ® MUMA from Evonik.

10 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.

15 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.

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

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

25 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
30 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
35 producing effective, acceptable, active and/or suitable end products.

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

In the discussion of the invention herein, unless stated to the contrary, the disclosure of alternative values for the upper and lower limit of the permitted range of a parameter coupled with an indicated that one of said values is
5 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.

10 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
15 various other embodiments and/or preferences of the invention whether or not the combination of such values has been specifically disclosed herein.

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

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

additional amount(s) of any additional component(s) that may not be explicitly described herein.

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

The term "substantially" and/or "substantially comprises" 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.

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,
5 cyano, methyl, halo, trihalomethyl and/or methoxy.

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
10 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
15 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,
20 nitrogen, oxygen, silicon and/or sulphur, more preferably from hydrogen, nitrogen, oxygen, phosphorus and/or sulphur.

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

The term 'hydrocarbo group' as used herein is a sub-set of 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.
35 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
5 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
10 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

15 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
20 multivalent hydrocarbo species linking two or more moieties (such as bivalent hydrocarbylene radicals e.g. alkylene).

Any radical group or moiety mentioned herein (e.g. as a substituent) may be a multivalent or a monovalent radical unless otherwise stated or the context clearly indicates otherwise (e.g. a bivalent hydrocarbylene moiety linking two other
25 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
30 organo moiety comprising from 1 to N carbon atoms. In any of the formulae herein if one or more substituents are not indicated as attached to any particular atom in a moiety (e.g. on a particular position along a chain and/or ring) the substituent may replace any H and/or may be located at any available position on the moiety which is chemically suitable and/or effective.

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

5 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.

10 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
15 geometric isomers); tautomers (e.g. keto and/or enol forms), conformers, salts, zwitterions, complexes (such as chelates, clathrates, crown compounds, cryptands / cryptates, inclusion compounds, intercalation compounds, interstitial compounds, ligand complexes, organometallic complexes, non-stoichiometric complexes, π -adducts, solvates and/or hydrates); isotopically substituted forms, polymeric
20 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
25 forms), different phases, solid solutions; and/or combinations thereof and/or mixtures thereof where possible. The present invention comprises and/or uses all such forms which are effective as defined herein.

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

Polymer precursors of the invention may comprise one or more
35 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.

5 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.

 A polymer is a polydisperse mixture of macromolecules of large molecular weight (for example many thousands of g/mole) prepared by a
10 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.

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

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

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

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

as UV; and/or with other types of radiation such as electron beams, alpha particles, neutrons and/or other particles .

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

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

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

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

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

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

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

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

The compositions of the invention are particularly useful as or for providing the principle component of coating formulations (i.e. composition intended for

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

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

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

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

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

The carrier medium may be removed from the compositions of the invention once they have been applied to a substrate by being allowed to dry naturally at ambient temperature, or the drying process may be accelerated by heat.

Crosslinking can be developed by allowing to stand for a prolonged period at ambient temperature (several days) or by heating at an elevated temperature (e.g. 50 °C) for a much shorter period of time.

A still further aspect of the present invention comprises paints
5 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
10 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
15 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 US4427836,
20 US4920160, US4594363, US4469825, US4468498, US4880842, US4985064, US5157084, US5041464, US5036109, US5409776 and US5510422. Other suitable pigments include, for example, Expancel™ 551 DE20 acrylonitrile / vinyl chloride expanded particles (Expancel Inc. Duluth Ga.); Sil-Cell™ 35/34 sodium potassium aluminium silicate particles (Silbrico Corporation, Hodgkins Ill.); Dualite™ 27
25 polyvinylidene chloride copolymer coated with CaCO₃ (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
30 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.
35 Combinations of the above ingredients are frequently preferred.

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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.

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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.

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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 Rhodamine™ 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.

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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 freeze/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 TiO₂ compatibility and stability. These would include surfactants from the Strodx™ line such as PK-90 or PK-0VOC.

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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.

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.

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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

5 rusting and long term corrosion.

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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™ I-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.

15 This is known to improve the tannin blocking character of the paint.

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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 100nm 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.

20 Combinations of Tinuvin 1130 with Tint-ayd CW5499 are particularly useful for semi transparent wood stains.

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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.

35

Paints prepared from emulsion polymer compositions comprising low molecular weight polymer 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 monoalkoxy. 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 γ -amino propyl-triethoxysilane. γ -amino propylmethyldimethoxysilane is a useful coupling agent for adhesion to metal oxides such as aluminium 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.

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

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

TESTS

MINIMUM FILM FORMING TEMPERATURE

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

KOENIG HARDNESS

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

GLASS TRANSITION TEMPERATURE (T_g)

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 T_g, or calculated from the Fox equation. Thus the T_g, in degrees Kelvin, of a copolymer having "n" copolymerised comonomers is given by the weight fractions W of each comonomer type and the T_gs of the homopolymers (in degrees Kelvin) derived from each comonomer according to the equation:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \dots + \frac{W_n}{T_{gn}}$$

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

SOLIDS CONTENT

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

20 pH VALUE

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

BLOCKING25 Block Resistance Measurement [Includes Blocking and Early Blocking]:Step 1: Blocking:

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

30

Step 1: Early Blocking:

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

35

Step 2: Blocking and Early Blocking:

After cooling down to room temperature two pieces of coated film are placed with the coated side against each other under a load of 1 Kg/cm² 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.

10 Gas Chromatography Mass Spectrometry (GCMS)

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

The GC-oven was programmed from 50°C (5 min) followed by different sequential temperature ramps of 5°C/min to 70°C (0 min), 15°C/min to 220°C (0 min), and ending with 25°C/min to 280°C (10 min). A continuous Helium flow of 1.2 ml/min was used. A hot split injection at 300°C was performed on a programmed temperature vaporizer (PTV). The injection volume was 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.

30 MOLECULAR WEIGHT

Unless the context clearly dictates otherwise the term molecular weight of a polymer or oligomer as used herein denotes number average molecular weight (also denoted as M_N). M_N 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

5 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

10 The SEC analyses were performed on an Alliance Separation Module (Waters 2690), including a pump, auto injector, degasser, and column oven. The eluent was tetrahydrofuran (THF) with the addition of 1.0 vol% acetic acid. The injection volume was 150µl. The flow was established at 1.0 ml/min. Three PL MixedB (Polymer Laboratories) with a guard column (3µm PL) were applied at a temperature of 40°C.

15 The detection was performed with a differential refractive index detector (Waters 410). The sample solutions were prepared with a concentration of 20 mg solids in 8 ml THF (+ 1vol% acetic acid), and the samples were dissolved for a period of 24 hours. Calibration is performed with eight polystyrene standards (polymer standard services), ranging from 500 to 4,000,000 g/mol. The calculation was performed with Millennium

20 32 software (Waters) with a third order calibration curve. The obtained molar masses are polystyrene equivalent molar masses (g/mol).

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

 The SEC analyses were performed on a Waters Alliance 2695 (pump,

25 degasser and autosampler) with a Shodex RI-101 differential refractive index detector and Shimadzu CTO-20AC column oven. The eluent was 1,1,1,3,3,3 hexafluoro isopropanol (HFIP) with the addition of 0.2M potassium trifluoro acetate (KTFA). The injection volume was 50µl. The flow was established at 0.8 ml/min. Two PSS PFG Linear XL columns (Polymer Standards Service) with a guard column (PFG PSS) were

30 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

35 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

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

10 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.

15 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
20 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.

25 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)
MMA denotes methyl methacrylate (may be (partly) bio-renewable)
30 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)
35 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.

5

Example I

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer are charged 43 parts of 2-butanone. The reactor contents are heated to 85 °C. As soon as the polymerization temperature is reached, a monomer feed consisting of 25 parts of dimethyl itaconate (DMI), 20 parts of styrene (STY), 25 parts of methyl methacrylate (MMA), 30 parts of acrylic acid (AA), and 0.3 parts of azobisisobutyronitrile (AIBN) is fed to the reactor in a period of 270 minutes. At the end of the monomer feed the polymerization temperature is kept at 85 °C for another 60 minutes after which the reactor contents are cooled back to room temperature.

15

Examples II to X

The Examples II to X are prepared analogously with reference to the method described in Example I above with reference to Table 1 below where the monomer feed in Example I is replaced with those ingredient and in the relative amounts listed in the Table 1.

20

Table 1

	II	III	IV	V	VI	VII	VIII	IX	X
DMI	25	62	55	43	61	55	55	55	55
STY	-	5	-	-	-	5	-	-	-
MMA	25	3	15	32	9	15	15	20	15
DEI	25	-	-	-	-	-	-	-	-
AA	-	30	-	-	30	-	30	-	30
iANH	25	-	-	25	-	25	-	25	-
MAA	-	-	30	-	-	-	-	-	-
AIBN	0.8	0.2	0.6	1.0	0.2	1.2	0.2	0.5	0.2

Example XI

To a high pressure polymerization kid, equipped with a stirrer, thermometer, pressure release valve, and high pressure monomer dosage pump are charged 43 parts of 2-butanone. The reactor contents are heated to 140 °C. As soon as the polymerization temperature is reached, a monomer feed consisting of 25 parts of dimethyl itaconate (DMI), 20 parts of styrene (STY), 25 parts of methyl methacrylate (MMA), 30 parts of acrylic acid (AA), and 0.15 parts of di-t-butyl peroxide (DTPO) is fed to the reactor in a period of 270 minutes. At the end of the monomer feed the polymerization temperature is kept at 85 °C for another 60 minutes after which the reactor contents are cooled back to room temperature.

Examples XII to XX

The Examples XII to XX may be prepared analogously with reference to the method described in Example XI above with reference to Table 2 below where the monomer feed in Example XI is replaced with those ingredient and in the relative amounts listed in the Table 2.

Table 2

	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX
DMI	25	62	55	43	61	55	55	55	55
STY	-	5	-	-	-	5	-	-	-
MMA	25	3	15	32	9	15	15	20	15
DEI	25	-	-	-	-	-	-	-	-
AA	-	30	-	-	30	-	30	-	30
iANH	25	-	-	25	-	25	-	25	-
MAA	-	-	30	-	-	-	-	-	-
DTPO	0.2	0.4	0.1	0.5	0.1	0.1	0.5	0.1	0.1

Example XXI

To a high pressure polymerization equipment, equipped with a stirrer, thermometer, pressure release valve, and high pressure monomer dosage pump are charged 34 parts of 2-butanone and 9 parts of 2-ethylhexyl alcohol. The reactor contents are heated to 140 °C. As soon as the polymerization temperature is reached, a monomer feed consisting of 25 parts of dimethyl itaconate (DMI), 20 parts of styrene (STY), 25 parts of methyl methacrylate (MMA), 30 parts of acrylic acid (AA), and 0.15

parts of di-t-butyl peroxide (DTPO) is fed to the reactor in a period of 270 minutes. At the end of the monomer feed the polymerization temperature is kept at 85 °C for another 60 minutes after which the reactor contents are cooled back to room temperature.

5

Examples XXII to XXX

The Examples XXII to XXX may be prepared analogously with reference to the method described in Example XXII above with reference to Table 3 below where the monomer feed in Example XXX is replaced with those ingredient and in the relative amounts listed in the Table 3.

10

Table 3

	XXII	XXIII	XXIV	XXV	XXVI	XXVII	XXVIII	XXIX	XXX
DMI	25	62	55	43	61	55	55	55	55
STY	-	5	-	-	-	5	-	-	-
MMA	25	3	15	32	9	15	15	20	15
DEI	25	-	-	-	-	-	-	-	-
AA	-	30	-	-	30	-	30	-	30
iANH	25	-	-	25	-	25	-	25	-
MAA	-	-	30	-	-	-	-	-	-
DTPO	0.2	0.4	0.1	0.5	0.1	0.1	0.5	0.1	0.1

Examples XXXI to XXXVI

15

The Examples XXXI to XXXVI may be prepared analogously with reference to the methods described herein above with reference to Table 4 below where the monomer feed may consists of the ingredients and the relative amounts listed in Table 4.

20

Table 4

	XXXI	XXXII	XXXIII	XXXIV	XXXV	XXXVI
DMI	55	55	55	30	30	30
DBI	-	-	20			
MMA	-	-	-	60	60	60
AA	15	15	15	10		
DAAM	10	10	10	-	-	-
BA	-	20	-	-	-	-
IA	-	-	-	-	10	-
IANH	-	-	-	-	-	10
PEG350	20	-	-	-	-	-
Tg (°C)	37.2	49.4	74.0	101.8	105.9	104.1

Examples XXXVII to XLIV

The following Examples XXXVII to XLIV were prepared as described
 5 below and some of their properties results are given in Table 5.

Example XXXVII MMA/DMI/AA

To a round-bottomed flask equipped with a condenser, thermometer,
 and a stirrer are charged 394.0 parts of 2-butanone. The reactor contents are heated to
 10 80 °C. As soon as the polymerization temperature is reached, 13.3 parts of azobis(2-
 methyl butyronitrile) are added and the monomer feed and catalyst feed are started.
 The monomer feed consists of 244.4 parts of methyl methacrylate, 244.4 parts of
 dimethyl itaconate, and 244.4 parts of acrylic acid. The catalyst feed consists of 31.1
 parts of azobis(2-methyl butyronitrile) dissolved in 125.9 parts of 2-butanone. Both
 15 feeds are added over a period of 180 minutes.

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

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

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

Example XXXVII S/DMI/AA

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

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

To 546.1 parts of polymer solution is added a mixture of 105.4 parts of a 25 wt-% of ammonia in water, and 1144.1 parts of water. Next, the 2-butanone is removed at 50 °C under reduced pressure. The solids content is corrected to 22.5 % using demineralized water and the pH is corrected to 8.6-8.8 using a 25 wt-% solution
20 of ammonia in water.

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

Example XXXIX MMA/DMI/AA

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

At the end of the feed the feed tank is rinsed with 90.9 parts of 2-butanone. 45 minutes after completion of the monomer feed 2.5 parts of t-butyl perbenzoate dissolved in 40 parts of 2-butanone are added and the mixture is stirred at
35 140 °C for another 45 minutes. Next, 2.5 parts of t-butyl perbenzoate dissolved in 40

parts of 2-butanone are added and the mixture is stirred for another 135 minutes at 140 °C.

The mixture is cooled to room temperature.

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

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

10

Example XL S/DMI/AA

To a high pressure reactor equipped with a thermometer, and a stirrer are charged 500.0 parts of 2-butanone. The reactor contents are heated to 140 °C. As soon as the polymerization temperature is reached, 4.4 parts of di-t-butyl peroxide and
15 40 parts of 2-butanone are added. 5 minutes later the monomer feed is started. The monomer feed consists of 331.8 parts of styrene, 331.8 parts of dimethyl itaconate, 331.8 parts of acrylic acid, 8.6 parts of di-t-butyl peroxide, and 10.0 parts of t-butyl perbenzoate, and is added over a period of 180 minutes at 140 °C.

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

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

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

Example XLI Sequential polymerization using the polymer from Example XXXVII

To a round-bottomed flask equipped with a condenser, thermometer, and a stirrer are charged 128.9 parts of the alkaline solution obtained from Example XXXVII. The mixture is heated to $80\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$.

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

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

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

Example XLII Sequential polymerization using the polymer from Example XXXVIII

A polymer was prepared analogous to the method described in Example XLI, using the alkaline solution obtained from Example XXXVIII. The final emulsion was highly viscous, requiring a dilution to a solids content of 35 %.

Example XLIII Sequential polymerization using the polymer from Example XXXIX

A polymer was prepared analogous to the method described in Example XLI, using the alkaline solution obtained from Example XXXIX.

30

Example XLIV Sequential polymerization using the polymer from Example XL

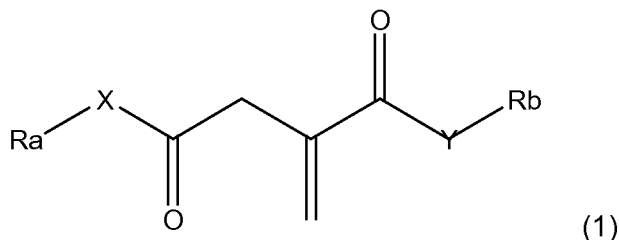
A polymer was prepared analogous to the method described in Example XLI, using the alkaline solution obtained from Example XL.

Results (Table 5)

	SC (%)	Viscosity (mPa.s)	pH
Example XLI	47.6	208	8.4
Example XLII	34.8	1006	8.4
Example XLIII	48.1	35	8.5
Example XLIV	48.1	201	8.4

CLAIMS

- 1 A copolymer having a low molecular weight and high glass transition
 temperature, the copolymer comprising (preferably consisting essentially of)
 5 moieties obtained and/or obtainable from the following components:
- (a) at least 20 wt-% of one or more itaconate functional monomer(s) not
 containing acidic groups or precursor acid groups),
 - (b) not more than 40 wt-% of an acid functional monomer(s) in an amount
 sufficient to achieve an acid value from 65 to 325 mg KOH per g of solid
 10 polymer,
 - (c) optionally not more than 72 wt-% of other monomers not being either (a)
 or (b);
- where the weight percentages of monomers (a), (b) and (c) total 100% and
 are calculated as a proportion of the total amount of monomers in the
 15 copolymer being 100%; and with the provisos:
- (I) the copolymer has a number average molecular weight (M_n) of no more
 than 15 kilograms / mole (also referred to herein as 'Low MW'); and
 - (II) the copolymer has a glass transition temperature of at least 75 °C (also
 referred to herein as 'High TG'),
- 20 and where either or both of provisos (III) and/or (IV) apply:
- (III) the copolymer contains less than 40 wt-% vinyl aromatic monomer(s)
 (also referred to herein as 'Low Vinyl Aromatic' or Low-Styrene'); and/or
 - (IV) the copolymer contains less than 40 wt-% methacrylate monomer(s)
 (also referred to herein as 'Low-MA').
- 25 2. A polymer composition as claimed in claim 1, in which component (a)
 comprises a compound of Formula 1:



where Ra and Rb independently represent any optionally substituted
 hydrocarbo moiety (such as any aliphatic, cycloaliphatic or aromatic moieties);
 30 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)

with the proviso that Formula 1 does not contain:

5 any acidic groups (such as carboxylic, phosphoric and/or sulphonic acid groups) or

any precursor acid groups, that is a group which readily generates an acid group under the conditions of polymerisation herein (such as an anhydride group).

10 3. A polymer composition as claimed in either preceding claim, in which component (b) is an acid functional monomer or precursor thereof selected from at least one ethylenically unsaturated carboxylic acid and/or derivatives thereof (such as anhydrides and/or salts).

15 4. A polymer composition as claimed in claim 3, in which the monomer composition is substantially free of arylalkylene and/or vinyl aromatic monomers.

5 A polymer composition as claimed in any preceding claim which is a solid grade oligomer (SGO).

20 6. A process for preparing a polymer composition as claimed in any of claims 1 to 5 comprising the steps of:

- (i) polymerising components (a), (b) and (c) (where present) in a solution polymerisation process in the presence of solvent,
 - (ii) removal of substantially all the solvent from step (i)
- to obtain a copolymer comprising at least 95% solids.

25 7. A process for preparing a polymer composition as claimed in any of claims 1 to 5 comprising the step of:
polymerising components (a), (b) and (c) (where present) in a bulk polymerisation process, where the bulk polymerisation is performed under at least one of the conditions (I) (II) and/or (III):

- 30 (I) in the presence of no more than 1 wt-% of chain transfer agent; relative to the total monomer composition (i.e. (a) + (b) + (c)) being 100%
- (I) in the presence of no more than 1 mole-% of initiator; relative to the total monomer composition (i.e. (a) + (b) + (c)) being 100%; and/or
- 35 (III) with a maximum polymerisation temperature of no more than 250 °C, preferably no more than 200 °C.

8. A polymer composition obtained and/or obtainable by a process as claimed in claim 6 or 7.
9. An aqueous composition comprising a polymer composition as claimed any of claims 1 to 5 and/or 8 and an aqueous medium.
- 5 10. A coating composition comprising a polymer composition as claimed any of claims 1 to 5 and/or 8 and/or an aqueous composition as claimed in claim 9.
11. A substrate and/or article having coated thereon an (optionally cured) coating composition of claim 10.
12. A method of using a polymer composition as claimed in any of claims 1 to 5 or
10 8 and/or an aqueous composition as claimed in claim 8 to prepare a coating composition.
13. A method for preparing a coated substrate and/or article comprising the steps of applying a coating composition of claim 10 to the substrate and/or article and optionally curing said composition in situ to form a cured coating thereon.
- 15 14. A substrate and/or article obtained and/or obtainable by a method of claim 13.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
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ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C09D

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

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

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/073417 A1 (DSM IP ASSETS BV [NL]; NABUURS TIJS [NL]; OVERBEEK GERARDUS CORNELIS []) 23 June 2011 (2011-06-23) cited in the application page 13 - lines 10, 24; example 1 -----	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011073417 A1	23-06-2011	CN 102656201 A	05-09-2012
		EP 2513176 A1	24-10-2012
		US 2013065070 A1	14-03-2013
		WO 2011073417 A1	23-06-2011



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权利要求书2页 说明书36页

(54) 发明名称

聚合物、方法和组合物

(57) 摘要

本发明描述了低数均分子量 ($M_n < 10\text{kD}$) 和高玻璃化转变温度 ($>75^\circ\text{C}$) 的共聚物 (任选地固体级低聚物 (SGO)), 其包含 (a) 至少 20 重量% 的衣康酸官能单体, (b) 不超过 40% 的亲水性单体, 优选地酸官能单体的量足以使酸值为 65 至 325mg KOH 每 g 固体聚合物; (c) 任选地不超过 70% 的非单体 (a) 或 (b) 的其他单体, 其具有 40 重量% 的乙烯基芳族单体最大含量和 40 重量% 的甲基丙烯酸酯最大含量; 其中单体 (a)、(b) 和 (c) 的重量百分数是以共聚物中单体总量 (为 100%) 的部分计算的。

1. 具有低分子量和玻璃化转变温度的共聚物,所述共聚物包含(优选地本质上由如下组分获得和/或能够获得的片段组成)由如下组分获得和/或能够获得的片段:

(a) 至少 20 重量%的一种或多种衣康酸官能单体,所述衣康酸官能单体不包含酸基团或前体酸基团,

(b) 不超过 40 重量%的酸官能单体,其量足以实现 65 至 325mg KOH 每 g 固体聚合物的酸值,

(c) 任选地不超过 72 重量%的非 (a) 或 (b) 的其他单体;

其中单体 (a)、(b) 和 (c) 的重量百分数总计 100%,并且是以所述共聚物中单体总量的部分计算的,所述共聚物中单体总量为 100%;前提是

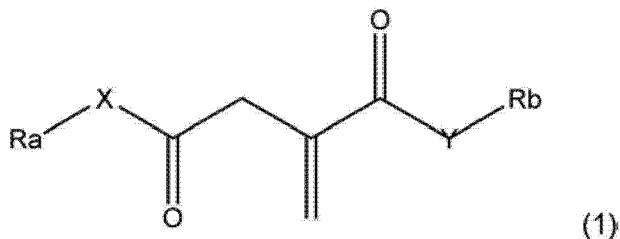
(I) 所述共聚物具有不超过 15 千克/摩尔的数均分子量 (M_n) (在本文中也称为“低 MW”);并且

(II) 所述共聚物具有至少 75°C 的玻璃化转变温度 (在本文中也称为“高 TG”),并且其中任选地适用前提条件 (III) 和/或 (IV) 中的一者或二者:

(III) 所述共聚物包含小于 40 重量%的乙烯基芳族单体 (在本文中也称为“低乙烯基芳族”或“低苯乙烯”);和/或

(IV) 所述共聚物包含小于 40 重量%的甲基丙烯酸酯单体 (在本文中也称为“低 MA”).

2. 如权利要求 1 中所限定的聚合物组合物,其中组分 (a) 包含式 1 的化合物:



其中 Ra 和 Rb 独立地表示任何可选地被取代的烃片段 (例如任何脂族、脂环族或芳族片段);并且

X 和 Y 独立地表示 -O- 和/或 -NRe-,其中在每种情况下 Rc 独立地表示 H 和/或任何可选地被取代的烃片段 (例如脂族、脂环族或芳族片段);

前提是式 1 不包含:

任何酸性基团 (例如羧酸、磷酸和/或磺酸基团) 或

任何前体酸基团,其是在本文中的聚合条件下容易产生酸基团的基团 (例如酸酐基团)。

3. 如前面权利要求中任意一项中所限定的聚合物组合物,其中组分 (b) 是酸官能单体或其前体,其选自至少一种烯属不饱和羧酸和/或其衍生物 (例如酸酐和/或盐)。

4. 如权利要求 3 中所限定的聚合物组合物,其中单体组合物基本上不含芳基烯烃和/或乙烯基芳族单体。

5. 如前面权利要求中任意一项中所限定的聚合物组合物,其为固体级低聚物 (SGO)。

6. 用于制备如权利要求 1 至 5 中所限定的聚合物组合物的方法,其包括如下步骤:

(i) 在溶液聚合工艺中在溶剂的存在下使组分 (a)、组分 (b) 和组分 (c) (当存在时) 进行聚合,

(ii) 去除来自步骤 (i) 的基本上所有溶剂,

从而获得包含至少 95% 固体的共聚物。

7. 用于制备如权利要求 1 至 5 中所限定的聚合物组合物的方法, 其包括如下步骤:

在本体聚合工艺中使组分 (a)、组分 (b) 和组分 (c) (当存在时) 进行聚合, 其中所述本体聚合是在条件 (I)、(II) 和 / 或 (III) 中的至少一个下进行的:

(I) 在不超过 1 重量% 的链转移剂的存在下; 相对于总单体组合物 (即 (a)+(b)+(c)), 其中所述总单体组合物为 100%; 和 / 或

(II) 在不超过 1 摩尔% 的引发剂的存在下, 相对于总单体组合物 (即 (a)+(b)+(c)), 其中所述总单体组合物为 100%; 和 / 或

(III) 采用不超过 250°C、优选地不超过 200°C 的最大聚合温度。

8. 通过如权利要求 6 或 7 中所限定的方法获得和 / 或能够获得的聚合物组合物。

9. 水性组合物, 其包含如权利要求 1 至 5 和 / 或 8 中任意一项所限定的聚合物组合物和水性介质。

10. 涂料组合物, 其包含如权利要求 1 至 5 和 / 或 8 中任意一项所限定的聚合物混合物和 / 或如权利要求 9 中所限定的水性组合物。

11. 基材和 / 或制品, 其上涂布有如权利要求 10 所限定的 (可选地固化的) 涂料组合物。

12. 使用如权利要求 1 至 5 或 8 中任意一项所限定的聚合物组合物或如权利要求 8 中所限定的水性组合物来制备涂料组合物的方法。

13. 用于制备经涂布的基材和 / 或制品的方法, 其包括以下步骤: 将如权利要求 10 所限定的涂料组合物涂覆到基材和 / 或制品上, 并任选地将所述组合物原位固化, 从而在其上形成经固化的涂层。

14. 通过权利要求 13 的方法获得和 / 或能够获得的基材和 / 或制品。

聚合物、方法和组合物

[0001] 本发明涉及由衣康酸酯和类似单体制成的聚合物；还涉及用于制备这些聚合物的方法以及它们在涂料、墨和粘合剂中的用途。

[0002] 衣康酸酯也被称为 2- 偏亚甲基丁二酸酯 (2-methylidenebutanedioate)，是能够由生物可再生来源获得的单体。尽管已被研究了许多年。然而，它们并没有广泛用于制备商业的聚合物，因为它们很昂贵并且通常难于加工。

[0003] 由于多种原因，人们期望具有低分子量（低 Mn）和高玻璃化转变温度（高 Tg）的聚合物。它们可以形成有用的涂料、可以用作稳定剂（例如在乳液聚合中）。它们可以生产具有改善的硬度和耐粘连性的膜。这种低 Mn、高 Tg 聚合物的例子为固体级低聚物（也被称为 SG0）。

[0004] 本申请人已经发现，衣康酸酯可以用于制备改善的聚合物，例如低 Mw/ 高 Tg 固体级低聚物。令人惊奇地，能够克服使用衣康酸酯单体的各种困难，并且这些衣康酸酯单体可以被引入到具有本文中所述的一些或所有优点的聚合物中。本发明的衣康酸聚合物还可以在室温下形成膜，其具有高韧性（弹性）且不易于粘连。

[0005] 本文中使用时，术语“固体级低聚物”（SG0）优选地表示包含低聚物（优选地所述低聚物具有通过 GPC 测得的不超过 100000g/mol 的重均分子量）的低聚物组合物，其中在标准条件下该组合物基本上由固体材料组成（优选地固体以大于或等于 95 重量%的低聚物组合物的量，更优选地所述组合物由固体材料组成）。术语“低聚物”、“基本上包含”和“标准条件”在下文中定义。

[0006] 通过甲基丙烯酸酯单体的本体聚合制得的聚合物通常很难转化或者需要不期望的处理条件。在本发明所解决的另一个问题中，本申请人已经发现这些甲基丙烯酸酯单体可以被衣康酸酯或类似单体完全或部分地替换。这会减小引发剂的浓度和 / 或降低生产聚合物所要求的聚合温度。所得到的聚合物是以高的单体转化率制得的，并且具有与由甲基丙烯酸酯单体制成的那些聚合物类似的性质。

[0007] 本发明还解决了另一个任选的问题。还已经发现，不使用苯乙烯单体会对聚合过程产生多个不期望的改变，尤其是当生产低分子量聚合物时。例如，提高引发剂浓度，使用链转移剂 (CTA) 和 / 或提高聚合温度。然而，由于其他原因，乙烯基芳族单体诸如苯乙烯也是不期望的，因为它们是可能的致癌物质，并且对健康具有其他潜在的慢性不利影响。优选地，使用尽可能少的乙烯基芳族单体，优选地完全不使用这些单体。先前已经用甲基丙烯酸酯单体替换苯乙烯单体（例如 EP156170 中所描述）。然而，如上文所述，使用甲基丙烯酸酯作为直接苯乙烯替换物时，存在许多问题。本申请人已经出人预料地发现，可以使用衣康酸官能单体来替换乙烯基芳族单体诸如苯乙烯（完全或部分），从而在所获得的聚合物中实现与通过乙烯基芳族单体所赋予的那些聚合物类似的性质。本文中使用时，除上下文外另有说明外，“苯乙烯”（例如不含苯乙烯）还可以指任何类似的乙烯基芳族单体。

[0008] 因此，总结本发明的一个方面，本申请人现已惊奇地发现，衣康酸酯单体可以用于替换或减少添加到聚合物中的苯乙烯和 / 或甲基丙烯酸酯 (MA) 单体的量，同时解决了使用低苯乙烯、低 MA、不含苯乙烯和 / 或不含 MA 的聚合物时造成的一些或所有问题。因此

(在本发明的一个方面),可以以非常低(或者甚至零)苯乙烯和/或MA含量以合理的单体转化率使用较之以前更低的链转移剂(CTA)的量、更低的引发剂浓度和/或更低的温度,来制备具有低水敏感性的低 M_w /高 T_g 聚合物。

[0009] 例如,本发明的一个优选的目的是提供一种具有小于15kg/摩尔的数均分子量和大于75°C的 T_g 的聚合物,该聚合物基本上不含乙烯基芳族单体。可以使用不超过1重量份(每100份单体)的CTA、小于1摩尔份(每100份单体)的引发剂和/或通过在不超过275°C的温度下的聚合,来制备这种聚合物。

[0010] 本文中描述了本发明还可以解决的其他问题,并且本发明的一个目标是解决本文中所指明的一些或所有问题。

[0011] 下面讨论一些现有技术文件。

[0012] W082/02387(SCJ)描述了用于制备低分子量乙烯基聚合物的本体聚合方法,该乙烯基聚合物具有小于2的分散指数和1000至6000的数均分子量。该聚合物通过如下制备:在235°C至310°C的温度下,向包含未反应的单体与乙烯基聚合物的熔融树脂混合物的反应器中,连续填充至少一种单烯基芳族单体与至少一种丙烯酸单体的混合物,同时保持流动速率,使得单体在反应器中的停留时间为2分钟并且反应混合保持在预定的水平。

[0013] EP156170(SCJ)描述了与上面描述的方法类似的单体聚合方法,其用于制备高产率的高固体、低分子量丙烯酸聚合物,该丙烯酸聚合物具有窄分子量分布和低生色团含量。该方法包括向包含未反应的丙烯酸单体与丙烯酸聚合物的熔融混合物的反应器中,连续填充聚合引发剂与至少一种丙烯酸单体(相对摩尔比为0.0005:1至0.06:1)以及反应溶剂(以丙烯酸单体的0至25重量%的量)的混合物,同时保持流动速率使得单体在反应器中的停留时间 ≥ 1 分钟,将反应混合保持在预定的水平,并且将熔融树脂混合物保持在足够高的反应温度下,从而加快向易于加工、均匀的、浓缩的聚合物产物的转化。

[0014] EP554783(BASF)描述了通过自由基引发的或热引发的聚合在环形模隙反应器内连续聚合乙烯基单体来形成乙烯基聚合物的方法,该反应器包含外管和插入其中的圆筒形转子,使得环形间隙为0.5至10mm宽,从而停留时间为1至10分钟。控制外管温度以使聚合在150至270°C下进行,从而提供具有1000至20000的分子量 M_n 和多分散度(M_w/M_n) < 3.5 的乙烯基聚合物。

[0015] US6346590描述了连续聚合以及向初级反应器中连续填充以下物质的混合物的缩合工艺:至少一种具有可自由基聚合基团和缩合反应性官能团(CRF)的可自由基聚合单体;至少一种具有与CRF反应的基团的改性剂(非单羟基醇);其中保持初级反应器中的温度水平来有效地聚合单体并使得至少一部分CRF与改性剂反应,来生成掺入了至少一些改性剂的无凝胶第一聚合物。向初级反应器中添加可自由基聚合单体,同时取出第一聚合物。将第一聚合物添加到维持在有效温度下的第二反应器中,以形成第二聚合物。

[0016] W02005/097854(DSM)描述了水性组合物,其包含:i)至少重均分子量在1000至80000g/摩尔的可交联乙烯基低聚物A,其通过以下物质的本体聚合获得:(a)5至45重量%的带有离子型或潜在离子型水分散基团的乙烯基单体;(b)0至30重量%的带有非离子型水分散基团的乙烯基单体;(c)2至25重量%的带有可交联基团的乙烯基单体;(d)0至40重量%的 α -甲基苯乙烯;(e)10至93重量%的非(a)、(b)、(c)或(d)的乙烯基单体;其中(a)+(b)+(c)+(d)+(e)=100%;以及ii)至少重均分子量 > 5000 g/摩尔的乙烯

基聚合物 B,其通过以下物质在乙烯基低聚物 A 的存在下的聚合获得:(f)0 至 5 重量%的带有离子型或潜在离子型水分散基团的乙烯基单体;(g)0 至 20 重量%的带有非离子型水分散基团的乙烯基单体;(h)0 至 15 重量%的带有可交联基团的乙烯基单体;(i)60 至 100 重量%的非(f)、(g)或(h)的乙烯基单体;其中(f)+(g)+(h)+(i)=100%;其中乙烯基低聚物 A 与乙烯基聚合物 B 的比例在 5:95 至 95:5 范围内;其中聚合物 B 比乙烯基低聚物 A 更疏水;其中乙烯基聚合物 B 的重均分子量大于乙烯基低聚物 A 的重均分子量;iii)0 至 20 重量%的助溶剂;和 iv)30 至 90 重量%的水;其中 i)+ii)+iii)+iv)=100%。

[0017] 其他现有技术文件一般性地描述了衣康酸酯的用途。

[0018] US4206292(Kureha Kagaku Kogyo Kabushiki Kaisha)描述了具有表面光滑性的氯乙烯树脂组合物,其包含:(1)100 份的氯乙烯聚合物;和(2)0.1 至 30 份的聚合物加工助剂,该聚合物加工助剂包含:(A)10 至 100 份的共聚物,该共聚物含有 20 至 99%的甲基丙烯酸烷基酯、1 至 70%的衣康酸二烷基酯和 0 至 60%的可共聚单体;和(B)0 至 90 份的共聚物,该共聚物含有 80 至 100%的甲基丙烯酸烷基酯和 0 至 20%的可共聚单体。这种氯乙烯树脂组合物与由生物基来源或其他环境友好来源制备的涂料组合物不太相关。

[0019] US4547428(Monsanto)描述了一种三元共聚物,其包含衍生自烯烃、可加成聚合的不饱和二羧酸的二酯和增溶性单体的重复单元,其中增溶性单体促进三元共聚物与卤乙烯聚合物之间的相容性。还公开了该加工助剂的颗粒形式及其制备方法。这些聚合物不适合涂料应用。

[0020] US4588776(Monsanto)描述了包含氯乙烯聚合物与颗粒状三元共聚物的共混物的聚合物组合物,该三元共聚物具有至少 100000 的分子量和至少 50°C 的玻璃化转变温度。该三元共聚物包含衍生自烯烃、可加成聚合的不饱和二羧酸的二酯和增溶性单体的重复单元,其中增溶性单体促进三元共聚物与卤乙烯聚合物的相容性。这些聚合物用于制备成形的塑料制品,而不能用于涂料应用。

[0021] US6951909(3M)描述了一种可聚合体系,其包含有机硼烷、至少一种可聚合单体和工作寿命延长剂。

[0022] W011/073417(DSM)公开了一种水性乳液,其至少包含乙烯基聚合物,所述乙烯基聚合物包含:a)45 至 99 重量%的具有式(I)的衣康酸酯单体,其中 R 和 R' 独立地为烷基和芳基;b)0.1 至 15 重量%的离子或潜离子不饱和单体;c)0 至 54 重量%的不同于 a)和 b)的不饱和单体;和在单体 a)、b)和 c)聚合之后接着加入并聚合的占总单体的 0.9 至 54.9 重量%的追加(chaser)单体组合物;其中 a)+b)+c)和追加单体组合物总计 100 重量%;并且其中基于水性乳液的总重量,水性乳液包含小于 0.5 重量%的式 I 的游离衣康酸酯单体。尽管该发明所声称的目标是提供具有高总浓度的衣康酸酯单体的乙烯基聚合物(参见第 2 页第 14-17 行),但是实际上较大比例的这种衣康酸酯是低级衣康酸酯(即小烷基的酯,诸如 DMI)。该文件并没有教导希望使用高浓度的高级衣康酸酯(即大烷基的酯,诸如 DBI)。事实上,W011/073417 指出衣康酸酯难于加工(参见第 2 页第 23-25 行),这与实施例的教导组合在一起使读者不会将大量疏水的高级衣康酸酯诸如 DBI 掺入到共聚物中。W011/073417 中描述 DBI 单体的使用的仅有的实施例是实施例 2、4、5 和 6。可以看出,DBI 仅以低的浓度在这些实施例中所制备的最终共聚物中用作共聚单体(最大 22.7 重量%),每一个实施例还使用了显著量的另一种疏水性单体丙烯酸丁酯(BA)来制备。苯乙烯追加

单体总是存在于最终产物中（至少 1.5 重量%）。这些实施例教导了不要使用 DBI 或其他高级衣康酸酯来替换常用的疏水性单体诸如 BA、EHA 和 / 或苯乙烯。在该文件中所制得的共聚物的膜性质诸如硬度和水敏感性方面,没有观察到明显改善。

[0023] GB1009486 (Borden) 描述了复合聚合颗粒的胶乳,其中核和壳可以包含偏氯乙烯与 α 不饱和脂肪酸的酯的共聚物（酯在壳中的量比在核中大）。一个实施例（实施例 3）描述了衣康酸二丁酯 (DBI) 以总单体的 17 重量%的总量（在外壳中 5%和在内部非核层中 12%）用作酯。这些复合多层聚合物颗粒解决了为纸或类似物提供水蒸汽阻隔涂层的问题,并且他们使用的 DBI 量比本发明中低得多。

[0024] US3766112 描述了用于地板蜡的高光泽胶乳,其包含具有聚乙烯吡咯烷酮保护胶体的氯化石蜡。用于制备胶体的四种单体组分:苯乙烯 (70 至 85%),丙烯酸 2-乙基己酯 (EHA) (5 至 15%), (甲基)丙烯酸 (3 至 10%) 和第四单体 (1 至 5%),所有百分数均为聚乙烯吡咯烷酮的总单体的重量百分数。建议作为第四单体的七个单体中的一个 DBI。这些聚合物解决了提供高光泽地板涂层的问题,并且以比本发明中低得多的量使用 DBI。

[0025] 因此,广义来说,根据本发明,提供具有低分子量（低 MW）和高玻璃化转化温度（高 TG）的共聚物,该共聚物包含（优选地本质上由如下组分获得和 / 或能够获得的片段组成）由如下组分获得和 / 或能够获得的片段:

[0026] (a) 至少 20 重量%的一种或多种不包含酸性基团和前体酸基团的衣康酸官能单体（本文中也称为“衣康酸单体”），

[0027] (b) 不超过 40 重量%的酸官能单体（本文中也被称为“酸性单体”），其用量足以获得 65 至 325mg KOH 每 g 固体聚合物的酸值

[0028] (c) 任选地不超过 72 重量%的非 (a) 和 (b) 的其他单体（本文中也被称为“其他单体”）;

[0029] 其中单体 (a)、(b) 和 (c) 的重量百分数总计 100%，并且是以共聚物中单体总量（为 100%）的部分计算的;

[0030] 并且前提是:

[0031] (I) 共聚物具有不超过 15 千克 / 摩尔的数均分子量 (Mn)（在本文中也被称为“低 Mw”）;并且

[0032] (II) 共聚物具有至少 75°C 的玻璃化转变温度（在本文中也被称为“高 TG”），

[0033] 并且,其中任选地适用前提条件 (III) 和 / 或 (IV) 中的一者或二者:

[0034] (III) 共聚物包含小于 40 重量%的乙烯基芳族单体（在本文中也被称为“低乙烯基芳族”或“低苯乙烯”）;和 / 或

[0035] (IV) 共聚物包含小于 40 重量%的甲基丙烯酸酯单体（在本文中也被称为“低 MA”）。

[0036] 任选地,本发明的共聚物是固体级低聚物 (SGO)。

[0037] 优选地,本发明的聚合物和 / 或衣康酸单体是由生物可再生来源获得的。

[0038] 本发明的另一个方面包括含有总组合物的 5 至 80 重量%的如本文中所描述的本发明的低 MW 和高 TG 共聚物。

[0039] 本发明的共聚物还可以独立地由下列可选的附加条件中的一个或多个来限制:

[0040] (V) 当组分 (a) 由以小于总单体的 30 重量%的量的 DBI 组成时,则共聚物基本上

不含任何氯基团 ;和

[0041] (VI) 当组分 (a) 由以小于总单体的 23 重量%的量的 DBI 组成时,共聚物不是通过其中使用追加(chaser)单体的乳液聚合方法制得的 ;和

[0042] (VII) 当组分 (a) 由以小于总单体的 23 重量%的量的 DBI 组成时,那么如果存在组分 (d) 的话,组分 (d) 不是苯乙烯或者由丙烯酸丁酯(混合物的 60 重量%)和苯乙烯(混合物的 40 重量%)组成的混合物 ;

[0043] (VIII) 共聚物基本上不含苯乙烯(优选地不含苯乙烯),更优选地如果存在的话组分 (d) 不是苯乙烯或者由丙烯酸丁酯(混合物的 60 重量%)和苯乙烯(混合物的 40 重量%)组成的混合物,更优选地如果存在的话组分 (d) 不是苯乙烯(S)、丙烯酸丁酯(BA)、丙烯酸 2-乙基己酯(EHA)或其混合物。(IX) 所述共聚物不是通过其中使用追加单体的乳液聚合方法制得的 ;和

[0044] (X) 只有当组分 (a) 由优选地以总单体 (a)+(b)+(c)+(d) 的 8.5 重量%至 15 重量%的量的 DBI 组成时,共聚物不是通过其中使用追加单体的乳液聚合方法制得的。

[0045] (XI) 当组分 (a) 由 DBI 组成时,则组分 (a) 不以总单体组合物的 8.5 重量%、21.8 重量%、22.5 重量%或 22.7 重量%的量存在,优选地不以 8 重量%至 23 重量%的量存在,

[0046] (XII) 当组分 (a) 由 DBI 组成时,则组分 (a) 不以总单体组合物的 4.7 重量%、5.0 重量%、8.5 重量%、21.8 重量%、22.5 重量%、22.7 重量%、25.0 重量%、28.7 重量%、30.0 重量%或 41.2 重量%的量存在,优选地不以 4 重量%至 42 重量%的量存在,

[0047] (XIII) 共聚物不是在聚衣康酸二乙酯种子聚合物存在下由以 15 比 85 的各自重量比的衣康酸二甲酯(DMI)和衣康酸二丁酯(DBI)的聚合获得的 ;更优选地共聚物不是在聚衣康酸二乙酯种子聚合物存在下由衣康酸二烷基酯的聚合获得的 ;最优选地共聚物不是在聚衣康酸二烷基酯种子聚合物存在下由聚合获得的 ;和 / 或

[0048] (XIV) 如果共聚物的聚合在包含有机硼烷络合物和活化剂的引发剂体系存在下进行,那么组分 (a) 以总单体 (a)+(b)+(c)+(d) 的大于 20 重量%、优选地至少 24 重量%的量存在。

[0049] 本文中使用时,术语“种子聚合物”如 US2011144265 中所定义(例如参见第 [007] 段),即聚合物种子颗粒分散于水性介质中从而该种子颗粒吸收又添加的(共聚)单体,并且该种子颗粒存在的浓度使得可以控制该(共聚)单体的颗粒尺寸。

[0050] 附加条件

[0051] (I) 低 MW

[0052] 本发明的共聚物优选地具有不超过 15 千克 / 摩尔(本文中被定义为低 MW)、适宜地小于 10 千克 / 摩尔的数均分子量(M_n)。本发明的优选共聚物具有 500 至 10000g / 摩尔、更优选地 500 至 7000g / 摩尔、最优选地 500 至 5000g / 摩尔、例如 700 至 3000g / 摩尔的数均分子量。

[0053] (II) 高 TG

[0054] 本发明的共聚物具有使用 Fox 方程计算得的至少 75℃ 的高玻璃化转变温度(本文中定义为高 TG)。本发明的优选高 TG 共聚物具有至少 80℃、更优选地至少 85℃、最优选地至少 90℃、例如至少 100℃ 的玻璃化转变温度。

[0055] (III) 低乙烯基芳族

[0056] 根据本发明的共聚物可以包含相对于总单体重量小于 40 重量%的乙烯基芳族单体,更优选地小于 20 重量%、最优选地小于 10 重量%且甚至最优选地小于 5 重量%、例如基本上不含(例如 0 重量%)的乙烯基芳族单体,总单体重量为 100%。本文中对“基本上不含”含义的限制也在下文中定义。任选地期望,限制本发明的组合物和共聚物中的乙烯基芳族单体的量,因为它们的存在会导致黄化、减少室外耐久性,并且对环境和/或健康具有潜在的不利影响。

[0057] 优选地期望,本发明的共聚物和组合物包含少量乙烯基芳族单体诸如苯乙烯和/或其他芳基烯烃(arylalkylene)单体。本文中使用时,术语“乙烯基芳族单体”表示诸如苯乙烯、 α -甲基苯乙烯、乙烯基甲苯、乙烯基萘、对甲基苯乙烯和氯甲基苯乙烯等的单体。术语“芳基烯烃”也定义如下。更优选地,诸如苯乙烯和 α -甲基苯乙烯的单体以少量存在(或不存在)于本发明的组合物中。本发明的更优选组合物是基本上不含乙烯芳族物质的那些。如果在本发明中使用乙烯基芳族单体,则适宜地为苯乙烯。

[0058] 然而,如酸性单体部分中所描述的,通过使用高 AV 的低分子量聚合物,可以使用大量乙烯基芳族单体(至多 40 重量%的单体)。然而,在本发明的一个适宜的实施方式中,共聚物仅包含少量乙烯基芳族单体(< 20 重量%的单体),并且适宜地,本发明的共聚物基本上不含任何乙烯基芳族单体。

[0059] 本申请人已经惊奇地发现了,在本发明的共聚物不包含乙烯基芳族单体或包含少量乙烯基芳族单体的实施方式中,共聚物还可以通过改善的聚合方法获得,这种改善的聚合方法展现出如下特征(I)至(III)中优选地一个、更优选地两个、最优选地三个特征:

[0060] (I) 使用不超过 1 重量份、优选地不超过 0.5、更优选地不超过 0.2、甚至更优选地不超过 0.1 重量%的链转移剂、最优选地不使用链转移剂;相对于总单体组合物(即(a)+(b)+(c)),总单体组合物为 100 重量份(本文中也表示为 wt 份每 100 单体)

[0061] (II) 使用不超过 1 摩尔份、优选地不超过 0.5、更优选地不超过 0.2、甚至更优选地不超过 0.1 摩尔份的引发剂,相对于总单体组合物(即(a)+(b)+(c)),总单体组合物为 100 摩尔份(本文中也表示为摩尔份每 100 单体),和/或

[0062] (III) 具有不超过 275°C、优选地不超过 225°C、更优选地不超过 200°C 的最大聚合温度。

[0063] (IV) 低甲基丙烯酸酯(低 MA)

[0064] 根据本发明的共聚物可以包含相对于总单体重量小于 40 重量%的甲基丙烯酸酯单体、更优选地小于 20 重量%、最优选地小于 10 重量%且甚至最优选地小于 5 重量%,例如基本上不含 MA 单体、诸如 0 重量% MA 单体,总单体重量为 100%。本文中对“基本上不含”含义的限制也在下文中定义。由于已经给出的原因,期望限制本发明的组合物和共聚物中的 MA 单体的量。

[0065] (III) 和 (IV) 低苯乙烯和低 MA

[0066] 本发明的共聚物和组合物还可以包含少量乙烯基芳族单体和 MA,有用地乙烯芳族单体和 MA 单体的总量相对于总单体重量小于 40 重量%、更有用地小于 20 重量%、最有用地小于 10 重量%且甚至最有用地小于 5 重量%、例如基本上不含(例如 0 重量%)这些单体,总单体重量为 100%。本文中对“基本上不含”含义的限制也在下文中定义。

[0067] 组成单体

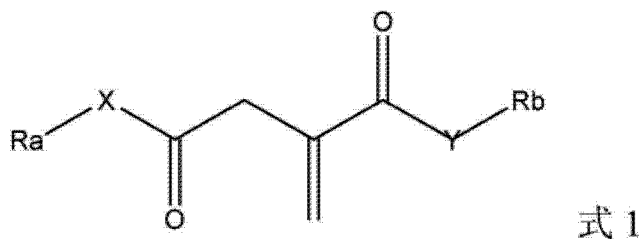
[0068] 组分 (a)、(b) 和 (c) 是互相排斥的。因此,应当理解,也可以衍生自衣康酸类物质(例如衣康酸、衣康酸酐、半衣康酸酯、其酸衍生物、其组合和 / 或混合物)的酸官能单体被看作是酸组分 (b) 的一部分,而不是衣康酸官能组分 (a) 的一部分。

[0069] 在本发明的一个优选实施方式中,组分 (a) 和 (b) 二者均衍生自衣康酸类物质和 / 或其衍生物、更优选地衍生自生物可再生来源。因此,例如组分 (a) 可以是衣康酸二 (C_{1-6} 二烷基) 酯(例如 DBI 和 / 或 DMI),并且组分 (b) 可以是衣康酸酐和 / 或其 C_{1-4} 烷基单酯(例如衣康酸)。在这种实施方式中,任选地不包含组分 (c),因此共聚物可以有利地由来自相同衣康酸来源的单体得到。

[0070] 组分 (a) 衣康酸单体

[0071] 衣康酸官能单体适合用作本发明中的组分 (a),其通常可以由式 1 表示:

[0072]



[0073] 其中 Ra 和 Rb 独立地表示任何可选地被取代的烃片段(例如任何脂族、脂环族或芳族片段);并且

[0074] X 和 Y 独立地表示 -O- 和 / 或 -NRc-,其中在每种情况下 Rc 独立地表示 H 和 / 或任何可选地被取代的烃片段(例如脂族、脂环族或芳族片段);

[0075] 前提是式 1 不包含:

[0076] 任何酸性基团(例如羧酸、磷酸和 / 或磺酸基团)或任何前体酸基团(其是在本文中的聚合条件下容易产生酸基团的基团,例如酸酐基团)。

[0077] 当 X 和 Y 均为 O 时,式 1 表示 2-偏亚甲基丁二酸二酯(2-methylidenebutanedioate diester)(本文中也称为衣康酸二酯)。X 和 Y 均为 NRc 时,式 1 表示衣康二酰胺。

[0078] 当 X 或 Y 中的一个为 O 且另一个为 NRc 时,式 1 表示具有一个酯基和一个酰胺基团的化合物。

[0079] 应当理解的是,本文中使用术语“衣康酸官能单体”指的是式 1(如本文中所定义)的任意衣康酸二酯和 / 或二酰胺单体,其他衣康酸酯、衣康酰胺。

[0080] 优选的衣康酸官能单体是具有以下特征的式 1 的那些,上述特征为其中:

[0081] Ra 和 Rb 独立地表示:

[0082] 可选地被取代的 C_{1-30} 烷基,

[0083] 更优选地 C_{1-20} 亚烷基(可以包含直链、支链和 / 或环状片段)和 / 或 C_{3-20} 亚芳基;

[0084] 最优选地 C_{1-10} 亚烷基。

[0085] 尽管 Ra 和 Rb 可以不同,但更适宜地它们表示相同片段。

[0086] 适宜地,式 1 可以表示衣康酸的二烷基或芳基酯、衣康酸的二烷基或芳基酰胺。更适宜地, R_a 和 R_b 可以独立地选自由以下组成的组:甲基、乙基、正丙基、异丙基、正丁基、异丁基、叔丁基、己基、环己基、2-乙基己基、癸基、十二烷基、苯基、2-苯乙基、2-羟乙基、2-羟丙

基、3-羟丙基和 4-羟丁基。更适宜地， R_a 和 R_b 选自甲基、乙基、正丁基和 2-乙基己基。最适宜地， R_a 和 R_b 选自甲基和乙基，例如甲基。

[0087] 衣康酸官能组分 (a) 以至少 20 重量%、有用地至少 25 重量%、更优选地至少 30 重量%、甚至更有用地至少 35 重量%以及最有用地至少 40 重量%的量，基于用于制备共聚物的单体 (a)、(b) 和 (c) 的总重量（为 100%）。

[0088] 适宜地，衣康酸官能组分 (a) 可以以小于 80 重量%、更适宜地小于 75 重量%、甚至更适宜地小于 70 重量%、最适宜地小于 65 重量%且例如小于 60 重量%的量存在于本发明的组合物和 / 或共聚物中；基于用于制备共聚物的单体 (a)、(b) 和 (c) 的总重量（为 100%）。

[0089] 优选地，衣康酸官能组分 (a) 可以以 20 至 80 重量%、更优选地 25 至 75 重量%、甚至更优选地 30 至 70 重量%、最优选地 35 至 65 重量%、例如 40 至 60 重量%的量存在于本发明的组合物和 / 或共聚物中；基于用于制备共聚物的单体 (a)、(b) 和 (c) 的总重量（为 100%）。

[0090] 衣康酸官能单体例如式 1 所示的那些单体也可以宽泛地分为两类：高级衣康酸酯，通常为疏水性的；和低级衣康酸酯，通常为亲水性的。

[0091] 在本发明的一个实施方式中，衣康酸官能单体可以是式 1 的衣康酸二酯，其中 R_a 和 R_b 独立地为可选地被取代的 C_{1-3} 烷基，例如 C_{1-3} 烷基，其中一个例子是衣康酸二甲酯 (DMI)。

[0092] 在本发明的另一个实施方式中，衣康酸官能单体可以是式 1 的衣康酸二酯，其中 R_a 和 R_b 独立地为可选地被取代的 C_{4-8} 烷基，例如 C_{4-6} 烷基，其中一个例子是衣康酸二丁酯 (DBI)。

[0093] 衣康酸官能单体 (a) 可以选自会形成具有优选地大于 40°C、更优选地大于 60°C 和最优选地大于 80°C 的 T_g 的均聚物的那些衣康酸单体。

[0094] 组分 (b) 酸性单体（也被称为“酸性组分”）

[0095] 应当理解，当本文中涉及酸官能和 / 或酸性组分时，其指的是酸性片段（例如羧酸、磷酸和 / 或磺酸基团）和 / 或在使用条件下可以形成酸性基团的前体酸性片段（例如酸酐）二者。携带酸的单体可以以游离酸或盐形式聚合，例如以其铵盐和 / 或碱金属盐形式。因此，本文中提及酸时也应理解为包括其合适的盐和 / 或其衍生物（例如其酸酐和 / 或酰氯）。

[0096] 因此，本发明的共聚物包含含有酸基团和 / 或前体酸基团的酸性官能单体（组分 (b)）。

[0097] 合适的酸单体以潜在酸官能基团形式可以是单官能或双官能的。优选的单体是丙烯酸、甲基丙烯酸、丙烯酸 β -羧乙酯、衣康酸、衣康酸酐、马来酸和马来酸酐。

[0098] 其他优选的酸具有一个烯属基团和一个或两个羧基。这种酸单体选自由以下组成的组：丙烯酸（及其可共聚的低聚物）、柠康酸、中康酸、巴豆酸、富马酸、衣康酸、马来酸、甲基丙烯酸、亚甲基丙二酸、其酸酐、其盐、其酰氯，磷酸化的甲基丙烯酸羟乙酯（磷酸化的 HEMA）、磷酸化的丙烯酸羟乙酯（磷酸化的 HEA）、磷酸化的甲基丙烯酸羟丙酯（磷酸化的 HPMA）、磷酸化的丙烯酸羟丙酯（磷酸化的 HPA）、磺化的苯乙烯（及其氯化物）、2-丙烯酰氨基-2-甲基丙磺酸 (AMPS) 和甲基丙烯酸乙酯-2-磺酸，多价酯的部分酸，更优选地二酯的

半酯、最优选地单酸半衣康酸酯（即式 A 中要么 Ra 要么 Rb 为 H 的那些酯），它们在相同物种中的组合和 / 或其混合物。

[0099] 更优选的单体是丙烯酸、甲基丙烯酸、丙烯酸 β -羧基乙酯和衣康酸酐。最优选的酸官能单体是衣康酸酐。

[0100] 合适的组分 (b) 的酸官能单体是能够与组分 (a) 的衣康酸官能单体共聚合的那些。适宜地，组分 (b) 的至少一个单体可以包含至少一个如本文中所限定的经活化的不饱和和片段。

[0101] 有用地，组分 (b) 的单体是酸官能烯属不饱和单体，例如酸官能（甲基）丙烯酸单体。

[0102] 优选的酸性单体包含至少一种烯属不饱和羧酸，有利地本质上由至少一种烯属不饱和和羧酸组成，但也可以使用其他酸性基团诸如可选地被取代的有机磷酸和 / 或磺酸。

[0103] 实例包括磷酸化的（甲基）丙烯酸烷基酯、芳基烯烃 (arylalkylenes) 的磺酸（及其衍生物）、（甲基）丙烯酸烷基酯的磺酸（及其衍生物）和 / 或其他有机取代的磺酸（例如丙烯酰氨基烷基磺酸 (acrylamidoalkyl sulfonic acid)）。

[0104] 有用的芳基烯烃磺酸是其中芳基烯烃片段包含可选地烃取代的苯乙烯、适宜地包含可选地 C_{1-10} 烃取代的苯乙烯、更适宜地包含可选地 C_{1-4} 烷基取代的苯乙烯的那些。有用的酸是苯乙烯化合物的磺酸取代的衍生物，该苯乙烯化合物选自自由苯乙烯、 α -甲基苯乙烯、乙烯基甲苯、叔丁基苯乙烯、二甲基苯乙烯和 / 或其混合物组成的组。尤其优选的是苯乙烯对磺酸及其相应的酰氯，苯乙烯对磺酰氯。然而，本发明的一个优选目标是减少（在一个实施方式中优选地消除）乙烯基芳族片段（例如苯乙烯及类似物）在本发明的共聚物中的量。因此，芳基烯烃磺酸优选地不用作酸性单体 (b) 或如果存在的话其量足以足够附加条件 (III) 本发明的共聚物包含小于 40% 的乙烯基芳族单体。

[0105] 优选的磷酸化的有机酸包括磷酸化的（甲基）丙烯酸酯，其可选地被例如一个或多个羟基取代，例如磷酸化的羟基（甲基）丙烯酸酯及其 C_{1-4} 烷基酯。

[0106] 尤其优选的酸单体是丙烯酸、甲基丙烯酸、丙烯酸 β -羧基乙酯、衣康酸和 / 或衣康酸酐。

[0107] 已知，可以直接聚合或者也可以不直接聚合形成本发明的共聚物的某些酸性组分也可以起到其他单体的前体的作用，其中其他单体进行聚合形成本发明的共聚物。例如，在本发明的一个实施方式中，在足够高的温度下，衣康酸脱水原位形成衣康酸酐，然后可以在形成本发明的共聚物的共聚中作为单体进行反应。

[0108] 对于乳液聚合来说，酸性单体诸如丙烯酸、甲基丙烯酸、丙烯酸 β -羧基乙酯和 / 或衣康酸可以是便利的。对于溶剂辅助分散 (SAD) 共聚来说，酸性单体诸如丙烯酸、甲基丙烯酸和 / 或衣康酸酐是优选的。

[0109] 有用地，基于用于制备共聚物的单体 (a)、(b) 和 (c) 的总重量（为 100%），酸性组分 (b) 可以以至少 10 重量%、更有用地至少 15 重量%、甚至更有用地至少 20 重量%、最有用地至少 25 重量%的量存在于本发明的组合物和 / 或共聚物中。

[0110] 酸性单体 (b) 以不超过 40 重量%、适宜地小于 35 重量%、更适宜地小于 30 重量%的量存在于本发明的组合物和 / 或共聚物中；该量基于用于制备共聚物的单体 (a)、(b) 和 (c) 的总重量（为 100%）。

[0111] 优选地（且受下文中与 AV 值有关的限制性条件限制），基于用于制备共聚物的单体 (a)、(b) 和 (c) 的总重量（为 100%），酸性组分 (b) 可以 10 至 40 重量%、更优选地 15 至 40 重量%、甚至更优选地 20 至 40 重量%、最优选地 25 至 40 重量%、例如 25 至 35 重量%的量存在于本发明的组合物和 / 或共聚物中。

[0112] 有用地，酸单体 (b) 可以以这样的量存在于本发明的组合物和 / 或共聚物中，其量足以实现至少 80mg KOH/g、更有用地至少 120mg KOH/g、最有用地至少 160mg KOH/g、例如至少 195mg KOH/g 固体聚合物的酸值 (AV)。

[0113] 适宜地，酸单体 (b) 可以以这样的量存在于本发明的组合物和 / 或共聚物中，其量足以实现不超过 325mg KOH/g 固体聚合物、更适宜地不超过 290mg KOH/g 固体聚合物、最适宜地不超过 260mg KOH/g 固体聚合物、例如不超过 200mg KOH/g 固体聚合物的酸值 (AV)。

[0114] 优选地，酸单体 (b) 可以以这样的量存在于本发明的组合物和 / 或共聚物中，其量足以获得 65 至 325mg KOH/g 固体聚合物的 AV。

[0115] 出于本文中所描述的各种原因，本发明的一个任选目标是尽可能地限制乙烯基芳族单体的量。然而，本申请人已经惊奇地发现了，可以通过提高 AV 数在一定程度上弥补使用较大量（至少 40 重量%）的乙烯基芳族单体所带来的加工困难。因此，在本发明的各种替换性实施方式中，当共聚物包含一定的相应乙烯基芳族单体总量（以共聚物的总单体的重量%计）时，酸单体可以以足够的量存在于本发明的组合物和 / 或共聚物中，该量足以实现一定酸值（以 KOH/g 每 g 固体聚合物计）：

[0116] 酸值 (AV) 乙烯基芳族单体

[0117] 200 至 325mg KOH/g 且 30 至 40 重量% ;或

[0118] 160 至 290mg KOH/g 且 20 至 30 重量% ;或

[0119] 120 至 260mg KOH/g 且 10 至 20 重量% ;或

[0120] 80 至 195mg KOH/g 使用 0 至 10 重量%。

[0121] 有用地，组分 (b) 既满足本文中的酸值 (AV) 限制又满足重量限制，但应当理解的是，根据所使用的单体，本文中所指定的 AV 可以通过使用本文中所给的优选重量%值以外的重量百分数来实现。当本文中的单体或其他组分的任意重量%与指定的酸值之间存在明显的不一致时，应当理解的是满足 AV 通常是更期望的目标。如果必要的话，可以以本领域技术人员所公知的方式适当地修改相关成分的重量%值。

[0122] 酸性官能单体 (b) 可以选自会形成具有优选地大于 40°C、更优选地大于 60°C 且最优选地大于 80°C 的均聚物的那些酸性单体（或其前体）。

[0123] 组分 (c) - 其他单体

[0124] 本发明的共聚物包含不超过 72 重量%、优选地不超过 70 重量%、优选地不超过 60 重量%、更优选地不超过 40 重量%的既非衣康酸官能单体 (a) 又非酸官能单体 (b) 的其他单体（组分 (c)）。组分 (c) 还可以满足如下限制性条件 (III) 和 / 或 (IV)：本发明的共聚物包含小于 40% 的乙烯基芳族单体和 / 或小于 40% 的甲基丙烯酸酯单体。因此，本文中所描述的诸如芳基烯基的单体和 / 或甲基丙烯酸酯单体是优选的，因为组分 (c) 仅限于本文中所描述的限制程度，并且任选地基本上不存在于本发明的组合物中。

[0125] 适宜地，基于用于形成共聚物的单体 (a)、(b) 和 (c) 的总量 (100%)，组分 (c) 的其他单体可以以小于 30 重量%、更适宜地小于 20 重量%、甚至更适宜地小于 10 重量%且

最适宜地小于 5 重量%的量存在于本发明的聚合物和 / 或共聚物中。

[0126] 有用地,基于用于形成共聚物的单体 (a)、(b) 和 (c) 的总量 (100%),组分 (c) 的其他单体当存在时以至少 0.1 重量%、更有用地至少 0.5 重量%、甚至更有用地至少 5 重量%的量存在于本发明的聚合物和 / 或共聚物中。

[0127] 优选地,基于用于形成共聚物的单体 (a)、(b) 和 (c) 的总量 (100%),组分 (c) 的其他单体当存在时以 0.1 至 40 重量%、更优选地 0.5 至 40 重量%、甚至更优选地 5 至 30 重量%、例如 5 至 20 重量%的量存在于本发明的聚合物和 / 或共聚物中。

[0128] 下面给出了合适的非衣康酸官能非酸官能单体。优选地,组分 (c) 包含少量 (更优选地不含) 乙烯基芳族单体和 / 或芳族烯烃单体。

[0129] 非衣康酸官能单体可以包含具有大于 40°C、更优选地大于 60°C 且最优选地大于 80°C 的均聚物 T_g 的任何丙烯酸或甲基丙烯酸酯或酰胺。

[0130] 这种单体的优选实例为甲基丙烯酸甲酯、甲基丙烯酸乙酯、双丙酮丙烯酰胺、丙烯腈、甲基丙烯酸羟乙酯、甲基丙烯酸环己酯、(甲基)丙烯酸异冰片酯、聚乙二醇(甲基)丙烯酸酯、聚丙二醇(甲基)丙烯酸酯、丙烯酰胺和甲基丙烯酰胺。可用于制备本发明的低分子量共聚物的尤其优选的交联单体描述于 WO2005/097854 (DSM) 中。

[0131] 组分 (c) 包含并非组分 (a) 或 (b) 的一部分的单体,该单体可与组分 (a) 和 (b) 以任意合适的技术共聚,例如本文中所描述的那些中的任意技术 (例如 SAD、溶液、本体和 / 或乳液聚合)。

[0132] 组分 (c) 可以包含合适的经活化的不饱和片段 (例如烯属不饱和),其中组分 (c) 的结构并不与组分 (a) 或 (b) 中任意一个重叠。

[0133] 优选地,组分 (c) 以小于 50 重量%且更优选地小于 40 重量%的量使用。

[0134] 组分 (c) 可以包含能够进行交联的单体、能够改善涂层对各种基材的粘附性的单体、能够增强聚合物乳液的胶体稳定性的单体、或者能够用来影响 T_g 或聚合物极性的单体。

[0135] 组分 (c) 还可以包含可以诱导共聚物组合物的交联的交联单体。交联能够如下发生:在室温下 (使用例如与己二酸二酰肼结合的双丙酮丙烯酰胺)、高温下 (烘烤条件,其中例如共聚的 (甲基)丙烯酸羟乙酯与六甲氧基甲基蜜胺反应) 进行,或者作为 2C 组合物 (共聚的 (甲基)丙烯酸羟乙酯与多异氰酸酯反应,例如 Bayhydur 3100)。交联单体的其他实例包括 (甲基)丙烯酸羟丙酯、硅烷官能单体,例如 3- 甲基丙烯酰氧基丙基三甲氧基硅烷 (Geniosil GF31, 来自 Wacker)。当本发明涉及使用该涂料组合物作为 UV 涂料时,包含根据本发明的低分子量聚合物的水性组合物可以与具有多个不饱和基团的聚合物或低聚物混合。典型的实例包括二官能或三官能的多官能丙烯酸酯,诸如三羟甲基丙烷三丙烯酸酯或者其乙氧基化物或丙氧基化物)。

[0136] 优选地,交联单体以小于 15 重量%、更优选地小于 10 重量%且最优选地 0 至 10 重量%的浓度使用。

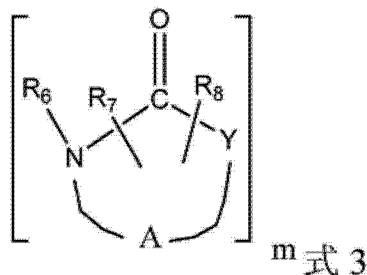
[0137] 组分 (c) 还可以包含改善 (湿) 粘附性质的单体。典型的单体包括脲基官能单体例如 Plex 6852-0 (来自 Evonik)、(甲基)丙烯酸异冰片酯、聚乙二醇(甲基)丙烯酸酯、聚丙二醇(甲基)丙烯酸酯。

[0138] 优选地,粘附促进单体以小于 15 重量%、更优选地小于 10 重量%且最优选地 0 至

10 重量%的浓度使用。

[0139] 可选地,组分 (c) 还可以包含至少一种式 3 的聚合物前体

[0140]



[0141] 其中 Y 表示电负性基团,

[0142] R_6 是 H、OH 或可选地羟基取代的 C_{1-10} 烃

[0143] R_7 是 H 或 C_{1-10} 烃;

[0144] R_8 是被至少一个经活化的不饱和片段取代的 C_{1-10} 烃基;并且;

[0145] 要么 A 代表既与 $-HN-$ 又与 $-Y-$ 片段相连的二价有机片段,因此 $-A-$ 、 $-NH-$ 、 $-C(=O)-$ 和 $-Y-$ 片段一起表示 4 至 8 个环原子的环,并且 R_7 和 R_8 与环上的任何合适的点相连;要么 A 不存在(并且式 3 表示不含杂环的直链和/或支链片段),在这种情况下 R_7 和 R_8 与 R_6 相连;并且

[0146] m 是 1 至 4 的整数。

[0147] 式 3 的一个或多个环片段均与 R_8 相连,并且在式 3 中当 m 是 2、3 或 4 时 R_8 是多价的(取决于 m 的值)。如果 m 不为 1,则 R_7 和 $-Y-$ 可以分别表示在每个环中的相同或不同的片段、优选地在每个环中的相同的相应片段。 R_7 和 R_8 可与环上的任意合适的位置相连。

[0148] 式 3 的优选单体包含其中具有以下特征的那些、适宜地本质上由其中具有以下特征的那些组成,所述特征为:A 表示可选的经取代的二价 C_{1-5} 亚烃基;和

[0149] $-Y-$ 是二价 $-NR_9-$ (其中 R_9 是 H、OH、可选地羟基取代的 C_{1-10} 烃或 R_8) 或二价 O。

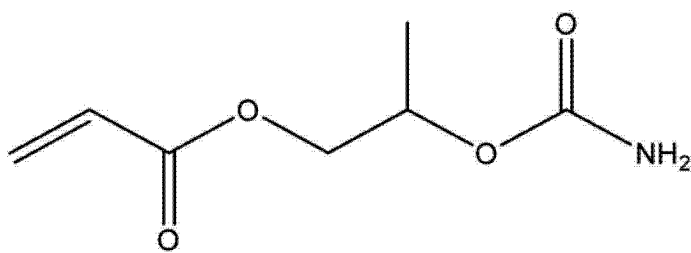
[0150] 式 3 的更优选单体包含其中具有以下特征的那些,所述特征为:m 为 1 或 2,

[0151] $-Y-$ 是 $-NR_8-$ (即其中式 2 经环氮与 R_8 相连),A 表示二价 C_{1-3} 亚烃基; R_6 是 H, R_7 是 C_{1-10} 烃;并且

[0152] R_8 包括(甲基)丙烯酰氧基烃基或其衍生物(例如马来酸酐)。

[0153] 式 3 所表示的单体包括通俗地被称为脲基单体的一些单体。式 3 的其他合适的脲基单体描述于“Novel wet adhesion monomers for use in latex paints”,Singh 等,Progress in Organic Coatings,34(1998),214-219,(尤其参见第 2.2&2.3 部分)和 EP 0629672(National Starch)中,二者均通过引用并入本文。适宜地,式 3 的单体可以以基本上纯的化合物(或化合物的混合物)形式使用或者可以溶解于合适的溶剂中,例如合适的(甲基)丙烯酸酯或丙烯酸衍生物,例如甲基丙烯酸甲酯。

[0154] 另一种合适的粘附促进单体为羟丙基氨基甲酸酯丙烯酸酯(hydropropylcarbamataacrylate, HPCA),例如可以从 BASF 作为在乙醇中的 70% 溶液(HPCA 70% EtOH)商业购得,HPCA 具有如下结构



并且可用作（湿）粘附促进剂和 / 或交

联剂。其可以是生物基的和 / 或通过酶生产的。

[0155] 在需要较高的分子量的那些情况中,可以使用其他组分和 / 或额外组分 (d),例如合适的多官能(甲基)丙烯酸酯或二乙烯基芳烃。典型的实例包括二官能、三官能或四官能的(甲基)丙烯酸酯,尤其是二官能的(甲基)丙烯酸酯和二乙烯基苯。基于总单体,典型的浓度小于 10 重量%、更优选地小于 5 重量%、甚至更优选地介于 0.05 重量%至 4 重量%、最优选地介于 0.1 至 2.5 重量%以及甚至最优选的基于 0.15 重量%至 1.5 重量%。

[0156] 本发明的其他方面

[0157] 方法

[0158] 本发明涉及单体的选择和所获得共聚物的性质。可以制备本发明的共聚物的聚合方法并不特别重要,因为可以使用任何合适的常规聚合方法。

[0159] 在本发明的一个优选实施方式中,共聚物是通过本体聚合工艺制备的。在本发明的另一个优选实施方式中,共聚物是通过溶液聚合工艺制备的。在本发明的另外一个优选实施方式中,共聚物是通过悬浮聚合工艺制备的。在本发明的另外还有一个优选实施方式中,共聚物是通过乳液聚合工艺制备的。这些技术的详细内容在下文中描述。

[0160] 链转移剂 (CTA)

[0161] 在本发明的任何实施方式中的一个优选方面中,当使用通常会需要链转移剂的聚合方法(例如但不限于自由基聚合,诸如乳液聚合,例如使用本文中所描述的低苯乙烯实施方式)时,本发明的方法以相对于总单体组合物(即(a)+(b)+(c)=100%)的如下总量使用链转移剂:不超过 1 重量%、优选地不超过 0.5%、更优选地不超过 0.2%、甚至更优选地不超过 0.1%、最优选地小于 50ppm、例如无链转移剂。

[0162] 在现有技术中已经使用的典型的链转移剂包括巯基酸及其烷基酯、四溴化碳、其混合物以及钴螯合剂、十二烷基硫醇(DDM)(最常用的一种)。巯基链转移剂通常以基于总单体含量的小于 1 重量%的量使用。典型地,以基于共聚物总重量的小于 50ppm 的量使用钴螯合剂 CTA。

[0163] 引发剂

[0164] 在本发明的任何实施方式中的一个优选方面中,当使用通常需要引发剂的聚合方法时,本发明的方法以相对于总单体组合物(即(a)+(b)+(c)=100%)的如下总量使用引发剂:

[0165] 对于本体聚合或溶液聚合方法来说,不超过 1 摩尔%、优选地不超过 0.5 摩尔%、更优选地不超过 0.2 摩尔%、甚至更优选地不超过 0.1 摩尔%。

[0166] 对于乳液聚合方法来说,不超过 1.5 摩尔%、优选地不超过 1 摩尔%、更优选地不超过 0.75 摩尔%、甚至更优选地不超过 0.5 摩尔%。

[0167] 用于使单体进行自由基聚合从而制备乙烯基聚合物的引发剂是公知的,并且是通

常适用于丙烯酸酯单体的自由基聚合的任何引发剂。它们可以是油溶性的,在水中具有低的溶解度,例如有机过氧化物、有机过氧酯和有机偶氮引发剂,并且以基于总单体含量的约 0.1 至 2 重量%的量使用。

[0168] 本申请人已经发现,一般来说,与其中(整体或部分)使用甲基丙烯酸酯单体而非衣康酸官能单体(组分(a))来制备聚合物的实施方式相比,尤其是对于具有较低量的乙烯基芳族单体的本发明的实施方式来说,可以使用较低量的引发剂,来制备本发明的衣康酸官能聚合物。

[0169] 受本文中所描述的对引发剂的任选限制条件限制,可用于经由溶液聚合或本体聚合生产低分子量聚合物的引发剂可以是任何有机过氧化物,包括氢过氧化物、二烷基过氧化物和/或烷基过氧链烷酸酯。

[0170] 合适的引发剂的实例还包括如下和/或其合适混合物中的任何一个(以及化学上类似和/或类同引发剂-例如具有相同结构类型-如下所列任意物质):

[0171] 可从 Akzo-Nobel 在 **Laurox®**、**Perkadox®** 和/或 **Trigonox®** 商标下和/或下面括号中所给出的商品名称下商购的所有那些:

[0172] 过氧化二异丁酰 (**Trigonox®** 187-C30 和/或 187-W40);

[0173] 过氧化新癸酸枯基酯 (**Trigonox®** 99-C75 和/或 99-W50);

[0174] 过氧化二碳酸二(3-甲氧基丁)酯 (**Trigonox®** 181);

[0175] 过氧化新癸酸 1,1,3,3-四甲基丁酯 (**Trigonox®** 423-C70 和/或 423-W50);

[0176] 过氧化新庚酸枯基酯 (**Trigonox®** 197-C75);

[0177] 过氧化新癸酸叔戊基酯 (**Trigonox®** 123-C75);

[0178] 过氧化二碳酸酯的混合物,在 **Trigonox®** ADC 和/或 **Trigonox®** ADC-NS60 的商标下获得;

[0179] 过氧化二碳酸二仲丁酯 (**Trigonox®** SBP、SBP-C60、SBPS 和/或 SBPS-C60);

[0180] 过氧化二碳酸二异丙酯 (**Perkadox®** IPP-NA30 和/或 IPP-NA27);

[0181] 过氧化二碳酸二(4-叔丁基环己基)酯 (**Perkadox®** 16S、16、16-W75 和/或 16-W40);

[0182] 过氧化二碳酸二(2-乙基己基)酯 (**Trigonox®** EHP-C75、EHP-W60、EHP-W50、EHP-W40S、EHPS 和/或 EHPS-C75);

[0183] 过氧化新癸酸叔丁酯 (**Trigonox®** 23、23-C75、23-C30 和/或 23-W50);

[0184] 过氧化二碳酸二丁酯 (**Trigonox®** NBP-C50);

[0185] 过氧化二碳酸二鲸蜡基酯 (**Perkadox®** 24-FL、24L 和/或 24-W35);

[0186] 过氧化二碳酸二肉豆蔻基酯 (**Perkadox®** 26);

[0187] 过氧化新戊酸 1,1,3-四甲基丁酯 (**Trigonox®** 425-C75);

[0188] 过氧化新庚酸叔丁基酯 (**Trigonox®** 257-C75);

[0189] 过氧化新戊酸叔戊基酯 (**Trigonox®** 125-C75);

[0190] 过氧化新戊基叔丁基酯 (**Trigonox®** 25-C75、25-C40 和/或 25-C25);

- [0191] 二(3,3,5-三甲基己酰基)过氧化物 (**Trigonox®** 36-C75、36-C40、36-C37.5 和 / 或 36-W50) ;
- [0192] 二月桂酰基过氧化物 (**Laurox®**、**Laurox®** S 和 / 或 **Laurox®** W-40) ;
- [0193] 二癸酰基过氧化物 (**Perkadox®** SE-10) ;
- [0194] 2,2-偶氮二(异丁腈) (**Perkadox®** AIBN) ;
- [0195] 2,2-偶氮二(2-甲基丁腈) (**Perkadox®** AMBN 和 / 或 AMBN-GR) ;
- [0196] 2,5-二甲基-2,5-二(2-乙基己酰过氧)己烷 (**Trigonox®** 141) ;
- [0197] 1,1,3,3-四甲基丁基过氧-2-乙基己酸酯 (**Trigonox®** 421) ;
- [0198] 叔戊基过氧-2-乙基己酸酯 (**Trigonox®** 121 和 / 或 121-C75) ;
- [0199] 过氧化二苯甲酰 (**Perkadox®** L-W75、L-W75SF、L-W40、CH-50、API 和 / 或 L-DFG) ;
- [0200] 叔丁基过氧-2-乙基己酸酯 (**Trigonox®** 21S、21-C70、21-C50 和 / 或 21-C30) ;
- [0201] 叔丁基过氧二乙基乙酸酯 (**Trigonox®** 27) ;
- [0202] 叔丁基过氧异丁酸酯 (**Trigonox®** 41-C50) ;
- [0203] 1,1'-偶氮二(六氢化苯腈) (**Perkadox®** ACCN) ;
- [0204] 1,1-二(叔丁基过氧)-3,3,5-三甲基环己烷 (**Trigonox®** 29、29-B90 和 / 或 29-C75) ;
- [0205] 1,1-二(叔戊基过氧)环己烷 (**Trigonox®** 122-C80) ;
- [0206] 1,1-二(叔丁基过氧)环己烷 (**Trigonox®** 22-B50、22-E50 和 / 或 22-C80) ;
- [0207] 叔戊基过氧 2-乙基己基碳酸酯 (**Trigonox®** 131) ;
- [0208] 叔戊基过氧乙酸酯 (**Trigonox®** 133-CK60) ;
- [0209] 叔丁基过氧-3,3,5-三甲基己酸酯 (**Trigonox®** 42S、42-C60 和 / 或 42-C30) ;
- [0210] 2,2-二(叔丁基过氧)丁烷 (**Trigonox®** D-C50 和 / 或 D-E50) ;
- [0211] 叔丁基过氧异丙基碳酸酯 (**Trigonox®** BPIC-C75) ;
- [0212] 叔丁基过氧 2-乙基己基碳酸酯 (**Trigonox®** 117) ;
- [0213] 叔戊基过氧苯甲酸酯 (**Trigonox®** 127) ;
- [0214] 叔丁基过氧乙酸酯 (**Trigonox®** F-C50) ;
- [0215] 丁基 4,4-二(叔丁基过氧)戊酸酯 (**Trigonox®** 17) ;
- [0216] 叔丁基过氧苯甲酸酯 (**Trigonox®** C 和 / 或 C-C75) ;
- [0217] 二枯基过氧化物 (**Perkadox®** BC-FF) ;
- [0218] 二(叔丁基过氧异丙基)苯 (**Perkadox®** 14S 和 / 或 14S-FL) ;
- [0219] 2,5-二甲基-2,5-二(叔丁基过氧)己烷 (**Trigonox®** 101、101-50D-PD、101-20PP、101-7.5PP-PD 和 / 或 101-E50) ;
- [0220] 叔丁基枯基过氧化物 (**Trigonox®** T) ;
- [0221] 2,5-二甲基-2,5-二(叔丁基过氧)己炔-3 (**Trigonox®** 145-E85) ;
- [0222] 二-叔丁基过氧化物 (**Trigonox®** B、B-C75、B-C50 和 / 或 B-C30) ;
- [0223] 3,6,9-三乙基-3,6,9-三甲基-1,4,7-三过氧壬烷 (**Trigonox®** 301 和 / 或

301-20PP) ;

[0224] 异丙基枯基过氧化物 (Trigonox® M-55) ;

[0225] 1,1,3,3- 四甲基丁基氢过氧化物 (Trigonox® TMBH-L) ;

[0226] 3,3,5,7,7- 五甲基 -1,2,4- 三氧杂环庚烷 (trioxepane) (Trigonox® 311) ;

[0227] 枯基氢过氧化物 (Trigonox® K-90) ;

[0228] 叔丁基氢过氧化物 (Trigonox® A-80 和 / 或 A-W70) ;

[0229] 叔戊基氢过氧化物 (Trigonox® TAHP-W85) ;和 / 或

[0230] 2,3- 二甲基 -2,3- 二苯基丁烷 (Perkadox® 30)。

[0231] 温度

[0232] 在本发明的任何实施方式中的一个优选方面中 (例如本发明的方法的低苯乙烯实施方式),所展现的最大聚合温度如下:

[0233] 对于本体聚合方法来说,不超过 275℃、优选地不超过 225℃、更优选地不超过 200℃。

[0234] 对于溶液聚合方法来说,不超过 180℃、优选地不超过 160℃且最优选地不超过 150℃。

[0235] 对于乳液聚合或分散体聚合方法来说,不超过 130℃、更优选地不超过 120℃且典型地不超过 100℃。

[0236] 应当理解的是,在其中聚合温度高于溶剂 (或在乳液聚合或分散体聚合情况下水) 的沸点的那些情况下,暗示了聚合是在高于 1bar 的压强下进行。

[0237] 任选地,本发明的某些共聚物还可以受如下附加条件限制:

[0238] (I) 当组分 (a) 由相对于总单体重量小于 30% 量的 DBI 组成时,共聚物基本上不含任何氯基团;和

[0239] (II) 当组分 (a) 由相对于总单体重量 8.5 至 15% 量的 DBI 组成时,共聚物是通过除其中使用追加单体的乳液聚合方法外的方法制备的。

[0240] 适宜地,组合物基本上不含聚氯乙烯聚合物和 / 或氯化石蜡,更优选地基本上不含任何含氯基团的单体,最优选地基本上不含任何含有 Cl 的物质 (无论是取代基、原子、二分子、离子或其他方式)。

[0241] 本发明的另一个方面,提供一种包含 5 至 80 重量%的低分子量聚合物的涂料组合物,其特征在于所述低分子量 (低 MW) 聚合物包含至少 20 重量%的衣康酸官能单体,并且具有 500 至 10000g/ 摩尔的数均分子量。

[0242] 本发明的聚合物具有低的数均分子量 (低 MW 聚合物),并且能够经由乳液聚合、分散体聚合、(连续) 本体聚合或经由溶液聚合制得。优选的聚合方法是本体聚合和溶液聚合。当本发明的低 MW 聚合物是经由乳液聚合、分散聚合和 / 或溶液聚合制得时,可以在不同的序列阶段中添加单体组合物。

[0243] 本发明的低 MW 聚合物优选地用作第二阶段乳液聚合中的胶体稳定剂。出于此目的,在开始乳液聚合阶段之前,低分子量聚合物的酸基团是 (部分) 中和的,并且低分子量聚合物 (部分地) 溶解。然而,低 MW 聚合物还可以有利地用作第二聚合乳液的添加剂。在这些情况下,混合在第二聚合物乳液的聚合过程完成以后,混合低 MW 聚合物的碱性溶液。

[0244] 本发明的优选共聚物具有 2 至 2.5、更优选地约 2.5 的多分散度。因此,对于本发明的共聚物的重均分子量来说,适合的期望相应值可以通过本文中数均分子量所给出的每个数值乘以 2.5 计算得到。这种计算得到的重均分子量数值和范围公开于本文中,不再明确描述。

[0245] 广义来说,在本发明的另外一个方面,提供了用于制备共聚物的方法,其包括如下步骤:在聚合方法中聚合聚合物前体来获得共聚物,该聚合物前体包含如上文中所描述的组分 (a)、组分 (b) 和任选地组分 (c),

[0246] 优选地,聚合方法选自本体聚合、溶液聚合、悬浮聚合和 / 或乳液聚合、更优选地本体聚合。

[0247] 本发明的另一个方面广义地提供通过本发明的方法获得和 / 或能够获得的共聚物。

[0248] 在本发明的另外一个实施方式,共聚物可以通过连续本体聚合来制备,例如使用如 W082/02387 或 EP554783 中所描述的类似的方法。由此,例如低 MW 聚合物可以使用 (连续) 本体聚合来制备,优选地使用小于 40 重量% (基于固体聚合物 (为 100%))、更优选地使用小于 20 重量%溶剂的溶剂浓度。合适的溶剂和合适的引发剂的实例 (受本文中所描述的任选限制条件限制) 也可以参见 W082/02387 或 EP554783,这两篇内容通过引用并入本文。

[0249] 在使用溶液聚合制备低分子量聚合物的情况下,优选的溶剂是具有不超过 130℃、更优选地不超过 100℃且最优选地不超过 90℃的沸点的那些溶剂。

[0250] 优选的溶剂是丙酮、甲基乙基甲酮、甲醇、乙醇、异丙醇、乙酸乙酯、乙酸丁酯和 / 或甲苯。其他合适的溶剂是本领域技术人员公知的。在这些情况下,当聚合温度超过溶剂和 / 或单体的沸点时,则在高压下进行聚合。

[0251] 优选地,溶液聚合物的固体含量为至少 40 重量%、更优选地 50 至 90 重量%、最优选地 60 至 85 重量%。有用地,本发明的固体聚合物是通过去除溶液聚合步骤中所使用的基本上所有溶剂来获得的,并且所分离得到的固体聚合物具有至少 95%、更优选地至少 98%、最优选地至少 99% 的固含量。适宜地,通过溶液聚合获得的本发明的固体聚合物是以无定形形式 (例如鳞片状或粒状物) 或以结晶形式 (例如作为针状结晶) 分离的。

[0252] 经由溶液聚合制备的低分子量聚合物可以通过提高 pH 来溶解,并接下来直接使用。然而,优选的是,在使用碱将低分子量聚合物溶解在水中之后去除聚合步骤中所使用的溶剂。溶剂的去除可以通过提高温度或降低压强来实现。优选组合这些方式。可以在溶解低分子量聚合物之后去除溶剂,然后进一步使用。然而,可以想到,也可以在低分子量聚合物用于下文详细说明的后续步骤中之后,去除溶剂。

[0253] 尽管不太优选,也可以经由乳液聚合或分散体聚合通过本领域技术人员公知的技术来制备低分子量聚合物。

[0254] 在一个特殊实施方式中,其中使用衣康酸酐或马康酸酐作为酸官能单体,可以在聚合完成之后对它们进行修饰。可以使用任何亲核官能团来进行酸酐基团的修饰。优选的官能团包括羟基、酰肼基、肼基、半-卡巴肼基和胺基。在所有情况下,修饰可以导致引入与羟基、酰肼基、肼基、半-卡巴肼基或胺基相连的片段,并且同时引入酸基团。随后可以使用剩余酸基团来溶解低分子量聚合物。

[0255] 可以使用单官能的羟基、酰肼、或肼、或者伯胺或仲胺来进行修饰,也可以使用双官能或更高官能的羟基、肼、酰肼、半-卡巴肼或者伯胺或仲胺来进行修饰。潜在的羟基官能团可以包括 C1-C20 脂族、芳族、或脂环族的单官能、双官能或高官能的醇。脂族、芳族、或脂环族基团可以包含其他官能团,例如能够用于改善粘合、交联或其他目的的官能团。这种官能团的典型实例可以包括磷酸酯/盐、磷酯/盐、硫酸酯/盐、磺酸酯/盐、酮、硅烷、(环状)脲基、(环状)碳酸酯/盐、酰肼、肼、半-卡巴肼、聚氨酯(urethane)、脲、氨基甲酸酯/盐和三聚氰胺。

[0256] 优选的(多)胺、(多)肼或(多)酰肼可以通过相同的描述来表征。

[0257] 当低分子量聚合物包含要用于修饰步骤中的衣康酸酐或马来酸酐时,特别优选地在与羟基或胺官能片段反应之前,酸酐是未水解的。因此,在那些情况下,优选聚合方法是本体聚合和/或溶液聚合,其中溶剂是非质子性的。

[0258] 根据各种程序,可以将本发明的低分子量聚合物溶解于水中,尤其在该低分子量聚合物包含酸官能基团(例如通过酸单体引入的)时如此。例如,可以将低分子量聚合物添加到水中,然后中和酸基团至足够高的水平,可以在添加到水中之前中和低分子量聚合物的酸基团,或者在低 MW 聚合添加之前将用来溶解低 MW 聚合物的水中和。这些步骤中每一步都可以在环境温度或高温(高于环境温度)下进行。

[0259] 本发明的另一个方面提供了包含如本文所描述的低分子量聚合物的涂料组合物。可以不同的方式将低分子量聚合物引入到涂料组合物中,不同方式的非限制性实例描述如下:

[0260] 低分子量聚合物可以例如与预先形成的胶乳共混或混合。这可以通过如下来实现:先溶解低分子量聚合物,再将其与第二乳液混合;或者将低分子量聚合物溶解于第二乳液中。第二乳液可以是任何类型的聚合物乳液,包括聚乙烯基组合物,包括序列、低聚物支持、梯度形态乳液,聚氨酯乳液,氨基甲酸酯-丙烯酸酯乳液,醇酸乳液和/或聚酯乳液。

[0261] 溶解于水中的低分子量聚合物可以用作乳液聚合步骤的表面活性剂和/或稳定剂。例如这种方法公开于 W02005/097854 中对比例 1 中。

[0262] 低分子量聚合物可以用作颜料分散剂,例如通过先将其混合在颜料分散体中从而添加到涂料组合物中。在这种情况下,将低分子量聚合物添加到包含无机颜料颗粒的颜料分散体,将混合物研磨直到获得稳定的颜料分散体。接下来,将颜料分散体添加到聚合物乳液中,以形成带颜料的涂料。

[0263] 本发明的组合物和/或涂料的优选应用领域包括木材涂料,例如窗框、工业木材、镶木地板;和装饰性应用,粘合剂和图形艺术应用,例如墨、粘合剂、复印清漆、膜涂料;在各种塑料(诸如聚苯乙烯、聚酯、PVC、聚丙烯、聚乙烯)上涂覆的涂料;或涂覆于玻璃或金属的涂料。

[0264] 可以使用多种方法来形成本发明的共聚物。这些方法包括乳液聚合、悬浮聚合、本体聚合和溶液聚合。这些方法都是极其公知的并且不需要非常详细地描述。

[0265] 在一个实施方式中,可以使用本体聚合方法来制备本发明的共聚物。烯属不饱和单体的本体聚合详细描述于 EP 0156170、W082/02387 和 US4414370,其内容通过引用并入本文。通常,在本体聚合方法中,两种或更多种单体的混合物被填充、优选地连续填充到反应器区域,该反应器区域包含具有相同比例的乙烯基单体作为单体混合物的熔融乙烯基聚

合物。将熔融的混合物保持在预定的温度下,以提供具有所期望分子量的乙烯基聚合物。以与将单体加入到反应区域的速度相同的速度,将产物从反应区域泵出,从而在体系中提供固定水平的乙烯基单体和乙烯基聚合物。所选择的具体流速取决于反应温度、乙烯基单体、所期望的分子量和所期望的多分散性。

[0266] 在另一个实施方式中,可以使用乳液聚合物来形成本发明的共聚物。传统的乳液方法包括,将单体分散于水性介质中,并使用自由基引发剂(通常水溶性的)、适当加热(例如 30 至 120°C)和搅拌来进行聚合。

[0267] 可以采用常规乳化剂(表面活性剂)来实现水性乳液聚合,被使用的常规乳化剂例如为阴离子型和/或非离子型乳化剂。基于所添加的全部单体的重量,所使用的量优选地很低、优选地 0.3 至 2 重量%、更常用地 0.3 至 1 重量%。

[0268] 水性乳液聚合可以采用常规的自由基引发剂,诸如本领域中所公知的过氧化物、过硫酸盐和氧化还原体系。基于所添加的全部单体的重量,所使用的引发剂的量通常为 0.05 至 3%。

[0269] 可以使用“一锅法”(“all in one”)批处理方法(即在聚合开始时要使用的所有组分均存在于聚合介质中的方法)或者半-批处理方法(在半-批处理方法中,一种或多种所采用的组分(通常至少一种单体)在聚合时全部或部分地进料到聚合介质中)来进行水性乳液聚合方法。尽管不优选,但原则上也可以使用完全连续的方法。优选地,采用半-批处理方法。

[0270] 所采用的聚合技术可以使得形成低分子量聚合物,例如通过采用链转移剂,诸如选自硫醇(巯醇)、某些卤代烃和 α -甲基苯乙烯的链转移剂;或者通过催化链转移聚合,使用例如非常常规的钴螯合物络合物。或者,可以使用受控的自由基聚合方法,例如通过利用合适的硝基氧化合物(nitroxide)或硫代羰基硫(thiocarbonylthio)化合物,诸如二硫代酯、二硫代氨基甲酸酯、三硫代碳酸酯和黄原酸酯,从而经由例如氮氧介导的聚合(NMP)、可逆加成断裂链转移方法(RAFT)或原子转移自由基聚合(ATRP)来介导聚合。

[0271] 当本发明的共聚物是乳液聚合物时,其可以与各种其他聚合物乳液混合,例如与不包含 DBI(或高级衣康酸酯)的那些聚合物乳液。这种第二聚合物乳液的例子可以是聚氨酯乳液、聚氨酯-聚(甲基)丙烯酸酯乳液、醇酸乳液、聚酯乳液和/或聚乙烯类乳液。后面的这些共聚物乳液集合可包括低聚物-聚合物乳液、梯度形态乳液、序列聚合的(sequentially polymerized)乳液或单相共聚物乳液。

[0272] 可以经由乳液聚合或者经由被称为溶剂辅助分散(SAD)聚合的方法来生产根据上面描述的乳液。

[0273] 当经由乳液聚合来生产共聚物乳液时,这可以根据单次进料方法、顺序进料多相共聚方法或粉末进料方法来进行,得到梯度颗粒形态。

[0274] 在溶液聚合方法的情况下,聚合在有机溶剂中进行。接下来,加入碱和/或表面活性剂,并且将聚合物溶液乳化。优选地,在整个方法结束时经由蒸发将溶剂去除。

[0275] 可以经由单次进料溶液聚合或者通过顺序进料多相聚合,来生产溶液聚合物。也可以设想,在可选地去除溶剂之前或者之后,将溶液聚合物用作乳液聚合阶段的种子。在这种情况下,将根据溶液聚合方法制得的聚合物乳液用作批处理或半-批处理聚合方法中的种子。

[0276] 优选的聚合方法是本体聚合。

[0277] 如本领域技术人员已知的,在乳液聚合物中使用表面活性剂。典型的表面活性剂已经在各种专利申请中广泛地描述了。表面活性剂的选择和浓度对于本发明来说并不关键。可以使用常规乳化剂(表面活性剂)例如阴离子型和/或非离子型乳化剂,来实现水性乳液聚合。基于用来制备聚合物所添加的全部单体的重量,所使用的量优选地很低、优选地 0.3 至 2 重量%、更常见地 0.3 至 1 重量%。

[0278] 优选地(并且受限于本文中的限制),在本发明的一个实施方式中,制备本发明的共聚物乳液的方法包括使用 W02011073417 中所描述的追加单体组合物。在另一个实施方式中,可以可选地不使用追加单体。

[0279] 在一个优选的情况下,低 MW 共聚物乳液的剩余单体含量小于 2000mg/L、更优选地小于 1500mg/L、最优选地小于 1000mg/L、以及尤其优选地小于 550mg/L。

[0280] 如果期望交联聚合物(例如在聚合物分散体中),相关低 MW 共聚物可以带有官能基团诸如羟基,并且分散体随后与诸如多异氰酸酯、三聚氰胺或甘脲的交联剂一起配制;或者在一种聚合物或两种聚合物上的官能基团可以包括酮羰基或醛羰基,并且在步骤 c) 中随后配制的交联剂可以是多胺(polyamine)或多酰肼(polyhydrazide),例如己二酸二酰肼、草酸二酰肼、邻苯二甲酸二酰肼、对苯二甲酸二酰肼、异佛尔酮二胺和 4,7-二氧杂癸烷-1,10 二胺。需要注意的是,由于形成共价键,这种交联剂会影响交联。

[0281] 尽管术语“乙烯基聚合物”通常用于指,从含乙烯基团($\text{CH}_2 = \text{CH}-$)的化合物聚合而获得的热塑性聚合物,但本文中使用时,术语“乙烯基聚合物”更广义地指包含一个或多个如下片段(例如作为其中的重复单元)的任何聚合物(无论是否热塑性)和/或由包含一个或多个如下片段的单体和/或聚合物前体获得的任何聚合物(无论是否热塑性),所述片段为:经活化的不饱和片段(例如丙烯酸酯和/或甲基丙烯酸酯);任何烯属不饱和片段(例如乙烯基片段);它们的混合物;和/或其在相同片段内的组合。

[0282] 为了改善诸如用在涂料应用中的聚合物的可持续性,对使用生物可再生单体的需求不断增长。考虑到化石燃料资源枯竭以及最近几年造成全球性环境问题的大气中二氧化碳的增加,由生物质来源生产这些聚合物的原料的方法吸引了大量关注。因为这些来源是可再生的因此具有碳平衡生物质(carbon-neutral biomass),所以预期这种方法未来尤其重要。因此,本发明以及本文中所描述的各个方面的一个优选特征是其中的单体(尤其是高级衣康酸二酯,例如 DBI)尽可能是生物可再生的。

[0283] 优选地,至少 20 重量%、更优选地至少 30 重量%以及特别地 40 重量%的用来形成本发明的聚合物的烯属不饱和单体是由至少一种生物可再生烯属不饱和单体获得的。生物可再生单体可以全部或部分地从生物可再生来源获得。在本发明的一个优选实施方式中,甲基丙烯酸酯单体被用作单体(c),其中醇是由生物可再生来源获得的。在另外一个优选实施方式中,(甲基)丙烯酸酯单元和可能的醇是由生物可再生来源获得的。因此,优选还测量碳 14 含量来确定生物可再生性。

[0284] 碳 14(C-14)的含量可以指示生物基材料的年代。本领域已知,C-14 具有约 5700 年的半衰期,其被发现于生物可再生材料中,而尚未在化石燃料中发现。因此,“生物可再生材料”是指其中的碳来自非化石生物来源的有机材料。生物可再生材料的例子包括但不限于糖,淀粉,玉米,天然纤维,甘蔗,甜菜,柑橘类水果,木本植物,纤维素,木质纤维素

(lignocellulosics), 半纤维素, 马铃薯, 植物油, 其他多糖诸如胶质、壳质、果聚糖以及支链淀粉 (pullulan), 以及它们的组合。

[0285] C-14 水平可以通过如下来确定: 通过液体闪烁计数法测定其衰变过程 (每克碳每分钟的衰变或 dpm/gC)。在本发明的一个实施方式中, 聚合物 A 和 / 或聚合物 B 包含至少约 1.5dpm/gC (每克碳每分钟的衰变)、更优选地至少 2dpm/gC、最优选地至少 2.5dpm/gC 以及尤其至少 4dpm/gC 的衰变的碳-14。

[0286] 丙烯酸可以由甘油制得 (如 Arkema 所公开), 或者由乳酸制得 (如 US7687661 所公开)。甲基丙烯酸可以由乙烯、甲醇和一氧化碳 (均是生物可再生的) 制备, 如 Lucite International Ltd 所公开。

[0287] 可以额外地有助于改善涂层性质的烯属不饱和生物可再生单体包括 α -亚甲基丁内酯、 α -亚甲基戊内酯、 α -亚甲基 γ -R³ 丁内酯 (R³ 可以是可选地被取代的烷基或可选地被取代的芳基); 衣康酸酯例如衣康酸二烷基酯 (包括 DBI) 和衣康酸单烷基酯, 衣康酸, 衣康酸酐, 巴豆酸及其烷基酯, 柠康酸及其烷基酯, 亚甲基丙二酸及其单烷基酯和二烷基酯, 柠康酸酐, 中康酸及其烷基酯。

[0288] 另一组可用的生物可再生单体包括 N-R², α -亚甲基丁内酰胺 (R² 可以是可选地被取代的烷基或可选地被取代的芳基); N-R², α -亚甲基 γ -R¹ 丁内酰胺; N-烷基衣康酰亚胺; (甲基) 丙烯酸糠酯; 和脂肪酸官能 (甲基) 丙烯酸酯, 例如从 Elementis 获得的 DAPRO FX-522 和从 Evonik 获得的 **Visiomer**® MUMA。

[0289] 可以理解的是, 为了清楚起见而描述于各自实施方式上下文中的本发明的某些特征也可以在单个实施方式中以组合形式提供。相反地, 为了简化起见而在单个实施方式上文中所描述的本发明的各种特征也可以分开提供或者以任意合适的子组合的形式提供。

[0290] 本发明的目的是解决现有技术中的问题或缺点 (例如本文中整个申请中所指出的) 中的一些或所有问题或缺点。

[0291] 除上下文中另有明确指明外, 本文中使用时, 本文中的术语的复数表达形式应解释为包括其单数表达形式, 反之亦然。

[0292] 本文中使用时, 术语“包括”或“包含”应理解为指的是随后的列表并非穷举性的, 并且可以包括或者可以不包括其他合适的项目, 例如合适地一个或多个其他特征、一种或多种组分、一种或多种成分和 / 或一个或多个取代基。

[0293] 术语“有效”、“可接受”、“活性”和 / 或“合适” (本文中适当描述的例如关于任何过程、用途、方法、施用、准备、产品、材料、配制品、化合物、单体、低聚物、聚合物预聚物和 / 或聚合物) 将理解为指的是: 发明的那些特性如果以正确的方式使用可以为本文中所描述的它们所添加和 / 或包含的效用提供所要求的性质。这种效用可以直接是例如材料具有用于前面提到的用途所要求的性质的情形, 和 / 或可以间接是例如材料在制备具有直接效用的其他材料中作为用作合成的中间体和 / 或诊断工具使用的情形。本文中使用时, 这些术语也表示官能基团是与产生有效的、可接受的、活性和 / 或合适的最终产品相协调的。

[0294] 本发明的优选的效用包括用作涂料组合物的组分。

[0295] 在本发明的讨论中, 除相反说明外, 公开一个参数的所允许范围的上限和下限的可供选择值再加上指明的所述值中的一个结合比其它值更优选, 这应当理解为暗示地记载了, 位于所述可供选择值的更优选值和不那么优选值之间的所述参数的每个中间值本身都

优于所述不那么优选的值,并且优于每个不那么优选的值和所述中间值。

[0296] 对于本文中给出的任意参数的所有上限和 / 或下限边界来说,边界值都包含于每个参数的值中。还应当理解的是,在本发明的各种实施方式中本文中所描述的各参数的优选的和 / 或中间的最小边界值与最大边界值的所有组合也都可以用于定义本发明的各种其他实施方式和 / 或优选方式中的每个参数的可供选择范围,无论这种值的组合是否已具体地在本文中公开了。

[0297] 因此,例如在本文中描述的以 0 至“x”的量(例如以质量和 / 或重量%为单位)的一种物质是指(除非上下文中另有明确说明)包含两种备选方案。首先,较广义的备选方案是该物质可以任选地不存在(当其量为零时)或者仅以低于能够检测量的微量允许量存在。第二个优选的备选方案(在物质量的范围内以 0 下限量表示))是指该物质存在,零表示下限量是非常小的痕量,例如足以通过合适的常规分析技术检测的任意量,更优选地,零表示物质的用量的下限大于或等于 0.001 重量%(如本文中计算的)。

[0298] 应当理解的是,本文中以百分数所表示的任何量的总和不能(允许舍入的误差)超过 100%。例如,在允许舍入误差的情况下,当以组合物(或其相同的一个或多个部分)的重量(或其他)百分数表示时,本发明的组合物(或其一个或多个部分)包含的所有组分的总和可以总计 100%。然而,当一系列组分未穷举时,每个这些组分的百分数的总和可以小于 100%,以允许一定百分数用于本文中未明确描述的一种或多种任意额外组分的额外量。

[0299] 在本发明中,除另有明确说明外,当以重量百分数表示时,用于描述存在于本发明的组合物中的组分的量是基于组合物中单体的总量(等于 100%,因此例如组分(a)+(b)+(c)+(d) 总共 100%)来计算的。为了方便起见,未落入组分(a)至(d)中任意一项的定义的某些非单体成分(例如链转移剂(CTA))也可以被计算为基于总单体的重量百分数(即其中总单体的重量单独设定为 100%)。由于单体的重量%(例如对于组分(a)至(d)来说)被定义为总共 100%,所以可以看出对非单体成分(即在(a)至(d)之外的那些组分)使用基于单体的重量%值会导致总百分数超过 100%。因此,以基于单体的重量百分数表示的非单体成分的量可以被看作是提供了,这些成分的重量相对于单体总重量的部分,其仅用作计算用的参考值而不是严格的百分数。当(a)+(b)+(c)+(d) 总共 100%时,其他成分并非从组合物中排除,并且基于总单体的重量百分数不应与相对于总组合物的重量百分数相混淆。

[0300] 本文中使用时,术语“基本上”和 / 或“基本包含”可以指,意味着具有较大量或比例的数量或实体(entity)。当在其中使用“基本上”的上下文中相关时,“基本上”可以理解为指的是,该数量或实体定量地(与说明书上下文中涉及的数量或实体相关)包含相关整体的至少 80%、优选地至少 85%、更优选地至少 90%、最优选地至少 95%、尤其至少 98%、例如约 100%的。类似地,术语“基本上不含”可以类似地表示,其所涉及的数量或实体包含不超过相关整体的 20%、优选地不超过 15%、更优选地不超过 10%、最优选地不超过 5%、尤其不超过 2%、例如约 0%。

[0301] 本文中使用的术语“可选的取代基”和 / 或“可选地被取代”(除非紧跟着一列其他取代基)表示一个或多个如下基团(或被这些基团取代):羧基、磺基(sulpho)、甲酰基、羟基、氨基、亚氨基、氮基(nitrilo)、巯基、氰基、甲基、甲氧基和 / 或其组合。这些可选的基

团包括多个（优选地两个）前述基团在相同片段中的所有化学上可行的组合（例如氨基和磺酰基，如果彼此直接相连，则表示氨磺酰基）。优选的可选取代基包括：羧基、磺基、羟基、氨基、巯基、氰基、甲基、卤、三卤甲基和 / 或甲氧基。

[0302] 本文中使用的同义术语“有机取代基”、“片段”和“有机基团”（本文中也缩写为“有机”(organo)）表示包含一个或多个碳原子并可选地包含一个或多个其他杂原子的任意单价或多价片段（可选地与一个或多个其他片段相连）。有机基团可以包含有机杂化原子（organoheteryl）基团（也被称为有机元素基团），其包含含碳的单价基团，因而是有机的，但是它们在除碳以外的原子上拥有其自由价（例如有机硫代基团）。或者或另外，有机基团可以包含有机基基团（organyl），其包括在碳原子上具有一个自由价的任意有机取代基团，不论官能团的类型如何。有机基团还可包括杂环基团，其包括通过从杂环化合物（一种环状化合物，它具有至少两种不同的元素作为环节原子，此时一种原子是碳）的任意环原子上除去一个氢原子而形成的一价基团。优选地，有机基团中的非碳原子可选自：氢、卤、磷、氮、氧、硅和 / 或硫，更优选地选自：氢、氮、氧、磷和 / 或硫。

[0303] 最优选的有机基团包括一个或多个如下含碳片段：烷基、烷氧基、烷酰基、羧基、羰基、甲酰基和 / 或其组合；它们可选地与一个或多个如下含杂原子的片段组合，该含杂原子的片段为：氧基、硫基、亚磺酰基、磺酰基、氨基、亚氨基、次氨基（nitrilo）和 / 或其组合。有机基团包括多个（优选地两个）前述含碳和 / 或杂原子片段在相同片段中的所有化学上可行的组合（例如烷氧基和羰基，如果彼此直接相连的话表示烷氧羰基基团）。

[0304] 本文中使用的术语“烃基”是有机基团的子集，其表示由一个或多个氢原子和一个或多个碳原子组成的任何单价或多价片段（可选地与一个或多个其他片段相连），并且可以包含一个或多个饱和的、不饱和的和 / 或芳族片段。烃基可以包含一个或多个如下基团。烃基包含通过从烃去除一个氢原子而形成的单价基团（例如烷基）。亚烃基（Hydrocarbylene）包含通过从烃去除两个氢原子而形成的二价基团，该基团自由价不形成双键（例如亚烷基）。偏亚烃基（Hydrocarbylidene）包括通过从烃的同一个碳原子上除去两个氢原子而形成的二价基团（其可以表示为“ $R_2C =$ ”），该基团的自由价形成双键（例如偏亚烷基）。次烃基（hydrocarbylidyne）包括通过从烃的同一碳原子上除去三个氢原子而形成的三价基团（其可以表示为“ $RC \equiv$ ”），该基团的自由化合价形成三键（例如次烷基）。烃基基团还可以包括饱和的碳碳单键（例如在烷基中）；不饱和的碳碳双键和 / 或三键（例如分别在烯基和炔基中）；芳族基团（例如在芳基中）和 / 或其在相同片段中的组合，在被指出的情况下，该烃基基团可以被其它官能团取代。

[0305] 本文中使用的术语“烷基”或其等同物（例如烷）在适当的情况下且除非另有声明，可以容易地被包含任何其它烃基团的术语替代，所述其它烃基团诸如为本文所述的那些基团（例如包含双键、三键、芳族片段（诸如分别为烯基、炔基和 / 或芳基）及 / 或其组合（例如芳烷基）以及连接两个或更多个片段的任何多价烃基（诸如二价亚烃基，例如亚烷基））。

[0306] 除非另有说明或者上下文中另有指明，本文中提到的任何基团或片段（作为取代基）可以是多价或单价的基团（例如连接两个其他片段的二价亚烃基片段）。然而，在本文指出的情况中，这种单价或多价基团仍可以包含可选的取代基。含有三个或更多个原子形成的链的基团表示这样的基团，该基团中，全部或者部分链可以是直链的、支链的和 / 或形

成环（包括螺环和 / 或稠环）。对某些取代基来说，指定了某些原子的总数，例如 C_{1-N} 有机基，表示包含 1 至 N 个碳原子的有机片段。在本文中的任意式中，如果未指明一个或多个取代基与片段中的任何具体原子相连（例如在沿链和 / 或环的具体位置上），则该取代基可以替代任何 H 和 / 或可以位于该片段上在化学上适宜和 / 或有效的任何可用位置上。

[0307] 优选地，本文中所列的任何有机基团包含 1 至 36 个、更优选地 1 至 18 个碳原子。尤其优选的是，有机基团中碳原子的数目为 1 至 12、尤其 1 至 10（包括端点）、例如 1 至 4 个碳原子。

[0308] 本文使用时，含有以括号给出的特征的化学术语（除了明确定义的化合物的 IUPAC 命名之外），例如（烷基）丙烯酸酯、（甲基）丙烯酸酯和 / 或（共）聚合物，表示括号中的那部分根据上下文的要求是任选的，因此例如术语（甲基）丙烯酸酯代表甲基丙烯酸酯和丙烯酸酯。

[0309] 构成和 / 或被用在本文所述的本发明的一些或全部的某些片段、物质、基团、重复单元、化合物、低聚物、聚合物、材料、混合物、组合物和 / 或配制品可以以一种或多种不同的形式存在，例如为如下非穷举性列表中的那些的任意一个：立体异构体（诸如对映异构体（例如 E 和 / 或 Z 形式）、非对映异构体和 / 或几何异构体）；互变异构体（例如酮式和 / 或烯醇式），构象异构体（conformer），盐，两性离子，络合物（诸如螯合物、笼合物、冠状化合物、穴状配体 / 穴状络合物（cryptands/cryptates）、包合物、嵌入化合物、填隙化合物（interstitial compound）、配体络合物、有机金属络合物、非化学计量络合物、 π -加合物、溶剂化物和 / 或水合物）；同位素取代的形式、聚合构型 [诸如均聚物或共聚物、无规聚合物、接枝聚合物和 / 或嵌段聚合物、直链和 / 或支链的聚合物（例如星形和 / 或侧链的）、交联和 / 或网状聚合物、可由两价和 / 或三价重复单元得到的聚合物、树枝状化合物、具有不同立构规整度的聚合物（例如全同立构聚合物、间同立构聚合物或无规立构聚合物）]；多晶形物（诸如间隙形式、结晶形式和 / 或无定形式），不同相态，固态溶液；若可行的话，和 / 或其组合和 / 或其混合物。本发明包括和 / 或使用所有这些如本文中定义的有效形式。

[0310] 本发明的聚合物可以由一个或多个合适的聚合物前体制得，该聚合物前体可以有机的和 / 或无机的并且包含任何合适的一个或多个（共聚）单体、一个或多个（共）聚合物 [包括一个或多个均聚物] 以及其混合物，而且该聚合物前体包含这样的片段，该片段能够与该聚合物前体或每个聚合物前体形成键以扩链，和 / 或能够经由本文中所指明的直接成键而与该聚合物前体或每个聚合物前体的另一个交联。

[0311] 本发明的聚合物前体可以包含一个或多个单体、低聚物、聚合物；及其组合，它们具有合适的可聚合官能团。应当理解的是，除上下文中另有规定外，本文中使用的术语“单体”涵盖了术语“聚合物前体”，并且不排除本身在性质上（in character）可以为聚合的和 / 或低聚的那些单体。

[0312] 单体是具有低分子量（例如小于一千 g/ 摩尔）的基本上单分散的化合物，其能够聚合。

[0313] 聚合物是通过聚合方法制得的具有大分子量（例如数千 g/ 摩尔）的大分子的多分散混合物，其中大分子包含多个重复的较小单元（其本身可以是单体、低聚物和 / 或聚合物），并且其中（除非性质严重依赖于分子结构的精细细节）添加或去除一个或几个单元对

大分子的性质的影响可以忽略。

[0314] 低聚物是具有单体与聚合物之间的中间分子量的分子的多分散混合物,这些分子包含少量单体单元,并且一个或几个单元的去除会显著地改变分子的性质。

[0315] 根据上下文,术语聚合物可以包含低聚物,或者可以不包含低聚物。

[0316] 本发明中的和/或本发明中使用的聚合物前体可以通过直接合成来制备或者(如果聚合前体本身是聚合型的话)通过聚合来制备。如果可聚合的聚合物本身用作本发明中的和/或本发明中使用的聚合物前体,优选的是这种聚合物前体具有低的多分散性、更优选地基本上是单分散的,从而使副反应、副产物的数目和/或由该聚合物前体形成的任意聚合材料中的多分散性降至最小。一种或多种聚合物前体在常温常压下可以是基本上非反应性的。

[0317] 除非本文中指明,本发明中的和/或本发明中使用的聚合物和/或聚合的聚合型聚合物前体可以通过本领域技术人员公知的任何合适的聚合手段来(共)聚合。合适方法的例子包括:热引发;通过添加合适试剂的化学引发;催化;和/或使用任选的引发剂然后辐照的引发,例如在适当波长诸如UV下采用电磁辐射(光化学引发);和/或采用其他类型的辐射诸如电子束、 α 粒子、中子和/或其他粒子。

[0318] 可以选择聚合物和/或低聚物的重复单元上的取代基,来改善具有该聚合物和/或树脂的材料相容性,其中出于本文中所描述的用途,聚合物和/或树脂可以配制和/或掺入到材料中。因此,可以选择取代基的尺寸和长度以便优化与树脂的物理缠绕或互穿(interlocation),或者它们可以包含或者可以不含其他反应性实体,这些其他反应性实体在适当情况下能够与这些其他树脂进行化学反应和/或交联。

[0319] 本发明的另一个方面广义地提供了涂料组合物,其包含本发明的和/或本文中所描述的聚合物和/或珠粒。

[0320] 本发明的另外一方面提供了由本发明的涂料组合物获得或者可以获得的涂层。

[0321] 本发明的另外一个方面广义地提供了其上涂布有本发明的(可选地固化的)涂料组合物的基材和/或制品。

[0322] 本发明的另外一个方面广义地提供了使用本发明的和/或本文中所描述的聚合物来制备涂料组合物的方法。

[0323] 本发明的另一个方面提供了用于制备经涂布的基材和/或制品的方法,其包括以下步骤:将本发明的涂料组合物涂覆到基材和/或制品上,并任选地将所述组合物原位固化,来在其上形成经固化的涂层。固化可以通过任何合适的手段,例如热固化,通过辐射和/或通过使用交联剂。

[0324] 优选的涂料组合物是溶剂涂料组合物或水性涂料组合物,更优选地是水性涂料组合物。

[0325] 可选地,水性涂料组合物还可以包含助溶剂(co-solvent)。本领域已知的助溶剂是在水性组合物中所采用的有机溶剂,其改善该组合物的干燥特性、尤其降低该组合物的最低成膜温度。助溶剂可以是在制备本发明的聚合物时结合或使用的溶剂,或者可以在配制水性组合物时已经添加过。

[0326] 本发明的组合物尤其用作或用于提供涂料配制物(即意图用于涂覆到基材而不需要对其进一步处理或添加的组合物)的主要组分,该涂料配制物诸如为保护性或装饰性

涂料组合物（例如漆料、亮漆或清漆），其中最初制备的组合物可选地可以用水和 / 或有机溶剂进一步稀释，和 / 或与其他成分组合，或者可以是更浓缩的形式，该更浓缩的形式通过可选地蒸发最初制备的组合物液体介质中的水和 / 或有机组分获得。

[0327] 本发明的组合物可以用于各种应用，并且出于这种目的，其可以任选地与其他添加剂和 / 或组分组合或配制，所述其他添加剂和 / 或组分诸如为消泡剂、流变控制剂、增稠剂、分散剂和 / 或稳定剂（通常为表面活性剂和 / 或乳化剂）、润湿剂、填料、增量剂（extender）、杀真菌剂、杀菌剂、聚结和润湿溶剂或助溶剂（尽管通常不需要溶剂）、增塑剂、防冻结剂、蜡、着色剂、颜料、染料、热稳定剂、流平剂、抗缩孔剂（anti-cratering agent）、填充剂、沉降抑制剂、UV 吸收剂、抗氧化剂、反应性稀释剂、中和剂、粘附促进剂和 / 或它们的任意合适混合物。

[0328] 前述添加剂和 / 或组分以及类似物可以在生产过程的任意阶段引入或者随后引入。可以引入阻燃剂（例如氧化锑），来增强阻燃性质。

[0329] 本发明的组合物还可以与其他聚合物共混，诸如乙烯基聚合物、醇酸树脂（饱和的或不饱和的）、聚酯和 / 或聚氨酯。

[0330] 本发明的涂料组合物可以通过任何常规方法涂覆到各种基材上，该基材包括木材、板、金属、石材、混凝土、玻璃、织物、皮革、纸、塑料、泡沫等等，所述常规方法包括刷涂、浸涂、流涂、喷涂等等。本发明的涂料组合物还可以用于涂布三维制品的内表面和 / 或外表面。还可以使用本发明的涂料组合物，如果需要的话适当配制，来提供膜、光泽剂、清漆、亮漆、漆料、墨和粘合剂。然而，它们尤其可用于且适用于为基材提供保护性涂层的主要成分，所述基材包括木材（例如木制地板）、塑料、聚合材料、纸和 / 或金属。

[0331] 一旦本发明的组合物已经被涂覆到基材上了，就可以通过使其在环境温度下自然干燥来将载体介质从本发明的组合物中去除，或者可以通过加热来加速干燥过程。通过环境温度下长时间静置（几天）或者通过在高温（例如 50℃）下加热短得多的时间，可以进行交联。

[0332] 本发明的另外一方面包括由本发明的聚合物组合物获得、能够获得的漆料和 / 或包含本发明的聚合物组合物的漆料，尤其在本发明的聚合物组合物是乳液聚合物时。因此，例如由本发明的乳液聚合物组合物制备的漆料可以以颜料体积浓度在 0 至 85% 范围内、优选地在 0 至 55% 范围内包含颜料。多种颜料颗粒的颜料体积浓度是基于由乳液聚合物组合物制备的干燥涂料的总体积，多种颜料颗粒所占的体积分数。合适的颜料包括无机颜料，例如二氧化钛、铁氧化物、锌氧化物、硅酸镁、碳酸钙、有机和无机着色颜料、铝硅酸盐、二氧化硅和各种粘土。二氧化钛是优选的，因为它能够提供不透明性。合适的有机颜料还包括塑料颜料，例如固体珠粒颜料和含空穴或囊泡的微球颜料。固体球粒颜料的实例包括聚苯乙烯和聚氯乙烯珠粒。微球颜料（其包括含一个或多个空穴的聚合物颗粒和囊泡化的聚合物颗粒）的实例公开于 US4427836、US4920160、US4594363、US4469825、US4468498、US4880842、US4985064、US5157084、US5041464、US5036109、US5409776 和 US5510422。其他合适的颜料包括例如 Expancel™ 551 DE20 丙烯腈 / 氯乙烯发泡颗粒（Expancel Inc. Duluth Ga.）；Sil-Cell™ 35/34 钠钾铝硅酸盐颗粒（Silbrico Corporation, Hodgkins Ill.）；Dualite™ 27 涂布有 CaCO₃ 的聚偏二氯乙烯共聚物（Pierce and Stevens Corporation, Buffalo N. Y.）；Fillitte™ 150 陶瓷球形颗粒（Trelleborg Fillite Inc. Norcross Ga.）；

Microbeads™4A 碱石灰颗粒 (Cataphote Inc.) ;Sphericell™ 中空玻璃颗粒 (Potter Industries Inc.Valley Forge Pa.) ;Eccosphere™ 中空玻璃球 (New Metals & Chemicals Ltd. ;Essex England) ;Z-light™ Zeeospheres W-410 和 W-610 陶瓷中空球 (3M St.Paul Minn.) ;Scotchlite™ K46 玻璃泡 (3M St.Paul Minn.) ;Vistamer™ UH 1500 聚乙烯颗粒 ;和 Vistamer™ HD1800 聚乙烯颗粒 (Fluoro-Seal Inc., Houston Tex)。Ropaque™ 聚合物是涂料中的优选组分。Z-light™ Zeeospheres W-410 和 W-610 陶瓷中空球也是优选组分。上述成分的组合往往是优选的。

[0333] 可以用各种水性增稠剂来增稠由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料。这些包括但不限于疏水改性的碱溶胀性乳液,例如 Acrysol™ TT-935、Acrysol™ TT-615、Acrysol™ RM-6、Polyphobe™ TR-116。也可以使用碱溶胀性乳液诸如 Acrysol™ ASE-60。也可以使用疏水改性的水溶性聚合物,诸如 Acrysol™ RM-2020、Acrysol™ RM-8、Aquaflow™ XLS-500、Aquaflow™ NHS-310、Rheolate™ CVS-11 和疏水改性的 HEC 诸如 Natrosol™ Plus 330。也可以使用羟乙基纤维素,诸如 Natrosol™ HBR 或 Cellosize™ QP-3000。也可以使用粘土用于下垂和沉降控制,诸如 Attagel™ 50 或 Bentone™ DE。

[0334] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料可以使用分散剂来帮助稳定该漆料中的颜料。可以使用多酸分散剂诸如 Hydropalat™ 44 或疏水性共聚物分散剂诸如 Tamol™ 681, Tamol™ 165, and Tamol™ 731。也可以使用苯乙烯马来酸酐共聚物。也可以使用小分子分散剂诸如多磷酸盐和柠檬酸。多磷酸盐的实例包括焦磷酸四钾、三多磷酸钾、六偏磷酸钠以及在商品名 Calgon™ 下售卖的高级磷酸盐。后面的多种磷酸盐与 ZnO 颜料结合使用,来帮助提供稳定性。

[0335] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料可以使用聚结助剂,来辅助胶乳乳液聚合物的成膜。这些聚结助剂可以是挥发性的,例如常见醇的乙氧基醚或丙氧基醚。实例包括乙二醇单丁醚、二甘醇单丁醚、丙二醇单丁醚和二丙二醇单丁基醚。常见且优选的聚结剂是 Texanol™。由本发明的乳液聚合物组合物制备的漆料还可以使用不产生 VOC 的非挥发性聚结剂。这些聚结剂可以包括多种材料,诸如 Optifilm™400、马来酸二辛酯、柠檬酸三乙酯或磷酸三丁酯。在一些情况下,可以使用氧化固化反应性增塑剂,诸如 Oxi-Cure™。此外,漆料还可以包含保湿材料,诸如乙二醇或丙二醇。还可以使用开放时间 (open time) 添加剂,诸如 Rhodaline™ OTE 或 Optifilm™ OT1200。优选的是,基于组合物的总重量,由乳液聚合物组合物制备的漆料包含小于 5 重量%的 VOC。更优选的是包含小于 2 重量% VOC 的漆料组合物,并且最优选的是包含小于 0.05 重量% VOC 的漆料组合物。

[0336] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料还将包含附件的表面活性剂。这些表面活性剂用于改善基材的润湿性、保证颜料和着色剂相容并且改善稳定性。经常添加非离子性表面活性剂诸如乙氧基化的醇,来改善冻融稳定性 (free/thaw stability) 和着色剂相容性。这些包含低 HLB 非离子型物质诸如 Igepal™ CO-430、Igepal™ CO-630,和较高 HLB 的非离子型物质诸如 Triton X-405。对于这些表面活性剂来说,也期望使用烷基醇 (诸如十三烷基醇) 或支链仲醇的类似物,诸如 Tergitol™ TMN-10。也往往使用 Tergitol™ TMN-10 来辅助颜料润湿。往往使用磺基琥珀酸二辛酯来增强基材润湿性,诸

如 Aerosol™ OT-100。还可以使用炔属二醇诸如 Surfynol™ 104, 并且由于它们低的动态表面张力, 有时期望使用炔属二醇。还可以使用磷酸基表面活性剂, 尤其用来改善 TiO₂ 相容性和稳定性。这些包括购自 Strodex™ line 的表面活性剂, 诸如 PK-90 或 PK-0VOC。

[0337] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料还可以包含能够改变表面粘连特性的添加剂。这种添加剂会包括氟碳表面活性剂, 诸如 Capstone™ FS-61。

[0338] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料还可以包含多价金属离子, 来提供成膜后的交联。这些多价金属离子会改善最终漆料的硬度和耐刮擦性以及改善耐化学性。尤其可以看出, 这会改善对有机溶剂的耐性。多价金属离子的实例包括 Zn、Mg、Zr 和 Ca。这些往往以水溶性盐的形式添加, 例如乙酸盐或碳酸盐。最有利地, 往往使用碳酸铵锌; 然而 Mg(OH)₂ 也是有效的, 并且有时是期望的。

[0339] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料可以包含磷酸盐基或硼硅酸盐基腐蚀抑制颜料, 诸如 Heucophos™ ZP0、Halox™ SPZ-391、Halox™ SZP-391JM、Halox™ 430 或 Halox™ CW-291。由本发明的乳液聚合物组合物制备的漆料可以包含有机腐蚀抑制剂, 诸如 Halox™ 510、Halox™ 520 或 Halox™ 570。由本发明的乳液聚合物组合物制备的漆料可以包含闪锈抑制剂, 诸如亚硝酸盐、磷酸盐、苯甲酸盐或 Halox™ Flash-X 330。这些成分通常直接添加到金属涂料中, 来减小闪锈和长期腐蚀。

[0340] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料可以包含阻断丹宁染色 (tannin stain blocking) 的添加剂, 来阻断丹宁迁移穿过涂层。这些添加通常基于多价阳离子, 诸如 Zr²⁺ 和 Zn²⁺ 或能够与带负电荷的丹宁类物质结合的固体无机材料。这种添加剂包括 Stainban™ 185、Stainban™ 186、Stainban™ 187、Halox™ BW-100、Halox™ L-44 和 Halox™ 1-66。此外, 往往向这些漆料中添加 ZnO, 来改善对丹宁染色阻断性。在许多情况下, 尤其期望制备包含具有高纵横比 (aspect ratio) 的无机颜料的漆料。一个实例是片状滑石, 诸如 Vertal™ 7。已知这些能够改善漆料的阻断丹宁特性。

[0341] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料可以包含 UV 吸收剂和自由基清除剂。这些用于改善涂料的长期户外耐久性、或者保护下面的基材以免 UV 降解。当配制澄清至半透明木材着色剂时, 这是尤其有用的。UV 阻断剂可以是有机材料诸如苯并三唑, 或者可以是无机 UV 阻断剂诸如低于 (sub) 100nm 金属氧化物。自由基清除剂基于受阻胺光稳定剂。UV 阻断剂的实例包括 Tinuvin 1130, 过渡铁氧化物 (trans iron oxide) 诸如 Tint-ayd CW5499 或 Tint-ayd CW5600、纳米锌氧化物和纳米钛氧化物。Tinuvin 1130 与 Tint-ayd CW5499 的组合尤其用于半透明木材染色。

[0342] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料可以蜡或表面改性添加剂, 诸如硅酮滑移助剂。蜡可以用于减小涂料的光泽度并保持高水平的耐咖啡、酒或茶污性。这些蜡还能够改善涂料的耐光泽性。这种蜡的实例包括 Ceraflour™ 916、Ceraflour™ 920 和 Ceraflour™ 962。蜡还可以用于改善漆料的耐擦伤和划伤性。实例为 Michem Emulsion™ 39235。硅酮滑移助剂也可用于改善耐擦伤和划伤性, 实例为 Tego Glide™ 410。

[0343] 由包含本发明的低分子量聚合物的乳液聚合物组合物制备的漆料可以包含含有环氧基或胺基的反应性硅烷。硅烷可以是三烷氧基的、二烷氧基的或单烷氧基的。烷氧基

团通常为甲氧基、乙氧基或丙氧基。在二烷氧基或单烷氧基材料的情况下,硅原子与甲基成键。例如,单甲基二甲氧基硅烷是常见的硅氧烷基团。基于甲氧基或乙氧基的三烷氧基和二烷氧基硅烷是优选的。乳液聚合物还可以包含能够与氨基硅烷的氨官能部分反应的反应性基团,例如环氧基或乙酰乙酰氧基。有用的氨基硅烷的实例为 Silquest A-1100,其为 α -氨基丙基三乙氧基硅烷。 α -氨基丙基甲基二甲氧基硅烷是有用的偶联剂,用于对金属氧化物诸如铝氧化物的粘附。有用的环氧硅烷的实例为 Silquest A-186 和 Silquest A-187。硅烷的用量通常为大约 1%,并且提供对金属和金属氧化物表面的粘附。它们还能够用于交联漆料。

[0344] 本发明的许多其他变种实施方式对于本领域技术人员来说是明显的,并且这些变种包含于本发明的宽范围内。

[0345] 本发明的其他方面以及其优选特征在本文中的权利要求书中给出了。

[0346] 测试

[0347] 最低成膜温度

[0348] 本文中所使用的分散体的最低成膜温度 (MFFT) 是采用 DIN 53787 且当使用 Sheen MFFT bar SS3000 涂覆时分散体形成光滑且无裂纹的涂层或膜时的温度。

[0349] KOENING 硬度

[0350] 本文中使用的 Koenig 硬度是硬度的一种标准量度,其测定了由分散体形成的膜的粘弹性质怎样将使膜表面变形的摆动运动慢下来,并且是根据 DIN 53157/NEN5319 测定的。

[0351] 玻璃化转变温度 (T_g)

[0352] 本领域公知的是,聚合物玻璃化转变温度是其从玻璃状、易碎状态变为塑性、高弹态时的温度。玻璃化转变温度可以使用差示扫描量热 (DSC) 来实验测得,取导数曲线的峰作为 T_g,或者可以由 Fox 方程计算得到。因此,具有“n”个共聚了的共聚单体的共聚物的 T_g(以开氏度数计)是通过每个共聚单体类型的重量分数 w 和由每个共聚单体获得的均聚物的 T_g(以开氏度数计)根据如下方程来给出的,该方程为:

$$[0353] \quad \frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \dots + \frac{W_n}{T_{gn}}$$

[0354] 计算得到的以开氏度数计的 T_g 可以容易地转化成 °C。

[0355] 固体含量

[0356] 本发明的水性分散体的固体含量通常在基于总重量的约 20 至 65 重量%、更常见 30 至 55 重量%的范围内。如果需要的话,可以通过添加水或去除水(例如通过蒸馏或超滤)来调节固体含量。

[0357] pH 值

[0358] 本发明的分散体的 pH 值可以为 2 至 10,并且通常 6 至 9.5。

[0359] 粘连 (BLOCKING)

[0360] 耐粘连测试 [包括粘连和早期粘连]:

[0361] 步骤 1:粘连:

[0362] 向本发明的水性乳液添加 10% 的丁基二甘醇,然后将该水性乳液的 100 微米湿膜

浇铸到纸基材上,并在 52℃ 下干燥 16 小时。

[0363] 步骤 1:早期粘连

[0364] 向本发明的水性乳液添加 10% 的丁基二甘醇,然后将该水性乳液的 250 微米湿膜浇铸到纸基材上,并在室温下干燥 24 小时。

[0365] 步骤 2:粘连与早期粘连:

[0366] 冷却至室温后,在 1Kg/cm² 的载荷下在 52℃ 下,将两片经涂布的膜的经涂布一侧彼此相对放置 4 小时。在此时间间隔后,去除在样品上的载荷,并使样品冷却至室温 (22±2℃)。当两个涂层可以彼此分离且对膜无任何损伤 (不粘) 时,耐粘连性就非常好而且评价为 5。然而当它们完全粘在一起时,耐粘连性非常差并且评价为 0。

[0367] 气相色谱质谱 (GCMS)

[0368] 为了确认聚合基本上完全,可以通过 GCMS 测定游离衣康酸酯单体的含量。在顶部空间 (head space) 装配有 CTC combi Pal 自动进样器的 Trace GC-DSQ MS (Interscience, Breda, the Netherlands) 上进行 GCMS 分析。载气为氦气,并且使用 CP Sil 5low bleed/MS, 25m x 0.25mm (内径), 1.0 μm (CP nr. 7862) 柱。

[0369] GC-烘箱被如下程序控制:从 50℃ (5min) 开始,随后通过不同的连续温度跃升,以 5℃/min 的速度升至 70℃ (0min)、以 15℃/min 的速度升至 220℃ (0min),最后以 25℃/min 升的速度 280℃ (10min)。使用 1.2ml/min 的连续氦气流。在 300℃ 下,在程序升温蒸发器 (PTV) 中进行热分流进样。进样体积为 1 μl。MS 输送线和离子源均保持为 250℃。采用单离子监测 (SIM) 来测量样品。对于具体的衣康酸二丁酯 (DBI) 案例,使用 127.0 和 59.0Da 的质量 (mass),对于内标 (丙烯酸异丁酯) 来说使用 55.0 和 73.0 的质量。样品溶液为约 500mg 在 3ml 内标溶液 (在丙酮中的丙烯酸异丁酯) 中。用 5 个从 0-500ppm 的不同浓度水平进行校准。使用 Microsoft Excel 用线性校准曲线来进行计算。

[0370] 分子量

[0371] 除上下文中另有明确说明外,本文中使用的聚合物或低聚物的术语分子量表示数均分子量 (也表示为 M_n)。可以通过任何合适的常规方法,例如通过气相色谱法 (GPC, 与上面描述的 GCMS 方法类似地进行) 和 / 或通过下述 SEC 方法,来测定 M_n 。GPC 方法是优选的。

[0372] 使用 SEC 测定聚合物的分子量

[0373] 还可以使用尺寸排阻色谱法 (SEC) 采用四氢呋喃作为洗脱剂或采用 1,1,1,3,3,3 六氟异丙醇作为洗脱剂,来测定聚合物的分子量。

[0374] 1) 四氢呋喃

[0375] SEC 分析是在 Alliance Separation Module (Waters 2690) 上进行的,其包含泵、自动进样器、脱气装置和柱温箱。洗脱剂是添加了 1.0 体积% 乙酸的四氢呋喃 (THF)。进样体积为 150 μl。流速定为 1.0ml/min。在 40℃ 的温度下使用带有保护柱 (guard column) 的 Three PL MixedB (Polymer Laboratories) (3 μm PL)。使用差示折光率检测器 (Waters 410) 来进行检测。制备具有 20mg 固体在 8ml THF (+1 体积% 乙酸) 中的浓度的样品溶液,并且将样品溶解 24 小时。使用范围在 500 至 4000000g/mol 内的 8 个聚苯乙烯标准品 (polymer standard services) 来进行校准。使用 Millennium 32 软件 (Waters) 采用三级校准曲线进行计算。所获得的分子量为聚苯乙烯当量摩尔质量 (g/mol)。

[0376] 2) 1,1,1,3,3,3,六氟异丙醇

[0377] SEC 分析在 Waters Alliance 2695(泵,脱气装置和自动进样器)上进行,采用 Shodex RI 101 差示折光率检测器和 Shimadzu CTO 20AC 柱温箱。洗脱剂为添加了 0.2M 三氟乙酸钾 (KTFA) 的 1,1,1,3,3,3 六氟异丙醇 (HFIP)。进样体积为 50 μ l。流速定为 0.8ml/min。在 40℃ 的温度下使用带有保护柱的两个 PSS PFG Linear XL 柱 (Polymer Standards Service) (PFG PSS)。采用差示折光率检测器来进行检测。制备具有 5mg 固体在 2ml HFIP(+0.2M KTFA) 中的浓度的样品溶液,并且将样品溶解 24 小时。使用范围在 500 至 2000000g/mol 内的 11 个聚甲基丙烯酸甲酯标准品 (polymer standard services) 来进行校准。使用 Empower Pro 软件 (Waters) 采用三级校准曲线进行计算。经由常规校准来获得摩尔质量分布,并且该摩尔质量是聚甲基丙烯酸甲酯当量摩尔质量 (g/mol)。

[0378] 标准条件

[0379] 本文中使用时,除上下文另有说明外,标准条件(例如用于干燥膜)指的是相对湿度 50% $\pm$ 5%、环境温度(本文中表示 23℃ $\pm$ 2℃ 的温度)以及空气流速 $\leq$ (小于或等于) 0.1m/s 和大气压强。

[0380] 提供如下实施例来进一步说明本发明的方法和组合物。这些实施例仅仅是示例性的,并且不意图以任何方式限制本发明的范围。除另有指明外,所有份数、百分数和比例均是基于重量的。实例前的前缀 C 表示其为对比例。

[0381] 各种注册的商标、其他名称和 / 或简称在本文中用来表示用来制备本发明的聚合物和组合物的一些成分。下面,通过化学名称和 / 或商品名称和可选地可以购买到这些成分的它们的制造商或供应商来对这些成分进行标识。然而,如果本文中未给出材料的化学名称和 / 或供应商,则可以在本领域技术人员所公知的例如参考文献中找到,例如 'McCutcheon' s Emulsifiers and Detergents', Rock Road, Glen Rock, N. J. 074521700, USA, 1997 和 / 或 Lewis, Richard J., Sr. 的 Hawley ' s Condensed Chemical Dictionary(第 14 版); John Wiley & Sons。

[0382] 在实施例中,可以使用如下简称 / 单体:

[0383] DBI 表示衣康酸二丁酯(可以是(部分地)生物可再生的)

[0384] DEI 表示衣康酸二乙酯(可以是(部分地)生物可再生的)

[0385] DMI 表示衣康酸二甲酯(可以是(部分地)生物可再生的)

[0386] MMA 表示甲基丙烯酸甲酯(可以是(部分地)生物可再生的)

[0387] BA 表示丙烯酸丁酯(可以是(部分地)生物可再生的)

[0388] STY 表示苯乙烯

[0389] IA 表示衣康酸(可以是生物可再生的)

[0390] IANH 表示衣康酸酐(可以是生物可再生的)

[0391] MMA 表示甲基丙烯酸(可以是生物可再生的)

[0392] AIBN 表示偶氮二异丁腈

[0393] DTPO 表示二叔丁基过氧化物

[0394] PEG350 表示甲氧基聚乙二醇甲基丙烯酸酯,可以从 Cognis(BASF 的一部分)在商品名 **Bisomer®** mPEG350MA 下购得。

[0395] 实施例 I

[0396] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中,添加 43 份 2- 丁酮。将反应器内

容器加热到 85℃。只要达到聚合温度,在 270 分钟的时间内,向反应器进料单体物料,该单体物料由 25 份衣康酸二甲酯 (DMI)、20 份苯乙烯 (STY)、25 份甲基丙烯酸甲酯 (MMA)、30 份丙烯酸 (AA) 和 0.3 份偶氮二异丁腈 (AIBN) 组成。在单体进料结束时,再将聚合温度保持在 85℃下 60 分钟,之后,将反应器内容物冷却到室温。

[0397] 实施例 II 至 X

[0398] 参照如上实施例 I 中所描述的方法按照下表 1 以类似方式来制备实施例 II 至 X,其中用表 1 中所列的那些成分及相对量替换实施例 I 中的单体物料。

[0399] 表 1

[0400]

	II	III	IV	V	VI	VII	VIII	IX	X
DMI	25	62	55	43	61	55	55	55	55
STY	-	5	-	-	-	5	-	-	-
MMA	25	3	15	32	9	15	15	20	15
DEI	25	-	-	-	-	-	-	-	-
AA	-	30	-	-	30	-	30	-	30
iANH	25	-	-	25	-	25	-	25	-
MAA	-	-	30	-	-	-	-	-	-
AIBN	0.8	0.2	0.6	1.0	0.2	1.2	0.2	0.5	0.2

[0401]

[0402] 实施例 XI

[0403] 向装配有搅拌器、温度计、压力释放阀和高压单体剂量泵的高压聚合容器,填充 43 份 2-丁酮。将反应器内容物加热到 140℃。只要达到聚合温度,在 270 分钟的时间内,向反应器进料单体物料,该单体物料由 25 份衣康酸二甲酯 (DMI)、20 份苯乙烯 (STY)、25 份甲基丙烯酸甲酯 (MMA)、30 份丙烯酸 (AA) 和 0.15 份二叔丁基过氧化物 (DTPO) 组成。在单体进料结束时,再将聚合温度保持在 85℃下 60 分钟,之后,将反应器内容物冷却到室温。

[0404] 实施例 XII 至 XX

[0405] 参照如上实施例 XI 中所描述的方法按照下表 2 以类似方式来制备实施例 XII 至 XX,其中用表 2 中所列的那些成分及相对量替换实施例 XI 中的单体物料。

[0406] 表 2

[0407]

	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	XX
DMI	25	62	55	43	61	55	55	55	55

STY	-	5	-	-	-	5	-	-	-
MMA	25	3	15	32	9	15	15	20	15
DEI	25	-	-	-	-	-	-	-	-
AA	-	30	-	-	30	-	30	-	30
iANH	25	-	-	25	-	25	-	25	-
MAA	-	-	30	-	-	-	-	-	-
DTPO	0.2	0.4	0.1	0.5	0.1	0.1	0.5	0.1	0.1

[0408] 实施例 XXI

[0409] 向装配有搅拌器、温度计、压力释放阀和高压单体剂量泵的高压聚合容器, 填充 34 份 2- 丁酮和 9 份 2- 乙基己醇。将反应器内容物加热到 140℃。只要达到聚合温度, 在 270 分钟的时间内, 向反应器进料单体物料, 该单体物料由 25 份衣康酸二甲酯 (DMI)、20 份苯乙烯 (STY)、25 份甲基丙烯酸甲酯 (MMA)、30 份丙烯酸 (AA) 和 0.15 份二叔丁基过氧化物 (DTPO) 组成。在单体进料结束时, 再将聚合温度保持在 85℃ 下 60 分钟, 之后, 将反应器内容物冷却到室温。

[0410] 实施例 XXII 至 XXX

[0411] 参照如上实施例 XXI 中所描述的方法按照下表 3 以类似方式来制备实施例 XXII 至 XXX, 其中用表 3 中所列的那些成分及相对量替换实施例 XXI 中的单体物料。

[0412] 表 3

[0413]

	XXII	XXIII	XXIV	XXV	XXVI	XXVII	XXVIII	XXIX	XXX
DMI	25	62	55	43	61	55	55	55	55
STY	-	5	-	-	-	5	-	-	-
MMA	25	3	15	32	9	15	15	20	15
DEI	25	-	-	-	-	-	-	-	-
AA	-	30	-	-	30	-	30	-	30
iANH	25	-	-	25	-	25	-	25	-
MAA	-	-	30	-	-	-	-	-	-
DTPO	0.2	0.4	0.1	0.5	0.1	0.1	0.5	0.1	0.1

[0414] 实施例 XXXI 至 XXXXVI

[0415] 参照如上所描述的方法按照下表 4 以类似方式来制备实施例 XXXI 至 XXXVI, 其中单体物料由表 4 中所列的那些成分及相对量组成。

[0416] 表 4

[0417]

	XXXI	XXXII	XXXIII	XXXIV	XXXV	XXXVI
DMI	55	55	55	30	30	30
DBI	—	—	20			
MMA	—	—	—	60	60	60
AA	15	15	15	10		
DAAM	10	10	10	—	—	—
BA	—	20	—	—	—	—
IA	—	—	—	—	10	—
IANH	—	—	—	—	—	10
PEG350	20	—	—	—	—	—
Tg(°C)	37.2	49.4	74.0	101.8	105.9	104.1

[0418]

[0419] 实施例 XXXVII 至 XLIV

[0420] 如下文描述制备如下实施例 XXXVII 至 XLIV, 并且表 5 中给出了它们的一些性质结果。

[0421] 实施例 XXXVII MMA/DMI/AA

[0422] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中, 填充 394.0 份 2- 丁酮。将反应器内容物加热到 80°C。只要达到聚合温度, 添加 13.3 份偶氮二 (2- 甲基丁腈), 并且开始添加单体物料和催化剂物料。单体物料由 244.4 份甲基丙烯酸甲酯、244.4 份衣康酸二甲酯和 244.4 份丙烯酸组成。催化剂物料由溶解于 125.9 份 2- 丁酮中的 31.1 份偶氮二 (2- 甲基丁腈) 组成。两种物料都在 180 分钟的时间段中添加。

[0423] 在进料结束时, 加入 2.5 份偶氮二 (2- 甲基丁腈), 并且在 80°C 下将混合物再搅拌 150 分钟。将混合物冷却至室温。

[0424] 向 615.8 份聚合物溶液中, 添加 99.6 份 25 重量%氨水溶液与 1080.5 份水的混合物。接下来, 在 50°C 下减压下去除 2- 丁酮。使用去矿物质水调整固体含量至 22.5%, 并且使用 25 重量%氨水溶液将 pH 调整到 8.6-8.8。

[0425] 最终聚合物溶液具有 22.5% 的固体含量和 8.7 的 pH。

[0426] 实施例 XXXVII S/DMI/AA

[0427] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中,装入 394.0 份 2-丁酮。将反应器内容物加热至 80℃。一旦达到聚合温度,加入 13.3 份偶氮二(2-甲基丁腈),并且开始添加单体物料和催化剂物料。单体物料由 244.4 份甲基丙烯酸甲酯、244.4 份衣康酸二甲酯和 244.4 份丙烯酸组成。催化剂物料由溶解于 125.9 份 2-丁酮的 31.1 份偶氮二(2-甲基丁腈)组成。两种物料都在 180 分钟的时间段中添加。

[0428] 在进料结束时,加入 2.5 份偶氮二(2-甲基丁腈),并且在 80℃下将混合物再搅拌 150 分钟。将混合物冷却至室温。

[0429] 向 546.1 份聚合物溶液中,添加 105.4 份 25 重量%氨水溶液与 1144.1 份水的混合物。接下来,在 50℃下减压下去除 2-丁酮。使用去矿物质水调整固体含量至 22.5%,并且使用 25 重量%氨水溶液将 pH 调整到 8.6-8.8。

[0430] 最终聚合物溶液具有 22.4%的固体含量和 8.6 的 pH。

[0431] 实施例 XXXIX MMA/DMI/AA

[0432] 向装配有温度计和搅拌器的高压反应器中,装入 500.0 份 2-丁酮。将反应器内容物加热至 140℃。一旦达到聚合温度,加入 2.9 份二叔丁基过氧化物和 40 份 2-丁酮。5 分钟后开始添加单体物料。单体物料由 331.8 份甲基丙烯酸甲酯、331.8 份衣康酸二甲酯、331.8 份丙烯酸、5.7 份二叔丁基过氧化物和 6.6 份过苯甲酸叔丁酯组成,并且单体物料是在 140℃下在 180 分钟的时间段中添加的。

[0433] 在进料结束时,用 90.9 份 2-丁酮冲洗物料罐。单体进料完成后 45 分钟,添加溶解于 40 份 2-丁酮中的 2.5 份过苯甲酸叔丁酯,并且将混合物在 140℃下再搅拌 45 分钟。接下来,加入溶解于 40 份 2-丁酮中的 2.5 份过苯甲酸叔丁酯,并且将混合物在 140℃下再搅拌 135 分钟。

[0434] 将混合物冷却至室温。

[0435] 向 619.3 份聚合物溶液中,添加 99.3 份 25 重量%氨水溶液与 1077.3 份水的混合物。接下来,在 50℃下减压下去除 2-丁酮。使用去矿物质水调整固体含量至 22.5%,并且使用 25 重量%氨水溶液将 pH 调整到 8.6-8.8。

[0436] 最终聚合物溶液具有 22.5%的固体含量和 8.6 的 pH。

[0437] 实施例 XL S/DMI/AA

[0438] 向装配有温度计和搅拌器的高压反应器中,装入 500.0 份 2-丁酮。将反应器内容物加热至 140℃。一旦达到聚合温度,加入 4.4 份二叔丁基过氧化物和 40 份 2-丁酮。5 分钟后开始添加单体物料。单体物料由 331.8 份苯乙烯、331.8 份衣康酸二甲酯、331.8 份丙烯酸、8.6 份二叔丁基过氧化物和 10.0 份过苯甲酸叔丁酯组成,并且单体物料是在 140℃下在 180 分钟的时间段中添加的。

[0439] 在进料结束时,用 90.9 份 2-丁酮冲洗物料罐。单体进料完成后 45 分钟,添加溶解于 40 份 2-丁酮中的 2.5 份过苯甲酸叔丁酯,并且将混合物在 140℃下再搅拌 45 分钟。接下来,加入溶解于 40 份 2-丁酮中的 2.5 份过苯甲酸叔丁酯,并且将混合物在 140℃下再搅拌 135 分钟。将混合物冷却至室温。

[0440] 向 617.8 份聚合物溶液中,添加 99.4 份 25 重量%氨水溶液与 1078.6 份水的混合物。接下来,在 50℃下减压下去除 2-丁酮。使用去矿物质水调整固体含量至 22.5%,并且使用 25 重量%氨水溶液将 pH 调整到 8.6-8.8。

[0441] 最终聚合物溶液具有 22.5% 的固体含量和 8.7 的 pH。

[0442] 实施例 XLI 使用来自实施例 XXXVII 的聚合物的序列聚合

[0443] 向装配有冷凝器、温度计和搅拌器的圆底烧瓶中,装入从实施例 XXXVII 获得的 128.9 份碱性溶液。将混合物加热到 $80^{\circ}\text{C} \pm 2^{\circ}\text{C}$ 。

[0444] 一旦达到反应温度,加入 0.2 份过硫酸钠与 0.4 份去矿物质水的混合物。5 分钟后,开始添加单体物料和引发剂物料,该单体物料由 43.8 份甲基丙烯酸甲酯和 43.8 份丙烯酸丁酯组成,该引发剂物料由 10.8 份去矿物质水和 0.4 份过硫酸钠(使用 25 重量%氨溶液调整到 pH 8)。两种进料应花费 120 分钟。在单体进料结束时,用 1.2 份水冲洗物料罐。两种进料完成后,将该批料在 80°C 下再搅拌 30 分钟,之后冷却到 50°C 。

[0445] 在 50°C 下,加入三分之一的由 0.1 份 70 重量%的叔丁基过氧化氢溶液组成的混合物,然后再加入三分之一的 0.1 份异抗坏血酸在 2.9 份水中的溶液。15 分钟后以及 30 分钟后,加入类似的物料部分,并且将该批料在 50°C 下再搅拌 15 分钟。

[0446] 检查 pH,并且如果需要的话使用 25 重量%的氨水溶液调节到 8.4 ± 0.1 。将该批料冷却至室温,之后使用去矿物质水将固体含量调节至 $48.5\% \pm 1\%$ 。

[0447] 实施例 XLII 使用来自实施例 XXXVIII 的聚合物的序列聚合

[0448] 采用与实施例 XLI 中所描述的方法相似的方法来制备聚合物,其中使用从实施例 XXXVIII 获得的碱性溶液。最终乳液是高粘性的,需要稀释剂使固体含量为 35%。

[0449] 实施例 XLIII 使用来自实施例 XXXIX 的聚合物的序列聚合

[0450] 采用与实施例 XLI 中所描述的方法相似的方法来制备聚合物,其中使用从实施例 XXXIX 获得的碱性溶液。

[0451] 实施例 XLIV 使用来自实施例 XL 的聚合物的序列聚合

[0452] 采用与实施例 XLI 中所描述的方法相似的方法来制备聚合物,其中使用从实施例 XL 获得的碱性溶液。

[0453] 结果(表 5)

[0454]

	SC(%)	粘度 (mPa. s)	pH
实施例 XLI	47.6	208	8.4
实施例 XLII	34.8	1006	8.4
实施例 XLIII	48.1	35	8.5
实施例 XLIV	48.1	201	8.4

Abstract

There is described a low number average molecular weight ($MN < 10$ kD) and high glass transition temperature (> 75 °C) copolymer (optionally a solid grade oligomer (SGO)) that comprises (a) at least 20 wt-% of itaconate functional monomer(s), (b) not more than 40 % of a hydrophilic monomer, preferably an acid functional monomer(s) in an amount sufficient to achieve an acid value from 65 to 325 mg KOH per g of solid polymer; (c) optionally not more than 70 % of other monomers not being either (a) or (b), having a max content of vinyl aromatic monomer(s) of 40 wt-% and/or max content of methacrylate(s) of 40 wt-%; where the weight percentages of monomers (a), (b) and (c) are calculated as a proportion of the total amount of monomers in the copolymer being 100 %.