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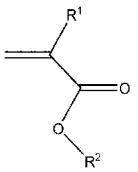
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(54) Title: BIO-BASED BINDER COMPOSITION FOR COATING APPLICATIONS



(I)

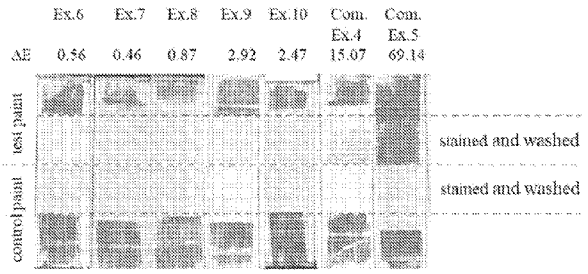


Figure 1

(57) Abstract: An aqueous polymeric dispersion of a copolymer including monomers a), b), c), and d). Monomer a) has Structure (I): where R^1 is hydrogen or a methyl group; and R^2 is a C1-C8 non-cyclic alkyl group. Monomer b) is an ethylenically unsaturated monomer other than a) selected from C1-C8 alkyl (meth)acrylates, ethylene, vinyl acetate, vinyl versatate, styrene, styrene derivatives, or combinations thereof. Monomer c) is an ethylenically unsaturated monomer including a functional group selected from carboxylate, phosphate, phosphonate; sulfonate, and/or acid, and/or salt, and/or anhydride forms thereof; hydroxyl; silane; or combinations thereof. Monomer d) is a nitrogen-bearing ethylenically unsaturated monomer. The copolymer includes at least 5%, biocarbon content as determined by ASTM D6866-22. The aqueous dispersion has a minimum film formation temperature less than 30°C.

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BIO-BASED BINDER COMPOSITION FOR COATING APPLICATIONS

FIELD OF THE INVENTION

Bio-based acrylate polymers suitable for use as binders for coatings.

BACKGROUND

Coatings are commonly used in architectural, industrial, and construction applications. Acrylic emulsion polymers are used as the binder in these applications due to their good balance of performance and cost. Desirable coating properties influenced by the binder are scrub resistance, tint strength, block resistance, and stain resistance. Acrylic emulsion polymers are derived from petroleum-sourced propylene. With dwindling supplies of petroleum and also the increased impacts of climate change, it is desirable to look for new ways to synthesize acrylic emulsion polymers that will have lower product carbon footprints.

One way to reduce petroleum-sourced content in acrylic emulsion polymers is to add bio-based materials via a blending approach. Many polymer pairs, however, are chemically incompatible. This incompatibility often causes performance deterioration, rather than synergistic performance benefits.

In order to increase the bio-carbon content (BCC) of the aqueous polymeric dispersion comprising acrylic polymer while maintaining or improving the performance of resulting coating compositions, an alternative approach is to polymerize acrylic monomers containing a certain degree of bio-renewable content via emulsion polymerization. The challenge, however, lies in producing an acrylic copolymer from available biobased acrylic monomers while simultaneously achieving the performance requirements for the intended application and the sustainability target of a minimum BCC threshold of 22% % measured according to ASTM-6866-22 Method B for the acrylic copolymer.

US 10662273 relates to an aqueous copolymer dispersion formed by emulsion polymerization of a monomer mixture including one or more (meth)acrylic acid esters whose homopolymer has a glass transition temperature (Tg) of greater than 25°C and at least one has a biorenewable carbon content of at least 50 wt. % of the total carbon content of the ester.

US 9593191 relates to the use of a polymer from the polymerization of 2-octyl acrylate of renewable origin and optionally at least one other monomer, as a binding agent in or for the production of a coating composition.

US 9505943 relates to an aqueous polymer coating composition including at least: a vinyl polymer A having a weight averaged molecular weight from 1000 to 150,000 and acid value of at least 5 mg KOH/g; and a vinyl polymer B having a molecular weight Mw of at least 80,000 g/mol and an acid value of less than 35 mg KOH/g; at least 20 wt % of at least one of polymer A and/or polymer B is derived from at least one bio-renewable olefinically unsaturated monomer.

US 9458346 relates to an aqueous polymer dispersion including a vinyl polymer with at least two phases comprising: A) 40 to 90 wt % of a vinyl polymer A having a glass transition temperature in the range of from −50 to 30° C.; and B) 10 to 60 wt % of a vinyl polymer B having a glass transition temperature in the range of from 50 to 130° C; and at least 20 wt % of the monomer composition used to form vinyl polymer A and vinyl polymer B is derived from at least one bio-renewable olefinically unsaturated monomer.

US 8642696 relates to copolymer compositions and methods for making these compositions. The copolymers include a vinyl aromatic monomer; a second monomer, and a biobased monomer comprising isobornyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate.

US 2021/0324114 relates to an aqueous dispersion as a biobased binder and an aqueous coating composition including the aqueous dispersion and showing stain resistance, freeze-thaw stability, and anti-clogging properties.

CN 112300343 A relates to a bio-based acrylate emulsion for building interior wall coating and a preparation method thereof. The bio-based acrylate emulsion disclosed by the invention has excellent physical and chemical properties, and the bio-based content exceeds 25% according to the test result of ASTM D6866.

EP 2626397 relates to polyacrylate-based pressure-sensitive adhesives.

WO2022/033945 relates to an aqueous vinyl polymer dispersion including a hydrophilic vinyl oligomer, a hydrophobic vinyl oligomer and a vinyl polymer obtained by the emulsion polymerization of ethylenically unsaturated monomers from petrochemical or renewable origin.

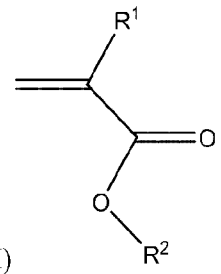
WO2023/148332 relates to aqueous polymer latex obtainable by polymerizing, optionally in the presence of a seed latex, a monomer composition M by radical emulsion polymerization

SUMMARY

An aqueous polymeric dispersion including bio-based monomer(s) provides a coating composition having a high bio carbon content while at the same time, when used as an aqueous polymeric dispersion binder in coating compositions, surprisingly provides a balance of scrub resistance, tint strength, block resistance, and stain resistance.

An aqueous polymeric dispersion is provided. The aqueous polymeric dispersion includes at least one copolymer formed by emulsion polymerization of a monomer mixture comprising the following monomers a), b), c), and d). The amounts are recited in wt%, based on a total dry weight of the copolymer.

a) 20-80wt% of at least one monomer of structure I:



(I)

where R^1 is a hydrogen or methyl group; and R^2 is a C1-C8, preferably C2- C6, more preferably C2- C4, non-cyclic alkyl group, and wherein a homopolymer of monomer a) has a glass transition temperature (Tg) less than 25 °C. Monomer a) preferably is biobased.

b) 20-80wt% of at least one ethylenically unsaturated monomer other than a) selected from the group consisting of C1-C8 alkyl (meth)acrylates, ethylene, vinyl acetate, vinyl versatate, styrene, styrene derivatives, or combinations thereof. Monomer b) is optionally biobased.

c) 0.1-10wt% of at least one ethylenically unsaturated monomer comprising at least one functional group comprising at least one of carboxylate, phosphate, phosphonate; sulfonate,

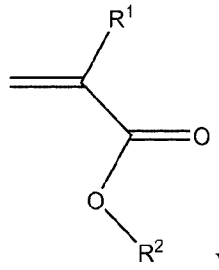
and/or acid, and/or salt, and/or anhydride forms of any of the forgoing thereof; hydroxyl; silane; or combinations thereof.

d) 0.1-10wt% of at least one nitrogen-bearing ethylenically unsaturated monomer.

The copolymer includes at least 5%, preferably at least 10%, more preferably at least 15%, most preferably at least 22% biocarbon content as determined by ASTM D6866-22 Method B. The aqueous polymeric dispersion has a minimum film formation temperature of 30°C or less.

A coating composition is also provided. The coating composition includes an aqueous polymeric dispersion including at least one copolymer formed by emulsion polymerization of a monomer mixture. The monomer mixture comprises, based on a total dry weight of the copolymer, monomers a), b), c), and d), as follows.

a) 20-80 wt% of at least one monomer of structure (I):



where R^1 is a hydrogen or methyl group; and R^2 is a C1-C8, preferably C2- C6, more preferably C2- C4, non-cyclic alkyl group, and wherein a homopolymer of monomer a) has a glass transition temperature (Tg) less than 25 °C. Monomer a) preferably is bio-based.

b) 20-80 wt% of at least one ethylenically unsaturated monomer other than a) selected from the group consisting of C1-C8 alkyl (meth)acrylates, ethylene, vinyl acetate, vinyl versatate, styrene, styrene derivatives, or combinations thereof. This monomer may optionally be bio-based.

c) 0.1–10wt% of at least one ethylenically unsaturated monomer comprising at least one functional group comprising at least one of carboxylate, phosphate, phosphonate; sulfonate, and/or acid, and/or salt, and/or anhydride forms of any of the forgoing thereof; hydroxyl; silane; or combinations thereof.

d) 0.1–10 wt% of at least one nitrogen-bearing ethylenically unsaturated monomer.

The copolymer includes at least 5%, preferably at least 10%, more preferably at least 15%, most preferably at least 22% biocarbon content as determined by ASTM D6866-22 Method B. The aqueous dispersion has a minimum film formation temperature of 30°C or less. A dried layer of the coating composition is improved with respect to one or more, preferably two or more, and most preferably all four of the following criteria, compared to a coating composition not including an aqueous dispersion of the present disclosure: scrub resistance, measured according to ASTM D2486-17 Method B and/or measured as described in the Examples; tint strength, measured according to ASTM D4838-88(2016) and/or measured as described in the Examples; block resistance, measured according to ASTM D4946-89(2017) and/or measured as described in the Examples; and/or stain resistance in terms of ΔE, measured according to ASTM D4828-94(2020) and/or measured as described in the Examples.

BRIEF DESCRIPTION OF THE DRAWINGS

The Figure shows a photograph of lipstick stain removal on a comparative coating composition and a coating composition according to an embodiment of the invention.

DETAILED DESCRIPTION

The terms "bio-based" or "biobased" as used herein mean products or materials that are derived in whole or in part from biomass resources, *i.e.* biomass-derived. Biomass resources are organic materials that are available on a renewable or recurring basis such as crop residues, wood residues, grasses, and aquatic plants. Products or materials, monomers, or polymers, containing any amount of bio-based content are referred to as "bio-based."

The terms, "non-bio-based" or "non-biobased" as used herein mean any product that does not contain any bio-based materials in it. For example, products made entirely from petrochemical resources are referred to as non-bio-based products.

Percent biocarbon content (BCC) or biobased (or bio-based) content is a measure of the amount of biomass-derived carbon in a product as compared to its total organic carbon content

(TOC). Percent biocarbon content is measured according to ASTM D6866-22, Method B. A product's biocarbon content is reported as a fraction of total organic carbon content (TOC) and not on its weight according to ASTM D6866-22 Method B.

Unless otherwise indicated, all percentages herein are weight percentages.

"Polymer" as used herein, is meant to include organic molecules with a weight average molecular weight higher than 20,000 g/mol, preferably higher than 50,000 g/mol, as measured by gel permeation chromatography.

BCC content of the copolymer

The copolymer includes at least 5%, preferably at least 10%, more preferably at least 15%, most preferably at least 22% biocarbon content as determined by ASTM D6866-22 Method B. According to some embodiments, the copolymer includes at least 22, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99 or up to 100 % BCC as determined by ASTM D6866-22.

Properties of the copolymer

An aqueous dispersion of the copolymer may have a minimum film formation temperature less than 30°C as measured according to ASTM D2354-10(2018). According to some embodiments, the aqueous dispersion of the copolymer may have a minimum film formation temperature less than 25, 20, 15, 10, 5, or less than 0°C.

According to some embodiments, the Tg of the copolymer may be less than 25, 20, 15, 10, 5, 0°C, as calculated by the Fox equation. As is known in the art, the Tg calculated by the Fox equation uses known values of homopolymers of the comonomers in the copolymer. These homopolymer Tgs are those as reported in the Polymer Handbook, 4th Edition; J. Brandrup (Editor), E. H. Immergut (Editor), E. A. Grulke (Editor); ISBN: 978-0-471-47936-9 May 2003.

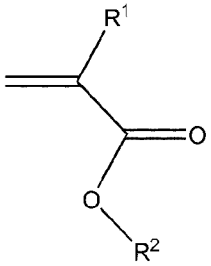
According to some embodiments, the copolymer may be a single stage polymer excluding a seed polymer. According to some other embodiments, the copolymer may be a two stage polymer, each stage having a different composition, excluding a seed polymer. According to some other embodiments, the copolymer may be a multi stage polymer, i.e. including three or more stages, each stage having a different composition, excluding a seed polymer.

According to an embodiment, the total percentages of the monomers a), b), c), d), and optionally an additional monomer in the copolymer add up to 100%.

Monomers in the copolymer

Monomer a)

The copolymer includes 20-80wt% of one or more monomers of structure (I):



(I) where R^1 is a hydrogen or methyl group; and R^2 is a C1-C8, preferably C2- C6, more preferably C2- C4, non-cyclic alkyl group, and wherein a homopolymer of monomer a) has a glass transition temperature (Tg) less than 25 °C. According to some embodiments, the Tg is preferably less than 20°C, more preferably less than 10°C.

The monomer a) is preferably bio-based. Biocarbon content of monomer a) may be at least 5%, preferably at least 10%, more preferably at least 20%, most preferably at least 30% biocarbon content as determined by ASTM D6866-22 Method B. According to some embodiments, the monomer a) includes at least 5%, preferably at least 10%, more preferably at least 20%, most preferably at least 30%, very most preferably at least 40 %,45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99%, or up to 100% biocarbon content (BCC) as determined by ASTM D6866-22.

According to some embodiments, the copolymer includes at least 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, or at least 75 wt% of monomer a) or a mixture of monomers a) based at total dry weight of copolymer. According to some embodiments, the copolymer includes at most 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, or at most 25 wt% of monomer(s) a) based on total dry weight of copolymer.

According to an embodiment, the copolymer includes from 45-60 wt% of monomer(s) a) and monomer(s) a) includes at least one of methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, 2-methylbutyl (meth)acrylate, isomers of pentyl

(meth)acrylates, isomers of hexyl (meth)acrylates, isomers of heptyl (meth)acrylates, isomers of octyl (meth)acrylates, 2-octyl (meth)acrylate, or combinations thereof.

According to an embodiment, monomer(s) a) includes at least one of ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylates such as n-butyl (meth)acrylate, iso-butyl (meth)acrylate, t-butyl (meth)acrylate; 2-methylbutyl (meth) acrylate, heptyl (meth)acrylates, octyl (meth)acrylates such as 2-octyl (meth)acrylate; or a combination thereof.

Other non-limiting examples of monomer a) are non-cyclic C1-C8 acrylates, non-cyclic C1-C8 methacrylates, or mixtures thereof in which the homopolymer or copolymer has the Tg range recited above. For example, the monomer(s) a) may be at least one of ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, 2-methylbutyl (meth)acrylate, 2-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-propylheptyl (meth)acrylate, ethylbutyl (meth)acrylate, isomers of pentyl (meth)acrylates, isomers of hexyl (meth)acrylates, isomers of heptyl (meth)acrylate such as n-heptyl (meth)acrylate, isomers of octyl (meth)acrylate, or combinations thereof. C1-C6 (meth)acrylates are more preferred, C1-C4 (meth)acrylate such as methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, iso-butyl acrylate are most preferred.

Monomer b)

The copolymer also includes 20-80wt% of at least one ethylenically unsaturated monomer or mixture of monomers, other than monomer(s) a). Monomer(s) b) may be selected from the group consisting of C1-C8 alkyl (meth)acrylates, ethylene, vinyl acetate, vinyl versatate, styrene, styrene derivatives, or combinations thereof, based on the total dry weight of the copolymer. Monomer b) is optionally bio-based. If the monomer b) is bio-based, it may include at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 99, or up to 100% BCC as measured according to ASTM D6866-22 Method B.

According to an embodiment, the monomer b) comprises methyl (meth)acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate.

According to some embodiments, the copolymer includes at least 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, or at least 75 wt% of monomer(s) b) based on a total dry weight of copolymer.

According to some embodiments, the copolymer includes at most 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30 or at most 25 wt% of monomer(s) b) based on total dry weight of copolymer.

According to an embodiment, the copolymer may include from 40-55 wt% of monomer b) and monomer b) comprises at least one of methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, vinyl acetate, styrene, or combination thereof.

Monomer c)

The copolymer includes 0.1-10wt%, based on a total dry weight of the copolymer of at least one ethylenically unsaturated monomer or mixture of monomers including at least one functional group including at least one of carboxylate and/or acid, and/or salt, and/or anhydride forms thereof; phosphate and/or acid, and/or salt forms thereof; phosphonate and/or acid, and/or salt forms thereof; sulfur bearing monomers and/or acid, and/or salt forms thereof; sulfonate and/or acid, and/or salt forms thereof; hydroxyl; silane; or combinations thereof.

According to an embodiment, monomer(s) c) includes at least one of carboxylic acid-functionalized monomers, phosphate-bearing monomers, sulfur-bearing monomers, or combinations thereof.

Non-limiting examples of monomer(s) c) are acrylic acid, methacrylic acid, or a combination thereof.

Other non-limiting examples include carboxylic acid-functionalized co-monomers such as (meth)acrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, citraconic acid, cinnamic acid, or combinations thereof.

An acid-functionalized co-monomer selected from phosphorus-based or sulfur-based acid-functionalized monomers or phosphate co-monomers may be used, including non-limiting examples such as: phosphoalkyl (meth)acrylates; phosphoalkyl (meth)acrylamides; phosphoalkyl crotonates, phosphoalkyl maleates, phosphoalkyl fumarates, phosphodialkyl (meth)acrylates, phosphodialkyl crotonates, vinyl phosphates or (meth)allyl phosphate; phosphate esters of polypropylene glycol mono(meth)acrylate or polyethylene glycol mono(meth)acrylate; polyoxyethylene allyl ether phosphate, or vinyl phosphonic acid.

Sulfur-based co-monomers include, without limitation, vinyl- and allyl-sulfonic acids; sulfoethyl (meth)acrylate, aryl-sulfonic acids; (meth)acrylamidoethane-sulfonic acids; methacrylamido-2-methyl propane-sulfonic acids; and the alkali metal salts of sulfonic acids.

Other functional monomer(s) c) are those including at least one hydroxyl and/or silane group. Preferred examples are 2-hydroxy-3-phenoxypropyl methacrylate, (meth)acryloxyalkyl trialkyloxysilanes, vinyltrialkoxysilanes, hydroxyalkyl (meth)acrylates, or combination thereof; preferably, 4-hydroxybutyl acrylate, methacryloxypropyl trimethoxysilane, methacryloxypropyl triethoxysilane, acryloxypropyl trimethoxysilane, acryloxypropyl triethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane and combinations thereof, more preferably, vinyltrialkoxysilanes, [3-(methacryloyloxy)propyl]trimethoxysilane, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl acrylate, or combinations thereof.

According to some embodiments, the copolymer includes at least 0.1, 0.2, 0.3, 0.4, 05, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9 or at least 9.5 wt% of monomer(s) c) based at total dry weight of copolymer. According to some embodiments, the copolymer may include at most 10, 9.5, 9, 8.5, 8, 7.5, 7, 6.5, 6, 5.5, 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, or at most 1 wt% of monomer(s) c) based on total dry weight of copolymer.

According to an embodiment, the copolymer may include from 0.1-2 wt% of monomer(s) c) and monomer c) may include at least one carboxylate functional group and/or acid, and/or salt, and/or anhydride form thereof.

Monomer d)

The copolymer includes 0.1–10 wt% of at least one nitrogen-bearing ethylenically unsaturated monomer d) or mixture of monomers d).

According to an embodiment, the copolymer includes at least one of (meth)acrylamide, diacetone acrylamide, ureido (meth)acrylate or a combination thereof.

Other nonlimiting examples of monomer(s) d) are ureido (meth)acrylates, (meth)acrylates with at least one of urea and thiourea in the side chains; acrylic allophanes, aminoalkyl (meth)acrylates, dialkylamino (meth)acrylates, aminoethyl acrylate and methacrylate; dimethylaminoethyl acrylate and methacrylate; diethylaminoethyl acrylate and methacrylate,

dimethylaminopropyl acrylate and methacrylate; 3-dimethylamino-2,2-dimethylpropyl acrylate and methacrylate; aminoethyl methacrylate, N-(2-aminoethyl)(meth)acrylamide, N-(3-aminopropyl)(meth)acrylamide, 2-(diethylamino)ethyl (meth)acrylate, 2-(diisopropylamino)ethyl (meth)acrylate, 2-(dimethylamino)ethyl (meth)acrylate, 2-(diethylamino)ethyl (meth)acrylate, 2-(dimethylamino)ethyl (meth)acrylate, N-[2-(diethylamino)ethyl](meth)acrylamide, 2-morpholinoethyl (meth)acrylate, N-morpholinoethyl acrylate and methacrylate; 2-N-piperidinoethyl acrylate and methacrylate; N-(3-dimethylaminopropyl)acrylamide and -methacrylamide; N-dimethylaminoethylacrylamide and -methacrylamide; N-diethylaminoethylacrylamide and methacrylamide; N-(4-morpholinomethyl)acrylamide and methacrylamide; vinylimidazole and also monoethylenically unsaturated derivatives of ethyleneurea, such as N-(2-(meth)acryloyloxyethyl)ethyleneurea, N-(β-acrylamidoethyl)ethyleneurea, N-2-(allylcarbamato)aminoethylimidazolidinone, N vinylethyleneurea, N-(3 allyloxy-2-hydroxypropyl)aminoethylethyleneurea, N-vinyloxyethyleneurea, N-methacryloyloxyacetoxyethylethyleneurea, N-(acrylamidoethylene)ethyleneurea, N-(methacrylamidoethylene)-ethyleneurea, 1-(2-methacryloyloxyethyl)2-imidazolidone, and N-(methacrylamidoethyl)ethyleneurea, N-(2 methacrloyloxyethyl) ethylene urea, N-(2 methacryloxyacetamidoethyl)-N, N' ethyleneurea, allylalkyl ethylene urea, N-methacrylamidomethyl urea, N-methacryoyl urea, N-[3-(1,3-diazacyclohexan)-2-on-propyl]methacrylamide, 2-(1-imidazolyl)ethyl methacrylate, 2-(1-imidazolidin-2-on)ethylmethacrylate, N-(methacrylamido)ethyl urea, urethane methacrylate, acrylamide, methacrylamide, acrylonitrile, vinyl cyanides, vinylpyrrolidone, or combinations thereof. According to an embodiment, monomer(s) d) includes a monomer including one or more carbonyl groups. If present, these carbonyl groups may react with a crosslinking additive that include one or more hydrazine or hydrazide groups to form crosslinks. Non-limiting examples of suitable such monomers are those including carbonyl or 1,3-dicarbonyl groups. Diacetone acrylamide is preferred.

According to some embodiments, the copolymer includes at least 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9 or at least 9.5 wt% of monomer(s) d) based at total dry weight of copolymer. According to some embodiments, the copolymer may include at most 10, 9.5, 9, 8.5, 8, 7.5, 7, 6.5, 6, 5.5, 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, or at most 1 wt% of monomer(s) d) based on total dry weight of copolymer.

According to an embodiment, the copolymer may include from 1-5 wt% of monomer(s) d) and monomer(s) d) comprises at least one of (meth)acrylamide, diacetone acrylamide or a combination thereof.

According to an embodiment the copolymer does not include acetoacetoxyethyl methacrylate (AAEM).

According to an embodiment, the copolymer includes less than 0.1, 0.05, 0.01 wt% of itaconates based on a total weight of the copolymer. According to an embodiment, the copolymer does not include itaconates.

According to an embodiment, the copolymer includes less than 0.1, 0.05, 0.01 wt% of itaconamides based on a total weight of the copolymer. According to an embodiment, the copolymer does not include itaconamides.

According to an embodiment, the copolymer includes less than 0.1, 0.05, 0.01 wt% of cyclic monomers such as isobornyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate , either alone or in combination based on a total weight of the copolymer. According to an embodiment, the copolymer does not include cyclic monomers such as isobornyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate , either alone or in combination.

Additional free radical reactive compounds:

The copolymer may optionally include 0-2wt% of at least one free radical reactive compounds other than monomer a), monomer b), monomer c) or monomer d). The additional free radical reactive compounds may optionally be completely or partially biobased or may not be biobased. The copolymer may include one, some or all of the following additional free radical reactive compounds. If more than one additional reactive compounds is present during emulsion polymerization, then the copolymer may include 0-2wt% of each additional free radical reactive compounds, or a total of 1-2wt % of a total of all of the additional free radical reactive compounds, based on a total weight of the copolymer. According to some embodiments, the copolymer may include at least 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.2, 1.3, 1.4, or at least 1.5wt% of each additional free radical reactive compounds, or a total of at least 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.2, 1.3, 1.4, or at least 1.5wt% of all of the additional free radical reactive compounds, based on a total weight of the copolymer. According to some embodiments,

the copolymer may include at most 2, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1 or at most 1wt% of each additional free radical reactive compounds, or a total of at most 2, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1 or at most 1wt% of all of the additional free radical reactive compounds, based on a total weight of the copolymer.

Non-limiting examples of additional free radical reactive compounds include chain transfer agents, especially sulfur-bearing chain transfer agents such as 3-mercaptopropionic acid, n-dodecyl mercaptan, t-dodecyl mercaptan, methyl 3-mercaptopropionate, butyl 3-mercaptopropionate, isooctyl 3-mercaptopropionate, benzenethiol, azelaic alkyl mercaptan, or mixtures thereof. Other non-limiting examples of chain transfer agents are mercaptans, polymercaptan, polyhalogeno, and allyl compounds in the polymerization mixture. Such chain transfer agents may be used to regulate the molecular weight of the polymer. Examples of suitable chain transfer agents include 3-mercaptopropionic acid, n-dodecyl mercaptan, t-dodecyl mercaptan, methyl 3-mercaptopropionate, butyl 3-mercaptopropionate, isooctyl 3-mercaptopropionate, benzenethiol, azelaic alkylmercaptan, or mixtures thereof. The chain transfer agent may be used in an effective amount to control the molecular weight of the emulsion polymer, for example, from 0 to 1%, from 0.1% to 0.5 %, or from 0.15% to 0.4%, by weight based on the total weight of monomers used for preparing the emulsion polymer.

Also suitable for the additional free radical reactive compounds are monomers comprising two or more unsaturated carbon-carbon double bonds, capable of being free- radical polymerized, including but not limited to tripropylene glycol diacrylate, 1,3-butylene glycol di(meth)acrylate, 1,12-dodecanediol di(meth)acrylate, decanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, trimethylolpropane tri(meth)acrylate, 1,3-butyleneglycol dimethacrylate, 1,4-butyleneglycol dimethacrylate, dipentaerythritol pentaacrylate, pentaerythritol tetraacrylate, 1,10-decanediol diacrylate, ethoxylated (2) bisphenol A diacrylate, 1,3-propanediol dimethacrylate, 1,4-butanediol diacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol diacrylate, 1,6 hexanediol dimethacrylate, dially phthalate, allyl methacrylate, divinylbenzene, or combinations thereof.

Copolymerizable surfactants may also be included in the final polymer as additional free radical reactive compounds. Nonlimiting examples of copolymerized stabilizers for the present

aqueous dispersions are copolymerizable nonionic and anionic surfactants such as those disclosed in US2014/0243552, the entire disclosure of which is incorporated by reference herein for all purposes. Other suitable copolmerizable surfactants are sold under the trade names Hitenol® BC, Hitenol® KH, Hitenol® AR, Adeka Reasoap SR and Adeka Reasoap ER, Oximulsion® React.

Any one or more or all or each of these additional monomers or free radical reactive compounds may be present in the copolymer at from 0-2wt%, based on a total dry weight of the copolymer.

Polymerization Methods:

Emulsion polymers and monomers useful to prepare polymeric emulsions or dispersions are known in the art (as discussed in texts on the subject such as "Emulsion Polymerization: Theory and Practice" by D. C. Blackley published by Wiley in 1975, "Emulsion Polymerization" by F. A. Bovey et al. published by Interscience Publishers in 1965, and "Emulsion Polymerization and Emulsion Polymers" by P.A. Lovell et al. published by Wiley Science in 1997).

The aqueous dispersion of the present invention comprises one or more emulsion polymers prepared by emulsion polymerization as is well known in the art.

The emulsion polymer may be prepared by emulsion polymerization of a mixture of monomers comprising the monomers a), b), c), and d), as well as optional additional monomer(s) described above. The mixture of monomers may be added neat or as an emulsion in water; or added in one or more additions or continuously, linearly or nonlinearly, over the reaction period of preparing the emulsion polymer. A monomer emulsion containing all or some portion of the monomers to be polymerized may be prepared using the monomers, water and surfactants.

The emulsion polymer may be prepared as a single stage or as a multistage polymer.

One or more surfactants may be added prior to, during, or after the polymerization of the monomer mixture, or combinations thereof. These surfactants may include anionic and/or nonionic emulsifiers. Examples of suitable nonionic emulsifiers include acyl, alkyl, oleyl, alkylaryl ethoxylates, and copolymers of ethylene oxide and propylene oxide. These products are

commercially available, for example, under the name Genapol®, Lutensol® or Emulan®, Rhodasurf®, Tergitol™, and Pluronic™. They include, for example, C4 to C12 mono-, di-, and tri-alkylphenols ethoxylates (EO range 3 to 70), C8 to C18 fatty alcohol ethoxylates, C11-C15 oxo-process alcohol ethoxylates, C16 to C18 fatty alcohol ethoxylates, C11 oxo-process alcohol ethylates, C13 oxo-process alcohol ethoxylates. Some of the commercially available anionic surfactants include sodium, potassium, and ammonium salts of linear and branched alcohol sulfates (e.g., Polystep® B-5, B-7 available from Stepan), alcohol ether sulfates (e.g., Disponil® FES 32, FES77 and FES993 available from BASF and Polystep B-11, B-12, B-19, B-20, B-22, B-23, B-40, B-41, etc. available from Stepan), linear and branched alkylbenzene sulfonates (e.g., Polystep® A-15 and A-16 available from Stepan), alpha-olefin sulfonates (e.g., Polystep® A-18 from Stepan and Rhodacal® DS-4 from Solvay), linear and branched alkyldiphenyloxide disulfonates (e.g., Dowfax 2A-1 available from The Dow Chemical Company and Calfax® DB-45 and Calfax® 16L-35 from Pilot Chemical); sulfosuccinates (e.g., Aerosol® A-102, OTPG-75, MA-80I, etc. available from Solvay), alcohol phosphate esters (e.g., Rhodafac® RS-610 from Solvay and Polystep® P-11, P-12, P-13 from Stepan), di- and tri-styrylphenol sulfates and phosphates (e.g., Polystep® TSP-16S and TSP-16S from Stepan). The amount of surfactants used can typically range from 0 to about 5%, from 0.1% to 3%, from 0.2 to 2%, by weight based on the total weight of monomer quantity.

As mentioned above, also suitable as stabilizers for the present dispersions are copolymerizable nonionic and anionic surfactants such as those disclosed in US2014/0243552. Other suitable copolmerizable surfactants are sold under the trade names Hitenol® BC, Hitenol® KH, Hitenol® AR, Adeka Reasoap SR and Adeka Reasoap ER, Oximulsion® React.

The polymerization process may be thermally initiated or redox initiated emulsion polymerization. Examples of suitable free radical initiators include hydrogen peroxide, t-butyl hydroperoxide, cumene hydroperoxide, ammonium and/or alkali metal persulfates, sodium perborate, perphosphoric acid, and salts thereof; potassium permanganate. The free radical initiators may be used typically at a level of 0.01 % to 3.0 % by weight, based on the total weight of monomers. Redox systems comprising the above described initiators coupled with a suitable reductant may be used in the polymerization process. Examples of suitable reductants include sodium sulfoxylate formaldehyde, ascorbic acid, isoascorbic acid, alkali metal and ammonium

salts of sulfur containing acids, such as sodium sulfite, bisulfite, thiosulfate, hydrosulfite, sulfide, hydrosulfide or dithionite, formadinesulfinic acid, acetone bisulfite, glycolic acid, hydroxymethanesulfonic acid, glyoxylic acid hydrate, lactic acid, glyceric acid, malic acid, tartaric acid and salts of the proceeding acids. Metal salts of iron, copper, manganese, silver, platinum, vanadium, nickel, chromium, palladium, or cobalt may be used to catalyze the redox reaction. Chelating agents for the metals may optionally be used.

The temperature suitable for polymerization process may be lower than 100°C, in the range of from 30°C to 95°C, or in the range of from 50°C to 90°C. Emulsion polymerization may be seeded or unseeded. In another aspect of the present invention the aqueous acrylic emulsion polymer may be prepared by a multistage emulsion polymerization process, in which at least two stages differing in composition are polymerized in sequential fashion, as noted above.

Additives in the aqueous dispersion:

The aqueous dispersion may also contain a water-soluble or water-dispersible crosslinking agent. These crosslinking agents may be referred to as latent crosslinking agents. Such cross-linking agent will react with specific polymer functionalities such as carbonyl or 1,3-dicarbonyl groups as water is removed from the coating compositions herein and as a film or coating is formed from the coating composition. A type of water-soluble crosslinking agent that can be used in the compositions herein comprises a compound which contains at least two hydrazine and/or hydrazide moieties. Particularly suitable are dihydrazine compounds of aliphatic dicarboxylic acids, for example, oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydazide, glutaric acid dihydrazide, adipic acid dihydrazide, maleic acid dihydrazide, fumaric acid dihydrazide and/or itaconic acid dihydrazide. Adipic acid dihydrazide (ADH) is a preferred water-soluble crosslinking agent for use in the compositions herein, especially those produced from monomer compositions containing diacetone acrylamide (DAAM). As noted above, DAAM may be included as at least one nitrogen-bearing ethylenically unsaturated monomer d) or mixture of monomers d). DAAM includes carbonyl groups reactive with the latent crosslinking agent.

In an embodiment, the aqueous dispersion described herein further comprises one or more additives to improve surface characteristics of dry coatings including the aqueous dispersion. Nonlimiting examples of such additives include waxes, fluorosurfactants, silicone

surfactants, Rhamnolipid-based surfactants, alcohol phosphate ester surfactants. These performance additives are commercially available, for example, under the name Capstone™, Aquacer®, Dowsil™, Stepcote®. Commonly used fluorosurfactants include, for example, fluoralkanes, perfluoralkanes, their derivatives, and the like. In an aspect, short chain fluorinated compounds are preferred. In a preferred aspect, the fluorosurfactant is an anionic C6-fluorocarbon compound (e.g., Capstone® FS-61), and is preferably substantially free of perfluorooctanesulfonic acid (PFOS) (perfluorooctanesulfonate) and perfluorooctanoic Acid (PFOA). Wax additives which can come from both fossil and renewable sources, are often included in aqueous dispersions and coatings to improve water repellency, surface slip and block resistance. Nonlimiting examples include paraffin-based wax emulsions (e.g., Aquacer 497 and Aquacer 539 from BYK, Michem® Emulsion 36840 from Michelman, Joncryl® Wax 35 from BASF). Examples of silicone surfactants may include DOWSIL™ 211S Additive from Dow. Examples of alcohol phosphate ester surfactants include Stepcote® W-877, W-839 and W-843 from Stepan. Non -limiting examples are potassium, sodium, or lithium n-octyl phosphate, more preferably potassium n-octyl phosphate Potassium salt of n-octyl phosphate (e.g., Stepcote® W-877) is most preferred. The additive used is usually from 50 ppm to 5000 ppm based on the total weight of coating composition, from 100 to 4000 ppm, preferably from 200 to 3000 ppm, most preferably from 250 to 2500 ppm. These additives may be added prior to, during, or after the polymerization.

The aqueous dispersion may further comprise one or more of the surfactants discussed in the section on polymerization.

According to some embodiments, it is desired that the resultant aqueous dispersion of the present invention comprises a low level of coagulum, for example, less than 1,000 ppm, less than 800 ppm, less than 500 ppm, less than 400 ppm, less than 300 ppm, or even less than 200 ppm. Coagulum is defined as filterables, meaning undesirable coarse materials formed by coagulated latex particles during the polymerizaton process.

Coating composition

A coating composition is also provided. The coating composition includes the aqueous polymeric dispersion including the at least one copolymer formed by emulsion polymerization of

a monomer mixture including, based on a total dry weight of the copolymer, monomers a), b), c), and d).

BCC content of the coating composition

The BCC of the coating composition is measured according to ASTM-6866-22 Method B. According to some embodiments, the coating composition includes at least 5, 10 15, 20, 22, 25, 30, 35, 40, 45, 50, 60, 65, 70, 75, or at least 80% BCC as measured according to ASTM-6866-22 Method B.

According to an embodiment, the BCC of the coating composition is based on all of the organic carbons in the coating composition, *i.e.*, carbons from the binder and carbons from any further additives to the coating composition.

According to another embodiment, the BCC of the coating composition is based on only the carbons from the binder in the coating composition.

Properties of the coating composition

A dried layer of the coating composition is improved in one, two, three or all four of the following key performance measures, compared to a coating formulation that does not include the aqueous polymeric dispersion is described herein: scrub resistance, for example measured according to ASTM D2486-17 and/or as described in the Examples, Test Method B; tint strength, measured according to ASTM D4838-88(2016) and/or as described in the Examples; block resistance, measured according to ASTM D4946-89(2017) and/or measured as described in the Examples; and/or stain resistance, measured according to ASTM D4828-94(2020) and/or as described in the Examples.

Other components in the coating composition

The aqueous coating composition may further include other components (additives) in addition to the copolymer dispersion. According to embodiments, some or all of these additional components may be completely or partially biobased.

Such additives include but are not limited to, crosslinking agents, pH adjustment agents, UV stabilizers, foam control agents, wetting agents, fillers, pigments, pigment extenders, fillers, dyes, matting and texturing agents, pigment enhancers, emulsifiers, surfactants, dispersants,

curing agents, coalescents, wetting agents, biocides, thickeners, rheology modifiers, plasticizers, waxes, anti-oxidants, antifoaming agents, antisettling agents, antiskinning agents, corrosion inhibitors, dehydrators, antigassing agents, dispersion aids, driers, antistatic additives, flash corrosion inhibitors, floating and flooding additives, in-can and in-film preservatives, insecticidal additives, optical whiteners, reodorants, water-soluble resins and other agents used in the art. These include, tints, emulsifiers, rheology control additives, additional polymers, pigments or colorants, fillers, dispersants or surfactants, plasticizers, defoamers, thickeners, biocides, solvents, rheology modifiers, wetting or spreading agents, leveling agents, conductive additives, thermal insulating fillers, adhesion promoters, anti-blocking agents, anti-cratering agents or anti-crawling agents, corrosion inhibitors, anti-static agents, flame retardants, optical brighteners, UV absorbers or other light stabilizers, antioxidants, chelating agents, flattening agents, humectants, insecticides, lubricants, odorants, oils, waxes or anti-slip aids, soil repellants, freeze-thaw and/or open time additives, and stain resistant agents.

Non-limiting examples of pigments that can act as colorants, fillers or dyes include but are not limited to: carbon black, colored organic pigments, and metal oxide pigments, such as titanium dioxide, zinc oxide, clay, aluminum silicate, zinc hydroxide, magnesium silicate, calcium silicate, amorphous silica, vapor phase silica, fumed silica, colloidal silica, alumina, aluminum hydroxide, zirconium oxide, and cerium oxide, as well as calcium carbonate, magnesium carbonate, kaolin, clay, talc, calcium sulfate, barium sulfate, and zinc carbonate.

Pigments include colored and opacifying pigments. Pigment volume concentration is used in an amount of less than 20 volume percent based on dry components of the coating composition. Pigment volume concentration = volume of pigment/volume of total solids.

Colored pigments are finely ground natural or synthetic, insoluble particles used to impart color when added to paints and coatings compositions. Pigment refers to a class of organic or inorganic matter that is insoluble in water, not soluble in the use of media, but has been highly dispersed so that the colored matter is colored. Pigments used for coatings are well known in the art. Non limiting examples of pigments include anatine, brookite, cadmium yellow, cadmium red, cadmium green, orange cobalt, cobalt blue, cerulean blue, aureolin, cobalt yellow, copper pigments, azurite, Han purple, Han blue, Egyptian blue, malachite, Paris green, phthalocyanine blue BN, phthalocyanine green G, verdigris, viridian, iron oxide pigments,

sanguine, caput mortuum, oxide red, red ochre, Venetian red, Prussian blue, clay earth pigments, yellow ochre, raw sienna, burnt sienna, raw umber, burnt umber, marine pigments (e.g., ultramarine, and ultramarine green shade), and zinc pigments (e.g., zinc white, and zinc ferrite).

Opacifying pigments reflect light and are used to make a coating opaque or less transparent. They prevent light transmission and provide ideal brightness and whiteness to the end product. The most commonly used are titanium dioxide (TiO_2), barium sulphate, zinc oxide, calcium carbonate, talc, nepheline syenite and combinations thereof. The most common and preferred is TiO_2. Extenders can also be added to the formulation. Suitable examples of extenders include precipitated grades of calcium carbonate, directly mined calcium carbonates, clean grades of magnesium calcium carbonate (dolomite), clean grades of calcined, pulverized clays (aluminosilicates), and clean purified grades of magnesium silicate.

A coalescing agent may be a component of the coating composition. As the coating dries after being applied to a substrate, the purpose of the coalescent agent in these compositions is to aid the discrete particles of polymer that are present in the aqueous dispersion to form into a continuous film. Coalescent works by softening the polymer particles, allowing them to fuse into a tough, continuous film. Common coalescents include ester alcohols, esters, and glycol ethers, esters, alcohols, amides, and polymers.

According to an embodiment, the coating composition may contain a water soluble or water dispersible latent crosslinking agent, as discussed above. According to some embodiments, this crosslinking agent is added when formulating the coating agent, rather than, or addition to, being added in to the aqueous dispersion of the copolymer binder.

In an embodiment, the coating composition described herein further comprises one or more additives to improve surface characteristics of dry coatings. Nonlimiting examples include waxes, flurosurfactants, silicone surfactants, Rhamnolipid-based surfactants, alcohol phosphate ester surfactants. These performance additives are commercially available, for example, under the name Capstone™, Aquacer®, Dowsil™, Stepcote®. Commonly used fluorosurfactants include, for example, fluoralkanes, perfluoralkanes, their derivatives, and the like. In an aspect, short chain fluorinated compounds are preferred. In a preferred aspect, the fluorosurfactant is an anionic C6-fluorocarbon compound (e.g., Capstone FS-61), and is preferably substantially free of PFOS and PFOA. Wax additives which can come from both fossil and renewable sources, are

often included in aqueous dispersions and coatings to improve water repellency, surface slip and block resistance. Nonlimiting examples include Paraffin-based wax emulsions (e.g., Aquacer 497 and Aquacer 539 from BYK, Michem® Emulsion 36840 from Michelman, Joncryl® Wax 35 from BASF). Examples of silicone surfactants may include DOWSIL™ 211S Additive from Dow. Examples of alcohol phosphate ester surfactants include Stepcote® W-877, W-839 and W-843 from Stepan. Stepcote® W-877 is most preferred. The additive used is usually from 50 ppm to 5000 ppm based on the total weight of aqueous dispersion, from 100 to 4000 ppm, preferably from 200 to 3000 ppm, most preferably from 250 to 2500 ppm.

The coating composition may further comprise one or more of the surfactants discussed in the section on polymerization.

Uses

The coating compositions of the present invention may be applied by conventional techniques, such as dipping, brushing, flowing, or spraying onto a variety of substrate surfaces. The substrates may include without limitation, wood, fabricated wood, paper, cardboard, textiles, synthetic resins, ceramics, ferrous metals, non-ferrous metals, stone, concrete, plaster, and the like.

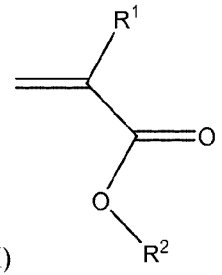
The coating compositions of the present invention may be used in indoor or outdoor applications. Useful applications may include, without limitation, interior and exterior wall coatings, garage floor coating, metal coating, rail car coating, agricultural machinery coating, automobile parts coating, log cabin coatings, deck stains, concrete coating, wood stains, porch or deck coatings, glossy top coats, traffic paints, kitchen cabinetry coatings, automobile refinish, lawn and garden equipment coatings, bus and truck top coatings, gloss trim enamels, metal primers, light duty maintenance coatings, furniture coatings, stain blocking coatings, appliance coatings, dumpster coatings, heavy duty equipment coatings, industrial equipment coatings, and sash and trim enamels.

The aqueous dispersion may be formulated into paints (coating compositions) of various colors when pigment is included. The coating composition may form a film on a substrate with or without the aid of coalescing agents when applied on the substrate at ambient conditions.

Non-limiting aspects of the invention are summarized as follows.

Aspect 1. An aqueous polymeric dispersion comprising at least one copolymer formed by emulsion polymerization of a monomer mixture comprising, based on a total dry weight of the copolymer, monomers a), b), c), and d):

a) 20-80wt% of at least one monomer of structure (I):



(I)

where R^1 is a hydrogen or methyl group; and R^2 is a C1-C8, preferably C2- C6, more preferably C2- C4, non-cyclic alkyl group, and wherein a homopolymer of monomer a) has a glass transition temperature (Tg) less than 25 °C;

b) 20-80wt% of at least one ethylenically unsaturated monomer other than a) selected from the group consisting of C1-C8 alkyl (meth)acrylates, ethylene, vinyl acetate, vinyl versatates, styrene, styrene derivatives, or combinations thereof, optionally bio-based;

c) 0.1-10wt% of at least one ethylenically unsaturated monomer comprising at least one functional group comprising at least one of carboxylate, phosphate, phosphonate; sulfonate, and/or acid, and/or salt, and/or anhydride forms thereof; hydroxyl; silane; or combinations thereof; and

d) 0.1-10wt% of at least one nitrogen-bearing ethylenically unsaturated monomer;

wherein:

the copolymer comprises at least 5%, preferably at least 10%, more preferably at least 15%, most preferably at least 22% biocarbon content as determined by ASTM D6866-22 Method B; and

the aqueous polymeric dispersion has a minimum film formation temperature of 30°C or less.

Aspect 2. The aqueous polymeric dispersion of Aspect 1, wherein monomer a) comprises at least 5%, preferably at least 10%, more preferably at least 20%, even more preferably at least 30%, most preferably at least 40 % biocarbon content as determined by ASTM D6866-22 Method B.

Aspect 3. The aqueous polymeric dispersion of Aspect 1 or Aspect 2, wherein the monomer a) comprises at least one of ethyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, 2-methylbutyl (meth) acrylate, t-butyl (meth)acrylates, heptyl (meth)acrylates, 2-octyl (meth)acrylate, or a combination thereof, said monomer a) comprising at least 40% biocarbon content as determined by ASTM D6866-22 Method B.

Aspect 4. The aqueous polymeric dispersion of any of Aspects 1-3, wherein the monomer a) is selected from the group consisting of ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, 2-methylbutyl (meth)acrylate, 2-octyl (meth)acrylate, or a combination thereof.

Aspect 5. The aqueous polymeric dispersion of any of Aspects 1-4, wherein the monomer b) comprises at least one of methyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, vinyl acetate, styrene, or a combination thereof.

Aspect 6. The aqueous polymeric dispersion of any of Aspects 1-5, wherein the monomer c) comprises at least one of carboxylic acid-functionalized monomers, phosphorus-bearing monomers, sulfur- bearing monomers, hydroxyl or silane or combinations thereof.

Aspect 7. The aqueous polymeric dispersion of any of Aspects 1-6, wherein the monomer c) comprises at least one of (meth)acrylic acid, phosphates, sulfates, hydroxyalkyl (meth)acrylates, 2- hydroxy-3-phenoxypropyl methacrylate, (meth)acryloxyalkyl trialkyloxysilanes, vinyltrialkoxysilanes, or combination thereof.

Aspect 8. The aqueous polymeric dispersion of any of Aspects 1-7, wherein the monomer c) is selected from the group consisting of acrylic acid, methacrylic acid, or a combination thereof.

Aspect 9. The aqueous polymeric dispersion of any of Aspects 1-8, wherein the monomer d) comprises at least one of acrylamides, (meth)acrylamide; diacetone acrylamide;

(meth)acrylates with at least one of ureido, urea, or thiourea in the side chains; acrylic allophanes; aminoalkyl (meth) acrylates; dialkylamino (meth)acrylates; or a combination thereof.

Aspect 10. The aqueous polymeric dispersion of any of Aspects 1-9, wherein the monomer d) is selected from the group consisting of acrylamides, (meth)acrylamide, diacetone acrylamide, ureido (meth)acrylate, or a combination thereof.

Aspect 11. The aqueous polymeric dispersion of any of Aspects 1-10, comprising at least 0.1wt% of at least one additional free radical reactive compound, the additional free radical reactive compound comprising at least one of a chain transfer agent; a copolymerizable surfactant; a monomer comprising two or more unsaturated carbon-carbon double bonds; or combinations thereof.

Aspect 12. The aqueous polymeric dispersion of any of Aspects 1-11, wherein the total percentages of the monomers a), b), c), d), and the optional free radical reactive compound add up to 100%.

Aspect 13. The aqueous polymeric dispersion of any of Aspects 1-12, wherein the copolymer comprises:

from 45-60 wt% of monomer a) and monomer a) comprises at least one of ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, 2-methylbutyl (meth)acrylate, 2-octyl (meth)acrylate, or a combination thereof.

from 40-55 wt% of monomer b) and monomer b) comprises at least one of methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, or combination thereof;

from 0.1-10 wt% of monomer c) and monomer c) comprises at least one carboxylate functional group and/or acid, and/or salt, and/or anhydride form thereof;

from 0.1-10 wt% of monomer d) and monomer d) comprises at least one of (meth)acrylamide, diacetone acrylamide or a combination thereof; and

wherein the copolymer comprises at least 22% biocarbon content as determined by ASTM D6866-22 Method B; and

the aqueous polymeric dispersion has a minimum film formation temperature less than 30°C.

Aspect 14. The aqueous polymeric dispersion of any of Aspects 1-13, wherein the copolymer comprises a monomer comprising at least one carbonyl group reactive with a latent crosslinking agent, the monomer preferably comprising at least one 1,3-dicarbonyl group, more preferably comprising diacetone acrylamide.

Aspect 15. The aqueous polymeric dispersion of any of Aspects 1-14, further comprising at least one additive.

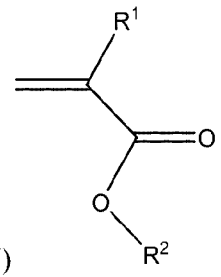
Aspect 16. The aqueous polymeric dispersion of Aspect 15, wherein the additive comprises at least two hydrazine and/or hydrazide moieties.

Aspect 17. The aqueous polymeric dispersion of Aspect 14 or Aspect 15, wherein the additive comprises alcohol phosphate ester surfactant or salt thereof, preferably potassium n-octyl phosphate, sodium n-octyl phosphate, or lithium n-octyl phosphate, more preferably potassium n-octyl phosphate.

Aspect 18. A coating composition comprising the aqueous polymeric dispersion of any of Aspects 1-17.

Aspect 19. A coating composition comprising an aqueous polymeric dispersion comprising at least one copolymer formed by emulsion polymerization of a monomer mixture comprising, based on a total dry weight of the copolymer, monomers a), b), c), and d):

a) 20-80wt% of at least one monomer of structure (I):



(I)

where R^1 is a hydrogen or methyl group; and R^2 is a C1-C8, preferably C2- C6, more preferably C2- C4, non-cyclic alkyl group, and wherein a homopolymer of monomer a) has a glass transition temperature (Tg) less than 25 °C;

b) 20-80wt% of at least one ethylenically unsaturated monomer other than a) selected from the group consisting of C1-C8 alkyl (meth)acrylates, ethylene, vinyl acetate, vinyl versatate, styrene, styrene derivatives, or combinations thereof;

c) 0.1-10wt% of at least one ethylenically unsaturated monomer comprising at least one functional group comprising at least one of carboxylate, phosphate, phosphonate, sulfonate; and/or acid, and/or salt, and/or anhydride forms thereof; hydroxyl; silane; or combinations thereof; and

d) 0.1-10wt% of at least one nitrogen-bearing ethylenically unsaturated monomer

wherein:

the copolymer comprises at least 5%, preferably at least 10%, more preferably at least 15%, most preferably at least 22% biocarbon content as determined by ASTM D6866-22; and

the aqueous dispersion has a minimum film formation temperature less than 30°C.

Aspect 20. The coating composition of Aspect 19, wherein the copolymer further comprises at least 0.1wt% of at least one free-radical reactive compound, the free-radical reactive compound comprising at least one of a chain transfer agent; a copolymerizable surfactant; a monomer comprising two or more unsaturated carbon-carbon double bonds; or combinations thereof.

Aspect 21. The coating composition of Aspect 19 or Aspect 20, wherein the copolymer comprises a monomer comprising at least one carbonyl group reactive with a latent crosslinking agent, the monomer preferably comprising at least one 1,3-dicarbonyl group, more preferably diacetone acrylamide.

Aspect 22. The coating composition of any of Aspects 19-21, further comprising at least one additive.

Aspect 23. The coating composition of Aspect 22, wherein the additive comprises at least two hydrazine and/or hydrazide moieties.

Aspect 24. The coating composition of Aspect 22 or Aspect 23, wherein the additive comprises alcohol phosphate ester surfactant or salt thereof, preferably potassium n-octyl phosphate, sodium n-octyl phosphate, or lithium n-octyl phosphate, more preferably potassium n-octyl phosphate.

EXAMPLES

Methods:

Latex coagulum

The amount of coagulum may be measured by pouring the aqueous dispersion polymer through 40 mesh and 250 mesh stainless steel wire mesh filters to capture fine solid material that was formed during the emulsion polymer production. The filter screens are carefully and thoroughly rinsed with water leaving only the filtered latex solids. The screens are dried in 135°C oven for at least 20 minutes. The filterable solids retained on the 40 and 250 mesh filters are determined gravimetrically and the total amount is calculated based on dry dispersion solids.

Glass transition temperature

Glass transition temperature may be measured using differential scanning calorimetry (TA Instrument Q2000) at a rate of 10°C/min. The half-height inflection point on the third heat cycle is reported as midpoint glass transition temperature. According to some embodiments, the glass transition temperature of homopolymers are those as reported in the Polymer Handbook, 4th Edition; J. Brandrup (Editor), E. H. Immergut (Editor), E. A. Grulke (Editor); ISBN: 978-0-471-47936-9 May 2003. According to some embodiments, the glass transition temperatures of copolymers are calculated from the Fox equation using the glass transition temperatures of homopolymers of the monomers thereof, as recited in the Polymer Handbook, 4th edition.

Minimum Film Formation Temperature

Minimum film formation temperature was measured on a customized rectangular aluminum bar with a hard coat anodized Teflon surface. The bar was equipped to heat and cool over a linear temperature gradient of 0°C to 60°C covering 34 inches at 1.77°C/inch. 1-2-ml wet

latex sample was pipetted into the well of a customized stainless steel drawdown bar to form a 0.3-mil wet film thickness. A smooth linear drawdown was made from one end to the other of the temperature gradient range. The clear top fitted over the bar was then immediately closed to allow the nitrogen purge to form the laminar flow of about 15-20 psig and the film to dry for 30-minutes to an hour. The minimum film formation temperature was identified as the point where the latex formed a clear and crack-free film.

Scrub Resistance

Relative scrub resistance was evaluated according to ASTM D2486-17, Test Method B on the Gardner Straight Line Washability and Wear Abrasion Machine. The coatings were applied side-by-side with a control paint using an applicator drawdown bar with a gap of 7 mils over Leneta black scrub test panels and allowed to dry for 7 days in a constant temperature and constant humidity (CT/CH) environmental chamber at 77±2 °F and 50% ±5% RH. After curing, the coated panel was placed over two 12.7 by 0.25 mm (0.5 in. by 0.01 in) shims that were positioned under each coating on the straight-line scrub machine. The coatings were then scrubbed with a bristle brush and an abrasive scrub medium until each paint film was removed in one continuous thin line across its own shim. The test was done in triplicate and the number of cycles to failure as well as the ratio between each test paint and the control paint was recorded.

Block Resistance

The test paints were prepared on the Leneta 3B opacity charts using a 3-mil bird drawdown bar. The films were dried in the controlled temperature and controlled humidity (CT/CH) chamber at 25°C and 50% relative humidity (RH) for one day. In the room temperature (RT) block test, two 2.54 cm x 2.54 cm square strips were placed together with paint film against paint film under a 454-gram weight. After 24 hours, the strips were separated and evaluated. For the elevated temperature (ET) block test, the paint strips after 1-day drying at CT/CH were placed in a 120°F oven for 30 minutes. A weight load of 1000 gram was transferred to the paint films via a 2.54-cm diameter rubber stopper. The films were allowed to cool for 30 minutes before the block ratings were given. Room and elevated temperature block were rated on the ASTM D-4946 scale from 0 (poorest) to 10 (best). The test was run in triplicate and the average value was reported.

Stain Resistance

Stain resistance was measured according to ASTM D4828-94 (2020). Each paint sample pair was prepared using an applicator drawdown bar with a gap of 7 mils where the paint sample and the control paint were drawn down side-by-side on a Black Leneta scrub chart. After drying for three days in the constant temperature and constant humidity (CT/CH) environmental chamber at 77±2 °F and 50% ±5% RH, the panel was stained with various stain media, covering both paints in a direction perpendicular to the direction the paints were applied. A strip of single ply paper towel was used to hold the liquid stains (e.g., coffee and wine) in place. To assure good contact with the sample, slight pressure was applied to the full length of the saturated strip. For this stain resistance test group, the following stain media were applied: mustard (French's), ketchup (Heinz), coffee (French roast coffee), red table wine (Carlo Rossi), grape juice (Concord), ball point pen (blue), pencil (No. 2B), purple crayon (Crayola), orange washable market (Crayola) and red lipstick (Covergirl). After the stains were applied, all samples were allowed to set with the stains for 2 to 2.25 hours from application of the last stain. After contact time, the excess stain material was rinsed under a stream of cold water and the panels were placed into the Scrub machine model D10 from Paul N. Gardner Company Inc. The use of two sponges, one for each paint, was used with special brush holders. Washing of the stains included the use of 10 mL of Formula 409® solution, added to the pre-moistened (with water) sponges. The Gardner scrub machine was run for 100 cycles. After testing, panels were rinsed and dried overnight. The change in ΔE value of the washed area where the stains were applied compared to a portion of the panel prior to staining and washing was reported. Lower ΔE values are indicative of less staining.

Tint strength

White paint tint strength was measured according to ASTM D4838-88(2016). In this test, 5.0 gram of phthalo blue colorant (Evonik's Colortrend 888-7214, colorant E) was added to 250.0 gram of base paint and then mixed for 5 minutes on a Red Devil shaker. The tinted paint was drawn down using an applicator bar with a 10-mil gap onto a Leneta 1B chart and immediately 30 cycles of rub-ups was performed on both sealed and unsealed sections. The CIE-Y reflectance was taken and the average of three measurements was reported. Comparative tint

strength was calculated from the Y reflectance data of the sample and a chosen control, according to the Kubelka-Munk formula:

$$\%TS_{KM} = \frac{[(1-Y\%_{batch})^2/(2Y\%_{batch})]}{[(1-Y\%_{control})^2/(2Y\%_{control})]}$$

Example 1: Production of Binder

Into a 1 gallon reactor was introduced an initial charge composed of 515 g of deionized water and 2.4 g of anionic surfactant I, 7.85 g acrylamide (30%) and 20 g pre-formed seed latex. 511.04 g of ethyl acrylate, 312.32 g of methyl methacrylate, 96.18 g of isobutyl acrylate, 18 g of diacetone acrylamide and 7.19 g of methacrylic acid were mixed with 33.65g of anionic surfactant II, 9.20 g of anionic surfactant III, 9.7 g of anionic surfactant IV, 4.2 g of anionic surfactant V and 252 g of deionized water to prepare monomer pre-emulsion. 0.53 g of sodium persulfate was weighed in a second glass beaker, dissolved in 8 g of deionized water to prepare initial initiator. 1.1 g of ammonium persulfate was dissolved in 41.5 g water in a third beaker to prepare delayed initiator. The contents of the reactor were heated to a temperature of 90 ± 2 °C. The initial initiator was first introduced into the reactor. Then the monomer pre-emulsion and the delayed initiator were fed into the reactor while keeping the reactor temperature at 90 ± 2°C over 210 mins. After the completion of the delayed initiator and monomer feeds, 27 gram of water was added to the reactor. The contents in reactor was cooked for 15 mins before allowing the medium to cool to 65 °C. During the 15 mins cook, a post oxidizer solution containing 1.9 g of 70% t-butyl hydroperoxide and 30 g of deionized water was prepared in a glass beaker. A post reducer solution containing 1.9 g of sodium metabisulfite and 31 g of deionized water was also prepared in a glass beaker. The post oxidizer and post reducer solutions were then fed into the reactor over 60 mins. The reactor was allowed to cool to room temperature. Then 9.2 g of adipic acid dihydrazide in 40 g of water and 22.5 grams of Stepcote® W-877 were added to the reactor. The pH of the latex was then adjusted to 7.5 with ammonia.

Examples 2-5

Latexes were prepared in the same manner as Example 1. Polymer compositions are shown in Table 1.

Comparative Example 1: Production of Binder

Latex was prepared in the same manner as Example 1. Polymer composition is shown in Table 1.

Comparative Example 2: Production of Binder

Latex was prepared in a similar manner as Comparative Example 1. Additional 19 g of Cavasol® W7 M TL (methyl-beta-cyclodextrin, solubilizing agent, Wacker) was charged to the reactor at the beginning of the reaction. Even in the presence of "phase transport catalyst" (US 5521266), the polymerization of the composition containing lauryl methacrylate did not produce as clean a product (higher filterable solids) as Examples 1-5 binders. Polymer composition is shown in Table 1.

Comparative Example 3: Production of Binder

Latex was prepared in a similar manner to Example 5, but without Stepcote® W-877.

Table 1. Polymer binder compositions by monomer weight percentage.

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5 Comp. Ex 3	Comp. Ex 1	Comp. Ex. 2
Monomer (a) (all bio-based)	EA	54	30	30	30		30	
	iBA	10	21			45		
	2-MBA			21				
	2-OA				21			
	BA					5		14
	LMA						21	36
Monomer (b)	MMA	33	46	46	46	47	46	47
Monomer (c)	MAA	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Monomer (d)	AM	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	DAAM	2	2	2	2	2	2	2
Calculated BCC (%)*		28	28	28	28	30	28	31
Measured BCC (%) by ASTM 6866-22 Method B		28				30		

Latex filterable (ppm)		<500	<500	<500	<500	<500	4727	778
Monomer (a) residual in latex (ppm)		<100	<100	<100	<100	<100	860	661

EA = ethyl acrylate, iBA = iso-butyl acrylate, 2-MBA = 2-methylbutyl acrylate, 2-OA = 2-octyl acrylate, LMA = lauryl methacrylate, MMA = methyl methacrylate, BA = butyl acrylate, MAA = methacrylic acid, AM = acrylamide, DAAM = diacetone acrylamide

* Calculation of BCC based on the total amount of biobased carbons from partially or fully biobased monomers a) and b) divided by the sum of total carbons in monomers a), b), c), d), and any additional monomer.

BCC = 100 x [(moles of biobased carbons)/(moles of total carbons)]

Examples 6-10. Preparation of coating compositions

The above aqueous dispersion examples 1-5 were evaluated in a coating composition shown in Table 2 and designated as Examples 6-10 in Table 3.

Comparative Examples 4-6: Preparation of coating composition

The above aqueous dispersion Comparative Examples 1, 2 and 3 were evaluated in a coating composition shown in Table 2 and designated as Comparative Examples 4, 5, and 6 in Table 3.

Table 2. Coating composition

Raw material	**Wet Pounds**	**Gallons**
Grind		
Water	40	4.8
Dispersant	7.0	0.78
Surfactant	2.0	0.24
Defoamer	2.0	0.27
Neutralizer	2.0	0.24
Pigment	360	18.46

Filler	12.5	0.57
Rheology modifier 1	24.0	2.71
Rheology modifier 2	3.0	0.35
Letdown		
Binder, 50% solids content (Ex. 1-5 or Comp. Ex. 1 or 2)	500	56.18
Coalescent	14	13.21
Water	110	1.77
Total paint	1076.5	99.58

The coating properties for each binder material are shown in Table 3.

Table 3. Coating properties.

(binder)	Ex. 6 (Ex. 1)	Ex. 7 (Ex. 2)	Ex. 8 (Ex. 3)	Ex. 9 (Ex. 4)	Ex. 10 (Ex. 5)	Comp. Ex. 4 (Comp. Ex. 1)	Comp. Ex. 5 (Comp. Ex. 2)	Comp. Ex. 6 (Comp. Ex. 3)
Scrub resistance (cycles)	>2500	>2500	>2500	>2500	>2500	>2500	>2500	
Tint strength (%) (higher is better)	104	105	101	101	99	100	96	
Total ΔE (lower is better)	38	32	33	36	38	52	100	
Block resistance (RT/ET) (higher is better)	9/7	7/6	9/6	9/7	8/8	8/8	9/8	0/0

It was surprising that the copolymer including the lauryl methacrylate has poorer tint strength and stain removal than the coating made with a binder including the lower alkyl (C1-C8) acrylate monomers. Most notably, clean removal of lipstick stain is a significant challenge with the copolymer comprising lauryl methacrylate as shown by the photo as well as the measured ΔE values on top of each photo. A higher ΔE indicates a greater degree of soiling due

to a deeper color left by the staining agents. The differences in stain resistance and stain removal between the inventive examples (Ex. 6-10) and comparative examples (Comp. Ex. 4 and Comp. Ex. 5) are also demonstrated by the total ΔE values in Table 3 which are the sums of 10 stains tested. Lower ΔE is more desirable. Comparative Example 6 compared to Example 10 shows the effect of alcohol phosphate ester surfactants on block resistance. Higher numbers are better in terms of block resistance.

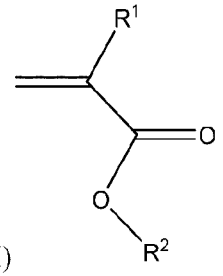
Within this specification embodiments have been described in a way which enables a clear and concise specification to be written, but it is intended and will be appreciated that embodiments may be variously combined or separated without departing from the invention. For example, it will be appreciated that all preferred features described herein are applicable to all aspects of the invention described herein.

The foregoing description of various forms of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise forms disclosed. Numerous modifications or variations are possible in light of the above teachings. The forms discussed were chosen and described to provide the best illustration of the principles of the invention and its practical application to thereby enable one of ordinary skill in the art to utilize the invention in various forms and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the scope of the invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally, and equitably entitled.

What is claimed is:

1. An aqueous polymeric dispersion comprising at least one copolymer formed by emulsion polymerization of a monomer mixture comprising, based on a total dry weight of the copolymer, monomers a), b), c), and d):

a) 20-80wt% of at least one monomer of structure (I):



(I)

where R^1 is a hydrogen or methyl group; and R^2 is a C1-C8, preferably C2- C6, more preferably C2- C4, non-cyclic alkyl group, and wherein a homopolymer of monomer a) has a glass transition temperature (Tg) less than 25 °C;

b) 20-80wt% of at least one ethylenically unsaturated monomer other than a) selected from the group consisting of C1-C8 alkyl (meth)acrylates, ethylene, vinyl acetate, vinyl versatates, styrene, styrene derivatives, or combinations thereof, optionally bio-based;

c) 0.1-10wt% of at least one ethylenically unsaturated monomer comprising at least one functional group comprising at least one of carboxylate, phosphate, phosphonate; sulfonate, and/or acid, and/or salt, and/or anhydride forms thereof; hydroxyl; silane; or combinations thereof; and

d) 0.1-10wt% of at least one nitrogen-bearing ethylenically unsaturated monomer;

wherein:

the copolymer comprises at least 5%, preferably at least 10%, more preferably at least 15%, most preferably at least 22% biocarbon content as determined by ASTM D6866-22 Method B; and

the aqueous polymeric dispersion has a minimum film formation temperature of 30°C or less.

2. The aqueous polymeric dispersion of claim 1, wherein monomer a) comprises at least 5%, preferably at least 10%, more preferably at least 20%, even more preferably at least 30%, most preferably at least 40 % biocarbon content as determined by ASTM D6866-22 Method B.

3. The aqueous polymeric dispersion of claim 1 or claim 2, wherein the monomer a) comprises at least one of ethyl (meth)acrylate, n-butyl (meth)acrylate, iso-butyl (meth)acrylate, 2-methylbutyl (meth) acrylate, t-butyl (meth)acrylates, heptyl (meth)acrylates, 2-octyl (meth)acrylate, or a combination thereof, said monomer a) comprising at least 40% biocarbon content as determined by ASTM D6866-22 Method B.

4. The aqueous polymeric dispersion of any of claims 1-3, wherein the monomer a) is selected from the group consisting of ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, 2-methylbutyl (meth)acrylate, 2-octyl (meth)acrylate, or a combination thereof.

5. The aqueous polymeric dispersion of any of claims 1-4, wherein the monomer b) comprises at least one of methyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, vinyl acetate, styrene, or a combination thereof.

6. The aqueous polymeric dispersion of any of claims 1-5, wherein the monomer c) comprises at least one of carboxylic acid-functionalized monomers, phosphorus-bearing monomers, sulfur-bearing monomers, hydroxyl or silane or combinations thereof.

7. The aqueous polymeric dispersion of any of claims 1-6, wherein the monomer c) comprises at least one of (meth)acrylic acid, phosphates, sulfates, hydroxyalkyl (meth)acrylates, 2- hydroxy-3-phenoxypropyl methacrylate, (meth)acryloxyalkyl trialkyloxysilanes, vinyltrialkoxysilanes, or combination thereof.

8. The aqueous polymeric dispersion of any of claims 1-7, wherein the monomer c) is selected from the group consisting of acrylic acid, methacrylic acid, or a combination thereof.

9. The aqueous polymeric dispersion of any of claims 1-8, wherein the monomer d) comprises at least one of acrylamides, (meth)acrylamide; diacetone acrylamide; (meth)acrylates with at least one of ureido, urea, or thiourea in the side chains; acrylic allophanes; aminoalkyl (meth) acrylates; dialkylamino (meth)acrylates; or a combination thereof.

10. The aqueous polymeric dispersion of any of claims 1-9, wherein the monomer d) is selected from the group consisting of acrylamides, (meth)acrylamide, diacetone acrylamide, ureido (meth)acrylate, or a combination thereof.

11. The aqueous polymeric dispersion of any of claims 1-10, comprising at least 0.1wt% of at least one additional free radical reactive compound, the additional free radical reactive compound comprising at least one of a chain transfer agent; a copolymerizable surfactant; a monomer comprising two or more unsaturated carbon-carbon double bonds; or combinations thereof.

12. The aqueous polymeric dispersion of any of claims 1-11, wherein the total percentages of the monomers a), b), c), d), and the optional free radical reactive compound add up to 100%.

13. The aqueous polymeric dispersion of any of claims 1-12, wherein the copolymer comprises:

from 45-60 wt% of monomer a) and monomer a) comprises at least one of ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, 2-methylbutyl (meth)acrylate, 2-octyl (meth)acrylate, or a combination thereof.

from 40-55 wt% of monomer b) and monomer b) comprises at least one of methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, or combination thereof;

from 0.1-10 wt% of monomer c) and monomer c) comprises at least one carboxylate functional group and/or acid, and/or salt, and/or anhydride form thereof;

from 0.1-10 wt% of monomer d) and monomer d) comprises at least one of (meth)acrylamide, diacetone acrylamide or a combination thereof; and

wherein the copolymer comprises at least 22% biocarbon content as determined by ASTM D6866-22 Method B; and

the aqueous polymeric dispersion has a minimum film formation temperature less than 30°C.

14. The aqueous polymeric dispersion of any of claims 1-13, wherein the copolymer comprises a monomer comprising at least one carbonyl group reactive with a latent crosslinking agent, the monomer preferably comprising at least one 1,3-dicarbonyl group, more preferably comprising diacetone acrylamide.

15. The aqueous polymeric dispersion of any of claims 1-14, further comprising at least one additive.

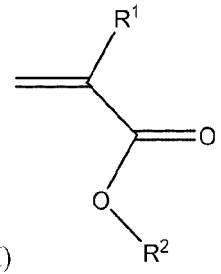
16. The aqueous polymeric dispersion of claim 15, wherein the additive comprises at least two hydrazine and/or hydrazide moieties.

17. The aqueous polymeric dispersion of claim 14 or claim 15, wherein the additive comprises alcohol phosphate ester surfactant or salt thereof, preferably potassium n-octyl phosphate, sodium n-octyl phosphate, or lithium n-octyl phosphate, more preferably potassium n-octyl phosphate.

18. A coating composition comprising the aqueous polymeric dispersion of any of claims 1-17.

19. A coating composition comprising an aqueous polymeric dispersion comprising at least one copolymer formed by emulsion polymerization of a monomer mixture comprising, based on a total dry weight of the copolymer, monomers a), b), c), and d):

a) 20-80wt% of at least one monomer of structure (I):



(I)

where R^1 is a hydrogen or methyl group; and R^2 is a C1-C8, preferably C2- C6, more preferably C2- C4, non-cyclic alkyl group, and wherein a homopolymer of monomer a) has a glass transition temperature (Tg) less than 25 °C;

b) 20-80wt% of at least one ethylenically unsaturated monomer other than a) selected from the group consisting of C1-C8 alkyl (meth)acrylates, ethylene, vinyl acetate, vinyl versatate, styrene, styrene derivatives, or combinations thereof;

c) 0.1-10wt% of at least one ethylenically unsaturated monomer comprising at least one functional group comprising at least one of carboxylate, phosphate, phosphonate, sulfonate; and/or acid, and/or salt, and/or anhydride forms thereof; hydroxyl; silane; or combinations thereof; and

d) 0.1-10wt% of at least one nitrogen-bearing ethylenically unsaturated monomer

wherein:

the copolymer comprises at least 5%, preferably at least 10%, more preferably at least 15%, most preferably at least 22% biocarbon content as determined by ASTM D6866-22; and

the aqueous dispersion has a minimum film formation temperature less than 30°C.

20. The coating composition of claim 19, wherein the copolymer further comprises at least 0.1wt% of at least one free-radical reactive compound, the free-radical reactive compound comprising at least one of a chain transfer agent; a copolymerizable surfactant; a monomer comprising two or more unsaturated carbon-carbon double bonds; or combinations thereof.

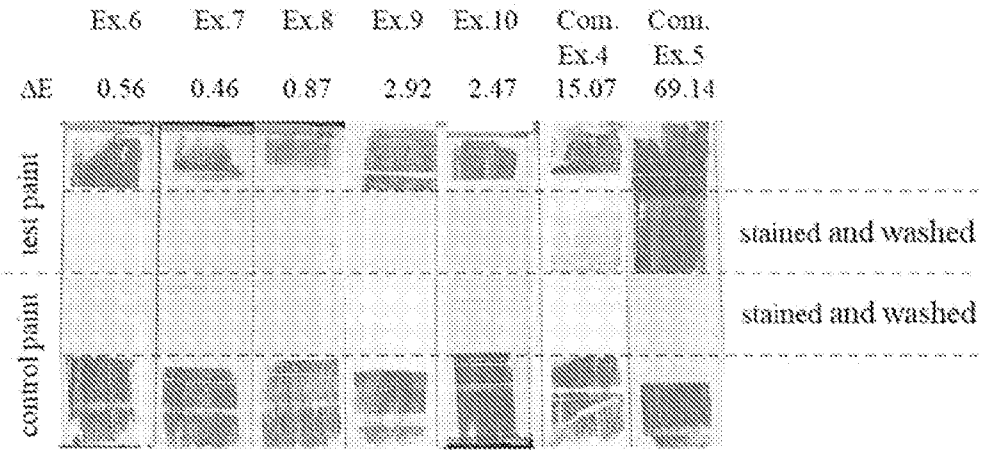
21. The coating composition of claim 19 or claim 20, wherein the copolymer comprises a monomer comprising at least one carbonyl group reactive with a latent crosslinking agent, the monomer preferably comprising at least one 1,3-dicarbonyl group, more preferably diacetone acrylamide.

22. The coating composition of any of claims 19-21, further comprising at least one additive.

23. The coating composition of claim 22, wherein the additive comprises at least two hydrazine and/or hydrazide moieties.

24. The coating composition of claim 22 or claim 23, wherein the additive comprises alcohol phosphate ester surfactant or salt thereof, preferably potassium n-octyl phosphate, sodium n-octyl phosphate, or lithium n-octyl phosphate, more preferably potassium n-octyl phosphate.

Figure 1


Ex.6
Ex.7
Ex.8
Ex.9
Ex.10
Com. Ex.4
Com. Ex.5
ΔE
0.56
0.46
0.87
2.92
2.47
15.07
69.14
test paint
control paint
stained and washed
stained and washed