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(54) **Title:** ALKENE VINYL ALKANOATE COPOLYMERS AND POLYMERIZATION METHODS THEREFOR

(57) **Abstract:** Hybrid copolymers are described having a particular utility for use in coatings such as latex paints, stains, lacquers, etc. The hybrid copolymers demonstrate improved washability and scrubability at the same, time as compared to copolymers and coatings with traditional binders. The hybrid copolymers may include a hybrid ethylene/styrene/vinyl acetate copolymer and methods of making such copolymers.



ALKENE VINYL ALKANOATE COPOLYMERS AND POLYMERIZATION METHODS THEREFOR

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. provisional application number 62/321,350 filed on April 12, 2016, the entirety of which is hereby incorporated by reference

BACKGROUND

1. Field

[0002] This application relates generally to alkene vinyl alkanoate copolymers and methods of making thereof and, more specifically, to hybrid alkene vinyl alkanoate copolymer binders for coatings such as paints, stains, lacquers, etc.

2. Description of Related Art

[0003] Paints and coatings typically contain four ingredients: a carrier liquid, a binder, one or more pigments, and additive(s) to provide the paint with desired properties. Each such ingredient may comprise a single component or several different components mixed into the paint.

[0004] The binder is a resinous or polymeric material that surrounds the pigment particles, binds them together, and gives the paint film its integrity. When paint is applied to a surface and dries, the binder adheres the pigment to that surface. The binder tends to effect many of the paint properties including, but not limited to, adhesion, resistance to bubbling, cracking and peeling, resistance to scrubbing and fading, and application properties such as flow/sag, leveling and gloss development to suggest but a few. In a latex paint, the binder traditionally comprises a latex resin, usually selected from copolymers employing an acrylic, vinyl acrylic (i.e., vinyl acetate and acrylate) or styrene acrylic (i.e., vinyl acetate and styrene) polymeric support resins or copolymers.

[0005] In some instances, styrene and vinyl acetate copolymers are difficult to produce by conventional polymerization methods because of their disparate reactivities. It is believed that vinyl acetate polymerizes very quickly relative to the polymerization rate of styrene because of its destabilized radical intermediate. Earlier efforts at styrene/vinyl acetate copolymerization have required the inclusion of additives, e.g. radical stabilizers or inhibitors, or complex polymerization methodologies. In addition, incorporation of ethylene presents special challenges given that ethylene is a gaseous monomer that requires high pressures for incorporation into the copolymer backbone.

BRIEF SUMMARY

[0006] The hybrid copolymers described herein have particular utility for use in coatings such as paints, stains, lacquers, etc. Specifically, the hybrid copolymers herein demonstrate improved washability and scrubbability at the same time as compared to copolymers and coatings with traditional compositions formed according to traditional methods.

[0007] According to one aspect, the subject application involves an ethylene/styrene/ vinyl acetate copolymer and methods of making such. More specifically, the subject application involves a hybrid ethylene/styrene/vinyl acetate copolymer that may employ a terpolymer support resin onto which ethylenically unsaturated monomers, such as styrene monomers, have been grafted. Also described are methods of making such hybrid ethylene/styrene/vinyl acetate copolymer via a mini-emulsion method. According to another aspect, the subject application involves a hybrid copolymer comprising a terpolymer support polymeric backbone onto which styrene and optionally (meth)acrylic and (meth)acrylate monomers have been grafted as polymeric side chains. An exemplary terpolymer for use with the present disclosure comprises a copolymer chain of ethylene/vinyl acetate/carbon monoxide monomer units. According to another aspect, the subject application involves methods of making the aforementioned hybrid copolymers via mini-emulsion processes and, in some instances, also using static mixer processes.

[0008] In one aspect, a hybrid copolymer suitable as a binder for latex coating compositions is provided herein. The hybrid copolymer may include a copolymer backbone including a poly (alkene-vinyl alkanoate-ketone) with carbon atoms adjacent a ketone carbonyl moiety and a polymeric side chain including at least one or more ethylenically unsaturated monomeric units grafted to the copolymer backbone. At least a portion of the ethylenically unsaturated monomer units are grafted to the carbon atoms adjacent the ketone carbonyl moiety in the poly (alkene-vinyl acetate- ketone).

[0009] In other approaches of this aspect, the hybrid copolymer of the preceding paragraph may be combined with one or more optional features. These optional features include wherein the poly (alkene-vinyl alkanoate-ketone) includes a plurality of vinyl alkanoate monomer units, a plurality of alkene monomer units, and carbon monoxide monomer units; wherein poly (alkene-vinyl alkanoate-ketone) includes vinyl alkanoate monomer units, alkene monomer units, and carbon monoxide monomer units randomly arranged along the copolymer backbone; wherein the vinyl alkanoate monomer units of the

poly (alkene-vinyl alkanoate-ketone) includes vinyl acetate; wherein the poly (alkene-vinyl alkanoate ketone) includes ethylene and vinyl acetate; wherein the hybrid copolymer includes up to about 30 weight percent of the poly (alkene-vinyl alkanoate-ketone); wherein the ethylenically unsaturated monomer units are selected from the group consisting of styrene, vinyl acetate, vinyl chloride, acrylic acid, (meth)acrylic acid, maleic acids, itaconic acid and their esters, amides with alcohols, and amines and mixtures thereof; wherein the weight percent of ethylenically unsaturated monomer in the hybrid copolymer is about 70 to about 98 weight percent and wherein at least a portion thereof are grafted to the copolymer backbone; wherein the hybrid copolymer further includes acrylic monomer units, methacrylic monomer units, or combinations thereof, and wherein at least a portion are grafted to the copolymer backbone; wherein a weight percent of the acrylic monomer units, methacrylic monomer units, or combinations thereof is about 5 to about 55 weight percent; wherein the hybrid copolymer further includes acrylic or methacrylic acid; wherein the hybrid copolymer further includes methacrylic and/or acrylic acid and wherein a weight percent of the methacrylic and/or acrylic acid is about 1 to about 5 weight percent; wherein the hybrid copolymer includes about 40 to about 65 weight percent styrene monomer units, about 2 to about 30 (in in other approaches, about 10 to about 20) weight percent poly(alkene-vinyl alkanoate ketone) monomer units, about 5 to about 55 weight percent acrylic monomer units, and about 1 to about 5 weight percent methacrylic or acrylic acid monomer units; wherein at least a portion of one or more of the styrene monomer units, the acrylic monomer units, the methacrylic acid monomer units, and mixtures thereof are mixed with the hybrid copolymer but not grafted thereto to form a hybrid copolymer composition including the hybrid copolymer and the ungrafted monomer units; and/or wherein the copolymer backbone includes ethylene, vinyl acetate, and ketone monomer units randomly polymerized within the copolymer backbone.

[0010] In another aspect, a method of making a hybrid copolymer of the preceding two paragraphs is provided. In one approach, the method includes free radical polymerization within a mini-emulsion blend having an average particle size of about 40 nm to about 700 nm.

[0011] In yet another aspect, a latex coating composition is provided. The latex coating composition includes about 4 to about 65 (in other approaches, about 4 to about 30; in other approaches about 30 to about 65) solids weight percent hybrid copolymer having a copolymer backbone including a poly (alkene-vinyl alkanoate-ketone) with carbon atoms adjacent a ketone carbonyl moiety and a polymeric side chain including at least one or more

ethylenically unsaturated monomeric units grafted to the copolymer backbone. The ethylenically unsaturated monomer units in the side chain are selected from styrene, vinyl acetate, vinyl chloride, acrylic acid, (meth)acrylic acid, maleic acids, itaconic acid and their esters, amides with alcohols, and amines and mixtures thereof. The latex coating composition further includes about 0 to about 2 weight percent solvent and about 0 to about 60 (in other approaches, about 0 to about 30, in other approaches about 30 to about 60, in yet other approaches about 16.2 to about 60, and in yet other approaches about 0 to about 50.9) weight percent inorganic particle

[0012] In other approaches of this aspect, the latex coating composition of the preceding paragraph may be combined with one of more optional features. These optional features may include any of those discussed previously and/or may further include at least a portion of the ethylenically unsaturated monomer units grafted to the carbon atoms adjacent the ketone carbonyl moiety in the poly (alkene-vinyl acetate- ketone); wherein the poly (alkene-vinyl alkanoate ketone) includes ethylene and vinyl acetate; wherein the hybrid copolymer includes up to about 30 weight percent of the poly (alkene-vinyl alkanoate- ketone); wherein the weight percent of ethylenically unsaturated monomer in the hybrid copolymer is about 70 to about 98 weight percent and wherein at least a portion thereof are grafted to the copolymer backbone; wherein the hybrid copolymer further comprises acrylic monomer units, methacrylic monomer units, and combinations thereof, and wherein at least a portion are grafted to the copolymer backbone; wherein a weight percent of the acrylic monomer units, methacrylic monomer units, and combinations thereof is about 5 to about 55 weight percent; wherein the hybrid copolymer further includes methacrylic and/or acrylic acid and wherein a weight percent of the methacrylic and/or acrylic acid is about 1 to about 5 weight percent; and/or wherein the hybrid copolymer includes about 40 to about 65 weight percent styrene monomers, about 2 to about 30 weight percent poly(alkene-vinyl alkanoate ketone), about 5 to about 55 weight percent acrylic monomers, and about 1 to about 5 weight percent methacrylic or acrylic acid.

[0013] The above summary presents a simplified summary in order to provide a basic understanding of some aspects of the copolymers, compositions, coatings and/or methods discussed herein. This summary is not an extensive overview of the copolymers, compositions, coatings, and/or methods discussed herein.

DETAILED DESCRIPTION

[0014] As mentioned above, latex paints and coatings may often include binders of acrylic, vinyl acrylic (i.e., vinyl acetate and acrylate) or styrene acrylic (i.e., vinyl acetate and styrene) polymeric support resins or copolymers. Styrene acrylic binders are often desired because they tend to be chemically or stain resistant, but such binders may often result in coatings that are not necessarily washable and often hard to clean. Ethylene vinyl acetate may also be incorporated into binders. Ethylene vinyl acetate binders may be more easily washable, but tend to have the shortcoming that they are not as chemically or stain resistant as other binders. Thus, many latex paints or coatings have good washability, but less than desired stain resistance and other latex paints or coatings have good stain resistance, but less than desired washability. A shortcoming of many prior binders is that coatings including such prior binders tend not to have high performance in both properties at the same time.

[0015] Disclosed herein are hybrid copolymers including a support resin or copolymer backbone of a poly (alkene-vinyl alkanoate-ketone) copolymer and grafted thereto at least one ethylenically unsaturated monomer unit(s) as a polymeric side chain. The binders of the present application include these hybrid copolymer compositions and surprisingly provide good washability and stain resistance at the same time.

[0016] Certain terminology is used herein for convenience only and is not to be taken as a limitation on the present disclosure. It is also to be noted that the phrase “at least one of” or “at least one”, if used herein, followed by a plurality of members herein means one of the members, or a combination of more than one of the members. For example, the phrase “at least one of a first widget and a second widget” means in the present application: the first widget, the second widget, or the first widget and the second widget. Likewise, “at least one of a first widget, a second widget and a third widget” means in the present application: the first widget, the second widget, the third widget, the first widget and the second widget, the first widget and the third widget, the second widget and the third widget, or the first widget and the second widget and the third widget.

Glossary of Terms

[0017] As used herein, the term “hybrid copolymer” or hybrid copolymer composition generally indicates a polymer or copolymer comprising at least two different polymeric materials or monomer units with at least a partially grafted arrangement. The copolymer is preferably a random copolymer. That is, the graft hybrid copolymer includes a substantially-linear backbone or support copolymer formed from a first polymeric or copolymer material with random polymeric or monomer units and regularly or randomly-

arranged side chains or branches of another polymeric material or monomer units extending transversely from the backbone as a side chain. In one approach, the branched polymeric side chains are structurally distinct from the polymeric material of the backbone, and each of the backbone and the side chain branches may be independently formed as segmented homopolymers or copolymers. The hybrid copolymer is at least partially grafted, and can optionally be fully grafted or less-than-fully grafted, meaning a hybrid copolymer composition can include both a grafted component comprising the graft copolymer (backbone and side chains) and an ungrafted component comprising the polymeric materials forming the backbone and/or the branches of the grafted component, but in an ungrafted state (e.g., suspended separately in the same medium or composition). In one embodiment, the hybrid copolymer utilizes a copolymer comprising poly (alkene-vinyl alkanoate-ketone) as a support resin or copolymer backbone, onto which one or more ethylenically unsaturated monomer units, such as styrene and other optional monomer units can be grafted in the same side chain. In another embodiment, the copolymer backbone or support resin is a terpolymer including a random arrangement of alkene, vinyl alkanoate and ketone monomer units, which may be ethylene, vinyl acetate, and carbon monoxide. Such ethylene/alkyl acetate /carbon monoxide copolymers are commercially available from E. I. du Pont de Nemours and Company (DuPont) under the ELVALOY tradename.

[0018] “Binder(s)” as used herein refers to long chain molecules of polymers or resins that are film-forming materials. Binders are generally responsible for gluing or binding coating materials together and to the substrate.

[0019] “Graft copolymer” or graft monomer unit(s) as used herein generally refers to branched or side chain polymers or monomer unit(s) thereof composed of different monomers to that of the support resin or copolymer backbone. The compositions herein may also include un-grafted copolymer side chains that are produced during the polymerization step. Preferably, the polymers and polymeric compositions herein are random polymers and the grafted copolymer side chains preferably have a random configuration as well. In one approach, at least a portion of the side chains are grafted to a carbon atom adjacent a ketone-carbonyl moiety of the support resin or copolymer backbone.

[0020] “Coatings” as used herein refer to compositions such as paints, stains, lacquers, etc. “Paint” as used herein generally refers to any mixture including different types of raw materials, each with its own function, which tend to be balanced to achieve the desired properties in the final product or film coating. The two primary functions of paint are decoration and protection. A paint may contain a solvent (which can include a volatile

component derived from a petroleum distillate for a solvent-based paint, or a low VOC, or no-VOC, or water for a water-based paint), a binder, a pigment, fillers (such as an extender or a plurality of extenders of different sizes) and an additive, which may impart different functionality to the paint or final coating. Embodiments of the present disclosure may include the hybrid copolymer and/or the hybrid copolymer compositions herein as a binder within coatings, optionally in combination with at least one of the solvent, pigment, fillers, and additive(s).

[0021] “Additives” as used herein refer to a general category of components or other raw materials that may be added to the coatings herein to promote various properties. Examples include, but are not limited to, surfactants, defoamers, biocides, mildewcides, algaecides, thickeners, anti-settling agents, pH buffers, corrosion inhibitors, driers, and/or anti-skinning agents.

[0022] “Pigment Volume Concentration” or “PVC” as used herein refers to a number that represents the volume of pigment compared to the volume of all solids. In the field of paints and coatings, PVC is a useful measure because the Binder acts as the material to unite all the pigment and other raw materials into the paint and the PVC value ensures there is enough Binder to enable the paint to adhere properly to whatever it has been applied over in addition to containing all of the other components of the paint. If a paint has no pigment at all it will usually be very glossy and have a PVC of zero. An example is clear gloss paints. Flat paints have a very high pigment loading and have high PVCs (usually in the range from about 35% up to about 80%). Another non-limiting exemplary range of PVC in which pigment can be loaded is from about 60% to about 75%. Primers and undercoats vary from 30% to about 50% PVC as do semi-gloss, satin and low sheen paints.

[0023] “Scrubbability” or “Scrub” as used herein generally refers to the ability of the coating to resist erosion caused by scrubbing. Scrub is based on ASTM D2486-06 as described further in the Examples below.

[0024] “Washability” as used herein refers to the ability of a coating to exhibit stain resistance and stain removal properties. Washability is based on ASTM D3450-15 as described further in the Examples below.

[0025] “Adhesion” or “Wet Adhesion” as used herein refers to the ability of a dried coating to adhere to a glossy polyester paint (such as Sherwin Williams ProMar 200 Alkyd Semi-gloss) when wet. Adhesion is based on ASTM D6900-10 (reapproved 2015) as described further in the Examples below.

Hybrid Copolymer

[0026] The present disclosure is generally directed to, in one aspect, a hybrid ethylene/styrene/vinyl acetate copolymer with a grafted polymeric side chain and methods of making such. More specifically, the subject application involves a hybrid ethylene/styrene/vinyl acetate copolymer that may employ a terpolymer support resin onto which ethylenically unsaturated monomer units, such as the styrene, have been grafted as polymeric side chains. Also described are methods of making such hybrid ethylene/styrene/vinyl acetate copolymer via a mini-emulsion polymerization method.

[0027] According to another aspect, the subject application involves a hybrid copolymer comprising a terpolymer support or copolymer backbone onto which styrene monomer units and optional (meth)acrylic and/or (meth)acrylate monomer units have been grafted as side chains (and in some approaches, the same side chain in a random fashion). An exemplary terpolymer for use with the present application comprises a random copolymer of ethylene, vinyl acetate, and carbon monoxide monomer units. According to another aspect, the subject application involves methods of making the aforementioned hybrid copolymers via mini-emulsion processes and, in some instances, also using static mixer processes.

[0028] According to yet another aspect, the subject application involves a hybrid copolymer composition suitable as a binder for coatings, such as paints, stains, lacquers and the like. In one approach, the hybrid copolymer binder composition includes a copolymer backbone or support copolymer including a poly (alkene-vinyl alkanoate-ketone) having carbon atoms adjacent a ketone carbonyl moiety; a polymeric side chain including at least one or more ethylenically unsaturated monomer unit(s), such as styrene and optional (meth)acrylics and/or alkyl (meth)acrylates, grafted to the copolymer backbone in the polymeric side chains; and at least a portion of the ethylenically unsaturated monomer units grafted to the carbon atoms adjacent the ketone carbonyl moiety in the poly (alkene-vinyl alkanoate ketone) backbone or support copolymer.

[0029] Turning to more of the specifics, examples of suitable poly(alkene-vinyl alkanoate-ketone) terpolymers for the backbone or support copolymer, such as poly(ethylene/alkyl acetate/carbon monoxide) terpolymers, are disclosed in U.S. Patent Nos. 3,780,140; 4,172,939; and 6,133,367; each of which is incorporated by reference herein. These copolymers are generally random terpolymers including about 10 to about 60 weight percent vinyl acetate (in other approaches, about 20 to about 30 weight percent vinyl acetate, and in yet other approaches, about 24 to about 28 weight percent vinyl acetate), about 40 to about 80 weight percent alkenes such as ethylene and the like, and about 3 to about 30 weight

percent carbon monoxide (in other approaches, about 5 to about 15 weight percent carbon monoxide). Examples of suitable terpolymers for use with the present disclosure is ELVALOY 742, ELVALOY 741 and/or ELVALOY 4924 (all from DuPont). According to other embodiments, the hybrid copolymer may include a terpolymer including an ethylene/vinyl acetate/acrylate copolymer as a support resin or copolymer. Such resins or copolymers may include about 9 to about 40 weight percent vinyl acetate and suitable examples are commercially available from DuPont under the tradename ELVAX.

[0030] Utilizing the terpolymer backbone as described herein is advantageous because it allows for the incorporation of ethylene and vinyl acetate into a hybrid copolymers for use as a paint binder at low pressures (e.g. ~ 1 atm.). Moreover, without being bound by theory, it is believed that the inclusion of carbon monoxide in an exemplary terpolymer chain promotes the grafting of other monomers, e.g. styrene and vinyl acetate polymeric side chains, to form the desirable hybrid copolymers described herein.

[0031] Terpolymers used in the backbone for the hybrid copolymers of the present disclosure have weight average molecular weights (Mw) of up to about 400,000. In one aspect, terpolymers of the present disclosure have average molecular weights of up to about 250,000, such as up to about 40,000; up to about 100,000; up to about 150,000; up to about 200,000; or about 250,000, including intermediate values and ranges. In other aspects, the terpolymers have weight average molecular weights ranging from about 40,000 to about 400,000; in other approaches, about 40,000 to about 270,000; and in yet other approaches, about 40,000 to about 100,000.

[0032] The hybrid copolymers of the present disclosure further include styrene and optional (meth)acrylic and alkyl (meth)acrylate as the ethylenically unsaturated monomer units of the grafted side chains, which are grafted as a polymeric side chain to the terpolymer backbone. As used herein, "styrene" includes styrene ($C_6H_5CH=CH_2$) as well as other functionalized styrene monomers, e.g. bromostyrene, methylstyrene, nitrostyrene, styrene sulfonate, divinyl benzene, etc. As used herein, alkyl (meth)acrylates in the grafted side chains include at least lower chain alkyl (meth)acrylates like C1 to C4 alkyl (meth)acrylates and includes both acrylates and methacrylates.

[0033] The hybrid copolymers of the present disclosure may further include optional (meth)acrylate monomer units. As used herein, "(meth)acrylate" includes both acrylate monomer units and methacrylate monomer units as well as functionalized (meth)acrylate monomer units suitable for incorporation into the hybrid copolymers disclosed herein. Examples of suitable (meth)acrylate monomer units include, but are not limited to,

alkyl (meth)acrylates, including methacrylate, butyl acrylate, 2-ethylhexylacrylate, C12/C18 alkylacrylate, polyethyleneglycol acrylate or diacrylate, acetoacetoxyethyl acrylates, diacetone acyl halides, benzophenone (meth) acrylates, etc. Additionally, vinylic monomers or other monomers may be functionalized or bear functional moieties that are utilized in post application functions, such as cross-linking, light or heat induced grafting. Functional moieties may also bear crosslinking groups, photo-reactive groups, anti-fouling agents, light absorbers, anti-corrosion agents, and the like.

[0034] Hybrid copolymers of the present disclosure (that is, backbone plus grafted side chains) may have weight average molecular weights (Mw) of up to about 1 million. In some aspects, the hybrid copolymers have average molecular weights of up to about 500,000. In other aspects, hybrid copolymers according to the present disclosure have average molecular weights of up to about 400,000, such as up to about 250,000; up to about 300,000; up to about 350,000; or about 400,000, including intermediate values and ranges of the above. In other aspects, the hybrid copolymers of the present disclosure may have weight average molecular weights of about 250,000 to about 1 million; in other approaches, about 250,000 to about 400,000; and in yet other approaches, about 250,000 to about 300,000.

[0035] Hybrid copolymers of the present disclosure preferably demonstrate single phase structures, despite (in some approaches) the inclusion of grafted and ungrafted (mixed) polymeric monomers, as evidenced by a single glass transition temperature (T_g). In one embodiment according to the present disclosure, the single T_g of the hybrid copolymers of the present disclosure is between about 10 to about 35 °C and, in other approaches, about 10 to about 31 °C, in other approaches about 30 to about 35 °C, and in other approaches about 10 to about 20 °C.

[0036] The hybrid copolymer herein may include ethylenically unsaturated monomer units (such as styrene and optional alkyl (meth)acrylate), ethylene/vinyl acetate/carbon monoxide monomer units, alkyl (meth)acrylate monomer units (such as butyl (meth)acrylate), and methacrylic acid monomer units as part of the binder copolymer or copolymer composition. In one approach, the copolymer includes about 70 to about 98 weight percent ethylenically unsaturated monomer units (such as styrene) as the grafted side chain copolymer unit, in another approach, about 70 to about 95 weight percent, in another approach, about 77 to about 90 weight percent, in yet other approaches, about 90 to about 95 weight percent, and in yet other approaches, about 80 to about 90 weight percent of the ethylenically unsaturated monomer units (such as styrene). The compositions may also include about 2 to about 30 weight percent poly (alkene-vinyl alkanoate-ketone) monomer

units, such as poly(ethylene-vinyl acetate-carbon monoxide) monomer units, in other approaches, about 5 to about 30 weight percent, in yet other approaches, about 10 to about 20 weight percent of the terpolymer monomer units, in other approaches, about 12 to about 20 weight percent of the terpolymer monomer units, in yet other approaches, about 15 to about 20 weight percent of the terpolymer, and in yet other approaches about 10 to about 15 weight percent of the terpolymer and other ranges within these endpoints. The copolymer may include about 7 to about 55 weight percent alkyl (meth)acrylate (such as butyl (meth)acrylate), in other approaches, about 42 to about 55 weight percent, and in yet other approaches, about 33 to about 47 weight percent alkyl (meth)acrylate (such as butyl (meth)acrylate). The composition may also include (meth)acrylic acid from about 1 to about 3 weight percent (meth)acrylic acid, in other approaches, about 1 to about 2 weight percent (meth)acrylic acid; and in yet other approaches, about 1 to about 1.4 weight percent of the (meth)acrylate acid.

Manufacture of Hybrid Copolymer and Compositions Thereof

[0037] The present disclosure also includes methods of making the hybrid copolymers and hybrid copolymer compositions described hereinabove. The hybrid copolymers can optionally be synthesized via a mini-emulsion polymerization technique. Mini-emulsion techniques provide for the incorporation of monomers into submicron (e.g., having an average droplet diameter from about 40 to about 700 nm, and in other approaches, approximately 50 nm to approximately 500 nm) droplets. According to one embodiment, the mini-emulsions are made using a micro-fluidizer having a chamber pressure approximately equal to about 10 to about 15K psi pressure during polymerization. The micro-fluidizer employs a high-shear mechanical technology to achieve uniform particle size reduction. In another embodiment, the mini-emulsions of the present disclosure are made using a static mixture, an instrument that provides continuous mixing of fluid materials within a cylindrical metallic mesh.

[0038] A mini-emulsion is typically obtained by shearing a mixture comprising, for example, an oil phase and a water phase. Mini-emulsion methods are particularly useful for incorporating hydrophobic monomers/polymers into sub-micron, mini-emulsion droplets. Individual mini-emulsion droplets can then be converted into individual copolymer units using conventional emulsion polymerization technologies. The mini-emulsions can be made by combining an oil (organic) phase comprising one or more hydrophobic polymers or copolymer precursors (e.g. monomers) with an aqueous (water) phase comprising water, one

or more buffers, and one or more surfactants. Examples of suitable surfactants can include both ionic and non-ionic surfactants with high, low or intermediate HLB values, such as nonylphenol ethoxylate (TERGITOL NP-10, Dow Chemical) and sodium lauryl ether sulfate (POLYSTEP B-23, Stepan Co.). The water phase is added to the oil phase (or vice versa) to form a coarse emulsion, from which the mini-emulsion is made through use of the aforementioned high shear divide.

[0039] According to one embodiment, the mini-emulsion described herein are produced using a micro-fluidizer such as those offered by Microfluidics Corp., for example. Micro-fluidization methods work by a high shear process whereby the coarse emulsion is divided into two or more fluid streams. Flow through a reaction chamber is characterized by high fluid velocities and subsequent impingement of fluid jets to the chamber walls or to one another. As a result, the fluid streams encounter highly turbulent conditions and interact at the nanometer level to produce exceptionally fine mini-emulsions with uniform particle size.

[0040] According to another embodiment, the hybrid copolymers can be made using a static mixer, such a Sulzer-type SMX mixer. A static mixer consists of in-line motionless mixing elements typically inserted in tubes or pipes allowing for continuous mixing of fluids. Mixing is achieved by splitting a multiphase (e.g. oil and water) stream into a large number of layers within each mixing element. The mixing elements are positioned in such a way as to change the mixing direction from one element to the next. The mixing flowrate can be varied as desired. The geometry of the system provides a high degree of homogeneity to the fluid and, as the feed stream proceeds through the system, it generates nano-droplets of the feed stream to provide the desired micro-emulsion. Large batches for industrial scale preparation of the hybrid copolymers can be processed using large diameter mesh cylinders.

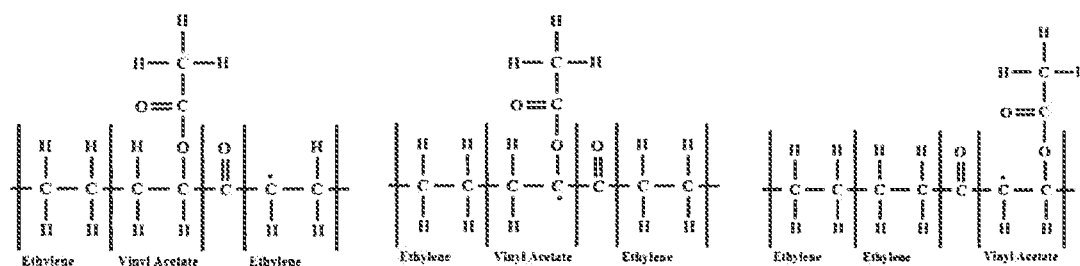
[0041] The average particle size of the mini-emulsion can be less than or equal to about 500 nm. However, other embodiments include average particle sizes less than or equal to about 400 nm, less than or equal to about 300 nm, less than or equal to about 200 nm or less than or equal to about 100 nm, including intermediate values and ranges. Yet other embodiments can include average particle sizes of the mini-emulsion from about 150 to about 200 nm, or from about 160 to about 190 nm. Once made, the mini-emulsion droplets can be converted into individual copolymer particles using any desired emulsion polymerization technique.

[0042] Without being bound by theory, it is believed that the inclusion of an electron withdrawing group, such as a ketone moiety, within the poly (alkene-vinyl alkanoate

ketone) promotes the grafting of copolymers onto the poly (vinyl alkanoate ketone) copolymer by stabilizing a carbon radical within the poly (vinyl alkanoate ketone) copolymer adjacent the electron withdrawing group within the poly (vinyl alkanoate ketone).

Copolymers or monomer units that may be grafted onto the poly(vinyl alkanoate ketone) due to such stabilizing of a carbon radical include, but are not limited to, styrene containing copolymers, acrylate containing copolymers and methacrylate containing copolymers.

[0043] The copolymers may be grafted onto the poly (alkene vinyl alkanoate ketone) copolymer by a termination reaction between the copolymer and a carbon radical within the poly (vinyl alkanoate ketone) copolymer adjacent a ketone moiety. In combination or the alternative, the copolymers may be grafted onto the poly (alkene vinyl alkanoate ketone) copolymer by a chain reaction between a single monomer of the copolymer and a carbon radical within the poly (vinyl alkanoate ketone) copolymer adjacent a ketone moiety. By some approaches, if the poly(vinyl alkanoate ketone) is a poly(alkene vinyl alkanoate ketone) the radical within the poly(vinyl alkanoate ketone) copolymer adjacent a ketone moiety may include a radical represented by one of the following general structures:



[0044] In some approaches, the method of making hybrid copolymers includes a) forming an oil phase by mixing styrene and other monomers and a terpolymer comprising ethylene/vinyl acetate/carbon monoxide; b) optionally adding one or more surfactants to the oil phase; c) forming a water phase by mixing water, a buffer and, optionally, one or more surfactants; d) forming a coarse emulsion by mixing the oil and water phases under agitation; and e) converting the coarse emulsion to a mini-emulsion. According to one illustrative embodiment, the coarse emulsion includes a combination of ingredients as listed in Table 1 below.

[0045] Table 1

Component	Amount, Grams
DuPont ELVALOY 742	5
butyl acrylate	54
methacrylic acid	1.4
styrene	40
water	88

[0046] In one approach, the latex copolymers of the present disclosure are prepared by free radical polymerization of the mini-emulsion blend. While the temperature in this step is not critical (in general, any temperature between the freezing point and the boiling point of the reaction components can be used), temperatures for conventional free radical emulsion polymerization range from about 20° C to about 90° C. Polymerization temperature can also depend on the choice of the free radical initiator. In some approaches, the particles of the mini-emulsion have average particle size in the range of about 40 nm to about 700 nm. The monomer content of the mini-emulsion is polymerized under free radical polymerization conditions in the presence of a free radical initiator. Both the initiator and the conditions may be conventional. Suitable free radical initiators are known in the art. These include, for example, the organic peroxides such as benzoyl peroxide, lauroyl peroxide and dicumyl peroxide; hydroperoxides such as tertiary butyl hydroperoxide, toluyl hydroperoxide, cumene hydroperoxide, amyl hydroperoxide; and inorganic persulfates such as potassium persulfate or ammonium persulfate; azobis-(isobutyro nitrile) (AIBN). The polymerization initiator may be either a water-soluble or an oil soluble compound. Persulfate initiator is preferred.

[0047] As mentioned, the latex copolymer particle size in the latex emulsion is in the range of about 40 nm to about 700 nanometers. Usually the latex copolymer particle size will be in the range from about 10 to about 1,000 nanometers. The preferred product copolymer particle size range is from about 80 to about 400 nanometers.

Coating Compositions Including the Hybrid Copolymers

[0048] The hybrid copolymers herein may be added to a coating composition, such as a latex paint composition, stains, lacquers, and the like. The coating compositions are preferably low VOC latex paint compositions having a VOC of about 50 or less grams/liter and most preferably no VOC. In one approach, a latex coating composition may include about 45 to about 60 weight percent water (in other approaches, about 30 to about 65 weight percent), about 0 to about 60 weight percent pigment or inorganic particle (such as titanium

dioxide) (in other approaches, about 16 to about 60; in other approaches, about 0 to about 30; and in yet other approaches about 30 to about 60 weight percent), and about 4 to about 65 solids weight percent of the hybrid copolymers herein (in other approaches, about 4 to about 30; in other approaches, about 30 to about 65; in yet other approaches, about 5 to about 50; and in yet other approaches, about 5 to about 25 solids weight percent).

[0049] The latex coating composition may also include other optional additives. Examples include, but are not limited to, surfactants, defoamers, biocides, mildewcides, algacides, thickeners, rheology modifiers, anti-settling agents, pH buffers, corrosion inhibitors, driers, and/or anti-skinning agents. The thickeners or rheology modifiers may be of the HASE, HEC, or HEUR.

[0050] The latex coating compositions herein with the hybrid copolymer may have a scrub number of at least about 500 (in other approaches, about 500 to about 1200) and a washability rating of at least about 3 for at least one stain including lipstick, mustard, teas, wine, and/or grape juice using the test methods as described herein. A latex coating composition with the hybrid copolymer may also exhibit a washability Delta E rating of about 6 or lower (in other approaches, about 1 to about 6) as measured with a GretagMacbeth Color-Eye 2145 spectrophotometer or equivalent using the test methods as described herein.

[0051] The latex paints of the present disclosure also include a pigment or inorganic particle. Suitable pigment particles or inorganic particles used in the copolymer compositions or complexes or the water-borne paint composition of the present disclosure may be titanium dioxide (TiO_2), zinc oxide (ZnO), calcium carbonate (CaCO_3), nepheline syenite, talc, clay materials, aluminum oxide, silicon dioxide, magnesium oxide, zinc sulfate, sodium oxide, potassium oxide, combinations thereof, or other known pigment or inorganic particles suitable for paints and other coatings. In some approaches, the pigment or inorganic particle is titanium dioxide, which may comprise anatase titanium dioxide or rutile titanium dioxide, or a mixture of the two. In other approaches, the pigment or inorganic particle comprises rutile titanium dioxide, to the exclusion of anatase titanium dioxide. In some approaches, the rutile titanium dioxide is surface treated with an inorganic oxide, such as silica (SiO_2). Generally, titanium dioxide has a particle size of from about 0.2 to about 0.3 microns in diameter and is provided in powder form, or in an aqueous slurry. An example of a titanium dioxide that is suitable for use in the present invention is Ti-Pure® R-706, which is commercially available from E.I. du Pont de Nemours and Company. Ti-Pure® R-706 titanium dioxide is a rutile titanium dioxide that is surface treated with silica.

[0052] The coating composition of the present invention using the hybrid copolymers herein may be produced using conventional latex paint forming techniques known to those skilled in the art of manufacturing paint. In addition to the copolymer or binder latex described above (which may be the sole binder latex in the paints), an optional dispersant latex, an optional extender, and an optional thickener, the water-borne coating composition may contain conventional additives such as coalescing aids, biocides, anti-foaming agents, freeze-thaw additives, rheology modifiers, surfactants, preservatives, and the like and combinations thereof. It should also be appreciated that in addition to pigment and extender, small amounts of other pigments or colorants may be used to provide desired coloration or to confer other optical effects.

EXPERIMENTAL

[0053] The following examples demonstrate the preparation of hybrid copolymers such as those described hereinabove. The examples are intended to be representative of the copolymers that can be made and are not intended to limit the scope of the present disclosure to the specific illustrative examples disclosed below. All percentages, ratios, and amounts in the Examples and throughout this disclosure are by weight unless otherwise specified.

[0054] EXAMPLE 1:

[0055] The composition of tested copolymers is detailed in Table 2 below. Each of hybrid copolymers 1 to 20 was made according to the following procedure. The hybrid copolymers in each of runs 1 to 20 were synthesized using varying amounts of styrene, butyl acrylate, and ELVALOY 742 (DuPont), as detailed on the left side of Table 2 in weight percent. For example, the amount of styrene monomer used to synthesize the hybrid copolymer can vary from about 49 wt. % to about 58 wt. % based on the total weight of the copolymer precursors (i.e. the total weight of styrene, butyl acetate and ELVALOY). According to an alternate embodiment, the amount of butyl acetate monomer used to synthesize the hybrid copolymer can vary from about 33 wt. % to about 47 wt. % based on the total weight of the copolymer precursors. In yet another embodiment, the amount of ELVALOY terpolymer used can vary from about 0 wt. % to about 10 wt. % based on the total weight of the copolymer precursors. In the Examples described herein, the remaining reactants used in the polymerization reaction for making hybrid copolymers 1 to 20 were kept constant for each run, as described in the right side of Table 2.

[0056] Table 2: Hybrid Copolymer Polymerization

Run	Styrene, wt. %	Butyl acrylate, wt. %	ELVALOY, wt. %	Additional Reactants for Runs 1-20	
1	49.11	44.11	5.39	MEHQ	50ppm
2	51.96	43.98	2.68	POLYSTEP B-23	1.68%
3	55.97	33.14	9.51	TERGITOL NP-10	2.40%
4	52.39	45.96	0.27	sodium carbonate	0.37%
5	49.11	41.16	8.35	oxidizer ($\text{Na}_2\text{S}_2\text{O}_8$)	0.60%
6	51.37	37.39	9.86	chase oxidizer (t-BHP)	0.22%
7	54.21	44.03	0.38	chase reducer (BRUGGOLITE FF6)	0.32%
8	54.23	41.85	2.54		
9	54.20	36.48	7.93		
10	56.31	37.07	5.23		
11	50.95	41.97	5.70		
12	54.20	36.48	7.93		
13	50.95	41.97	5.70		
14	54.03	39.60	4.99		
15	51.37	37.39	9.86		
16	56.16	42.46	0.00		
17	49.45	45.96	3.22		
18	54.23	41.85	2.54		
19	51.78	39.47	7.37		
20	56.31	39.53	2.78		

[0057] Table 3 below provides further parameters of the copolymers described in runs 1 to 20 of Table 2 above. Viscosity is measured with a Brookfield DV+1 viscometer at ambient temperature (approximately 25°C) using spindle #3.

[0058] Table 3:

Run	Emulsion Droplet Size (nm)	Latex Particle Size (nm)	pH	NVM (% Volume Solids)	Viscosity (cP)	Density (Pounds/Gallon)	Tg°C
1	415	161	6.32	55.21	540	8.69	5.91
2	425	187	6.27	55.76	273	8.69	9.25
3	551	168	6.61	53.52	200	8.67	17.79
4	610	184	6.74	52.47	188	8.69	9.10
5	603	160	6.58	53.30	235	8.68	6.87
6	904	156	6.57	53.85	208	8.66	10.75
7	804	178	6.60	53.63	267.5	8.69	11.88
8	443	162	6.45	53.44	288.8	8.68	12.66
9	503	153	6.36	53.56	309	8.67	14.45
10	491	158	6.23	52.97	194	8.66	16.83
11	448	163	6.40	54.58	288	8.67	8.74
12	482	153	6.22	53.98	196	8.63	14.45
13	-	158	6.35	53.37	330	8.68	8.74
14	-	162	6.32	53.58	303	8.68	13.18
15	567	152	6.47	53.57	246	8.69	10.75
16	1295	177	6.40	53.12	220	8.69	14.78
17	487	173	6.48	53.25	262	8.66	5.70
18	474	179	6.45	53.65	199	8.68	12.66
19	576	163	6.48	53.42	233	8.68	10.53
20	448	175	6.41	53.39	230	8.65	15.97

[0059] Another exemplary small-scale batch process includes the following process steps: (1) The ELVALOY is premixed with styrene and other monomers until completely dissolved therein. The combination may be heated (up to about 70 °C) to promote dissolving of the ELVALOY to form oil phase. (2) MEHQ (methyl hydroquinone or the like) is then added to the premix solution forming the oil phase. (3) Butyl acrylate, methacrylic acid and surfactant (nonylphenol ethoxylate, TERGITOL NP-10, Dow Chemical) are also incorporated into the premix. (4) Water is combined with a buffer (e.g., sodium carbonate) and the combination stirred until the sodium carbonate is dissolved, thereby forming the water phase. (5) A surfactant (e.g., sodium lauryl ether sulfate, POLYSTEP B-23, Stepan Co.) is then added to the water phase. (6) Under agitation and at atmospheric pressure, the oil phase is added to the water phase slowly until the coarse emulsion is formed, and mixed for three (3 min.) minutes to four (4 min.) minutes after combined under high shear to form the mini-emulsion. (7) An oxidizer (e.g., Na₂S₂O₈) is added along with water to the microfluidizer at room temperature and pressure. (8) The mini-

emulsion is then placed in a water bath and heated to a temperature of about 80 °C. (9) The mixture is held at temperature for about 3 hours, and gently agitated every 30 minutes, before being cooled to about 65°C. (10) A chase oxidizer (e.g., t-BHP) is added with water and the combination is mixed. (11) In three equal portions, the chase reducer (e.g., BRUGGOLITE, Bruggemann Chemical) is added in water over a period of 45 minutes, and the temperature is maintained at 65 °C. (12) The combination is cooled to room temperature and the pH adjusted to a value of about 5.5 to 6.5. (13) An optional biocide and defoamer can be added if desired.

[0060] When incorporated into latex paint, paints including a binder comprising the hybrid copolymers herein demonstrate improved washability and scrubability at the same time as compared to traditional paint compositions with a conventional binder. Hybrid copolymers were used as binders for paints, coatings, stains, lacquers, etc.

[0061] EXAMPLE 2:

[0062] The hybrid copolymer compositions of runs 1 to 20 set forth in Example 1 above were made into latex paint compositions. Exemplary paint compositions included approximately 4.39 pounds/gallon to 4.68 pounds/gallon of the hybrid copolymer composition of Example 1 as a binder as set forth in Table 4 below (noted as pounds/100 gallons in the Table). The paint may also include conventional components including water, defoamer, thickener, surfactants, titanium dioxide, and other additives. As shown in Table 4 below, each of the samples was prepared into a paint composition using the amount of Table 4. Each paint also had the same amounts of other conventional components as shown in Table 4A and 4B.

[0063] Table 4: Paint Compositions with Hybrid Copolymer

Paint Sample	Hybrid Copolymer Run #	Amount of Hybrid Copolymer Composition, pounds per 100 gallons
1	1	443.48
2	2	439.11
3	3	456.77
4	4	468.83
5	5	459.64
6	6	453.43
7	7	457.69
8	8	458.84
9	9	456.19
10	10	461.18
11	11	446.98
12	12	448.85
13	13	459.50
14	14	457.23
15	15	458.66
16	16	463.10
17	17	458.58
18	18	456.59
19	19	458.72
20	20	456.12

[0064] Table 4A: Paint Compositions

Ingredient	#/100 gal	% Volume
WATER	228.43	27.49
MINERAL OIL DEFOAMER	2.00	0.26
TEXANOL	15.00	1.89
CELLOSIZ QP-300 (HEC THICKENER)	1.75	0.15
Dupont TiPure R-746 Titanium Dioxide Slurry (75%)	230.00	12.04
ACRYSOL RM-2020 NPR	3.50	0.40
ACRYSOL TT-935	12.00	2.03
AQUEOUS AMMONIA	2.00	0.26
EXPERIMENTAL COPOLYMER of Table 4	Per table	-
WATER	30.00	4.47
SUM	964.68	100.00

[0065] Table 4B: Approximate Calculated Characteristics of the Paint from Table

4A

Calculated Characteristics	
Density (Lb/gal)	9.65
Percent Weight Solids (NVM - wt%)	44.16
Percent Volume Solids (NVV - vol%)	33.25
Pigment Volume Concentration	15.36
VOC (g/l)	> 50 g/l

[0066] EXAMPLE 3

[0067] The 20 paint samples of Example 2 were tested for scrub resistance and washability. Scrub Resistance is based on ASTM D2486-06 using Leneta SC-2 Standardized Scrub Medium (Abrasive Type). To reduce the known variability in the test, all samples were run on the same machine with the same brush. To reduce error further an established "500-Scrub" control paint was run with each test paint. The control paint was a commercially available paint: Sears Easy Living Semi-Gloss.

[0068] In this data set, the "500-Scrub" control paint scrubbed an average of 646 cycles to failure (Standard Deviation = 90). To get the average, normalized scrub values the actual Experimental test scrub values are divided by the actual scrub values of the defined "500-Scrub" control and multiplied by 500. Each paint was tested in duplicate and reported as an averaged and normalized value.

[0069] Washability follows ASTM D3450-15 with two modifications. First, Formula 409 Multi Surface Spray Cleaner (Clorox) was used as a non-abrasive medium. Second, the panels were not read on a Color-eye spectrophotometer. For this study, the panels were rated on a 0 to 5 scale with 0 is defined as not being able to wash the stain off compared to the non-washed area and 5 is define as no trace of stain remains. Any rating ≥ 3 is judged to be acceptably washable. The stains used were common household products of Red Lipstick, Mustard, Tea, Red Wine, and Grape Juice. Test results are provided in Table 5.

[0070] Table 5: Normalized Scrub to a defined 500 scrub standard (Modified ASTM D2486-06) and Stain Washability (Modified ASTM D3450-15) Test Results.

Paint Sample ID	Copolymer Sample ID	Average Normalized Scrubs	Washability Rating 0-5 (5=Excellent)				
			Lipstick	Mustard	Tea	Wine	Grape Juice
1	1	994.76	3	3	3	2	3
2	2	812.34	3	3	3	3	3
3	3	470.69	3	3	3	3	3
4	4	606.38	3	3	3	3	3
5	5	648.44	3	3	4	3	3
6	6	576.37	3	3	4	3	3
7	7	742.12	3	3	3	3	3
8	8	918.44	3	3	3	3	3
9	9	834.50	3	3	3	2	3
10	10	663.47	3	2	3	3	3
11	11	1044.54	3	3	2	2	2
12	12	665.28	2	3	3	3	3
13	13	997.03	3	3	2	2	3
14	14	739.10	3	3	2	2	3
15	15	812.14	3	3	3	3	3
16	16	851.42	3	3	3	3	3
17	17	995.10	3	3	3	3	3
18	18	929.57	3	4	3	2	3
19	19	877.83	3	3	3	3	3
20	20	782.86	3	3	3	3	3

[0071] EXAMPLE 4

[0072] Based on the previous results another hybrid copolymer was made and incorporated into a latex paint composition. The latex paint composition was then compared with two external control latexes in the next Example. A hybrid copolymer was prepared as in Example 1 and as presented in Table 6.

[0073] Table 6: hybrid latex composition.

Elvaloy Melt Index g/10 min	Elvaloy Molecular weight	Styrene Wt %	BA Wt %	Elvaloy Wt %	MAA Wt %	Latex Particle Size (nm)	pH	NVM	Density (lb/gallon)
535	~72000	41.00	55.00	11.00	1.52	167	6.21	53.7	8.68

[0074] EXAMPLE 5

[0075] Three white paints were made and tested using a common formula in Table 7 from the Example 4 hybrid copolymer and two commercially available control latexes (Airlfex EF811 or Encor 481). These formulas were also targeting very low Volatile Organic Components (VOC). One control latex was Airlfex EF-811 (Wacker), which is an ethylene vinyl acetate copolymer known to have exceptionally high scrubbability. The other control latex was Encor481 (Arkema), which is a styrene acrylate copolymer known to have exceptional stain resistance and washability as well as good wet adhesion.

[0076] Table 7: Paint Formulas

	EVA Control		Styrene Acrylic Control		Inventive Hybrid Copolymer	
	#/100 gal	% Volume	#/100 gal	% Volume	#/100 gal	% Volume
WATER	228.43	27.49	190.00	22.86	228.43	27.49
MINERAL OIL DEFOAMER	2.00	0.26	2.00	0.26	2.00	0.26
HEC THICKENER (Cellosize QP-300)	1.75	0.15	1.75	0.15	1.75	0.15
TiO ₂ (DuPont Tioxide R-746)	230.00	12.04	230.00	12.04	230.00	12.04
ACRYSOL RM-2020 NPR	3.50	0.40	3.50	0.40	3.50	0.40
ACRYSOL TT-935	12.00	2.03	18.00	2.03	12.00	2.03
AQUEOUS AMMONIA, 26 BE	2.00	0.26	2.00	0.26	2.00	0.26
Airflex EF811 EMULSION	466.00	52.36	-	-	-	-
ENCOR 481	-	-	528.50	60.75	-	-
Example 4 Hybrid Copolymer	-	-	-	-	459.64	52.98
WATER	41.55	5.00	10.28	1.24	31.36	3.74
SUM	987.23	100.00	986.03	100.00	970.68	99.37
Calculated Characteristics						
Density (Lb/gal)	9.87		9.86		9.77	
Percent Weight Solids (NVM - wt%)	44.16		43.68		44.16	
Percent Volume Solids (NVV - vol%)	33.25		33.25		33.25	
Pigment Volume Concentration	15.36		15.36		15.36	
VOC (g/l)	0		0		0	

[0077] The paint compositions in Example 5 were tested using the same methods previously discussed with a couple of additions. In addition to the scrub and washability tests, wet adhesion testing was also performed. Wet adhesion was measured using a modified version of ASTM D6900-10 (Reapproved 2015). The glossy substrate in the wet adhesion tests was Sherwin Williams ProMar 200 Alkyd Semi-gloss Enamel. The wet adhesion test was modified to be scrubbed for no more than 50 cycles and the rating is in % paint Adhered (= 100 – ASTM) and not % failure as required for ASTM D6900-10. The reported values are adhesion after 24 hour dry. Also, the washability results for Example 5 paints are presented in Delta E values using the unstained area of the panel as the standard and reading the stained/washed area as the batch using a GretagMacbeth Color-Eye 2145 spectrophotometer or equivalent. Delta E is as reported by the GretagMacbeth spectrophotometer. Scrubbability tests were performed and recorded the same as reported earlier for this

evaluation the “500 Scrub” control averaged 475 scrubs to failure. (Standard deviation = 154). Table 8 below is the test results of the comparison

[0078] Table 8: Paint Tests

Paint Sample ID	24 hour Wet Adhesion	Average Normalized Scrubs	Washability Delta E (Lower is Better)				
			Lipstick (Delta E)	Mustard (Delta E)	Tea (Delta E)	Wine (Delta E)	Grape Juice (Delta E)
EVA Control	0	2202	0.73	4.09	5.80	8.62	6.71
Styrene Acrylate Control	100%	58	(Failed) Paint washed off with the Stains				
Example 5	100%	1486	1.82	2.14	4.46	6.33	4.43

[0079] Table 8 illustrates the improvements using the hybrid copolymer of the present disclosure. Latex paints using the hybrid copolymers herein have comparable Scrubs to the EVA control but with significantly improved stain washability (that is, lower Delta E) without sacrificing the paint. It also demonstrates excellent adhesion and superior scrubs to the styrene acrylic control.

[0080] For the paints in example 5 and throughout this disclosure, unless otherwise specified, all measurements herein are made at $23 \pm 1^\circ\text{C}$ and 50% relative humidity. All publications, patent applications, and issued patents mentioned herein are hereby incorporated in their entirety by reference. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed disclosure. The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, such as dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as “40 mm” is intended to mean “about 40 mm”.

[0081] Illustrative embodiments have been described, hereinabove. It will be apparent to those skilled in the art that the above devices and methods may incorporate changes and modifications without departing from the general scope of this disclosure. It is intended to include all such modifications and alterations within the scope of the present disclosure. Furthermore, to the extent that the term “includes” is used in either the detailed description or the claims, such term is intended to be inclusive in a manner similar to the term “comprising” as “comprising” is interpreted when employed as a transitional word in a claim.

CLAIMS

What is claimed is:

1. A hybrid copolymer suitable as a binder for latex coating compositions, the hybrid copolymer comprising:
 - a copolymer backbone including a poly (alkene-vinyl alkanoate-ketone) with carbon atoms adjacent a ketone carbonyl moiety;
 - a polymeric side chain including at least one or more ethylenically unsaturated monomeric units grafted to the copolymer backbone; and
 - wherein at least a portion of the ethylenically unsaturated monomer units are grafted to the carbon atoms adjacent the ketone carbonyl moiety in the poly (alkene-vinyl acetate- ketone).
2. The hybrid copolymer according to claim 1, wherein the poly (alkene-vinyl alkanoate-ketone) includes a plurality of vinyl alkanoate monomer units; a plurality of alkene monomer units; and carbon monoxide monomer units.
3. The hybrid copolymer according to claim 2, wherein poly (alkene-vinyl alkanoate-ketone) includes vinyl alkanoate monomer units, alkene monomer units, and carbon monoxide monomer units randomly arranged along the copolymer backbone.
4. The hybrid copolymer according to claim 3, wherein the vinyl alkanoate monomer units of the poly (alkene-vinyl alkanoate-ketone) includes vinyl acetate.
5. The hybrid copolymer according to claim 3, wherein the poly (alkene-vinyl alkanoate ketone) includes ethylene and vinyl acetate.
6. The hybrid copolymer according to claim 1, wherein the hybrid copolymer includes up to about 30 weight percent of the poly (alkene-vinyl alkanoate-ketone).
7. The hybrid copolymer according to claim 1, wherein the ethylenically unsaturated monomer units are selected from the group consisting of styrene, vinyl acetate,

vinyl chloride, acrylic acid, (meth)acrylic acid, maleic acids, itaconic acid and their esters, amides with alcohols, and amines and mixtures thereof.

8. The hybrid copolymer according to claim 1, wherein the weight percent of ethylenically unsaturated monomer in the hybrid copolymer is about 70 to about 98 weight percent and wherein at least a portion thereof are grafted to the copolymer backbone.

9. The hybrid copolymer according to claim 1, wherein the hybrid copolymer further includes acrylic monomer units, methacrylic monomer units, or combinations thereof, and wherein at least a portion are grafted to the copolymer backbone.

10. The hybrid copolymer according to claim 9, wherein a weight percent of the acrylic monomer units, methacrylic monomer units, or combinations thereof is about 5 to about 55 weight percent.

11. The hybrid copolymer according to claim 8, wherein the hybrid copolymer further includes acrylic or methacrylic acid.

12. The hybrid copolymer according to claim 11, wherein the hybrid copolymer further includes methacrylic and/or acrylic acid and wherein a weight percent of the methacrylic and/or acrylic acid is about 1 to about 5 weight percent.

13. The hybrid copolymer according to claim 1, wherein the hybrid copolymer includes about 40 to about 65 weight percent styrene monomer units, about 2 to about 30 weight percent poly(alkene-vinyl alkanoate ketone) monomer units, about 5 to about 55 weight percent acrylic monomer units, and about 1 to about 5 weight percent methacrylic or acrylic acid monomer units.

14. The hybrid copolymer of claim 1, wherein at least a portion of one or more of the styrene monomer units, the acrylic monomer units, the methacrylic acid monomer units, and mixtures thereof are mixed with the hybrid copolymer but not grafted thereto to form a hybrid copolymer composition including the hybrid copolymer and the ungrafted monomer units.

15. The hybrid copolymer of claim 1, wherein the copolymer backbone includes ethylene, vinyl acetate, and ketone monomer units randomly polymerized within the copolymer backbone.

16. A method of making a hybrid copolymer of claim 1, the method comprising free radical polymerization within a mini-emulsion blend having an average particle size of about 40 nm to about 700 nm.

17. A latex coating composition comprising:
about 4 to about 65 solids weight percent hybrid copolymer having a copolymer backbone including a poly (alkene-vinyl alkanoate-ketone) with carbon atoms adjacent a ketone carbonyl moiety and a polymeric side chain including at least one or more ethylenically unsaturated monomeric units grafted to the copolymer backbone, wherein the ethylenically unsaturated monomer units in the side chain are selected from styrene, vinyl acetate, vinyl chloride, acrylic acid, (meth)acrylic acid, maleic acids, itaconic acid and their esters, amides with alcohols, and amines and mixtures thereof;
about 0 to about 2 weight percent solvent; and
about 0 to about 60 weight percent inorganic particle.

18. The latex coating composition of claim 17, further comprising at least a portion of the ethylenically unsaturated monomer units are grafted to the carbon atoms adjacent the ketone carbonyl moiety in the poly (alkene-vinyl acetate- ketone).

19. The latex coating composition of claim 17, wherein the poly (alkene-vinyl alkanoate ketone) includes ethylene and vinyl acetate.

20. The latex coating composition of claim 17, wherein the hybrid copolymer includes up to about 30 weight percent of the poly (alkene-vinyl alkanoate-ketone).

21. The latex coating composition of claim 17, wherein the weight percent of ethylenically unsaturated monomer in the hybrid copolymer is about 70 to about 98 weight percent and wherein at least a portion thereof are grafted to the copolymer backbone.

22. The latex coating composition of claim 17, wherein the hybrid copolymer further comprises acrylic monomer units, methacrylic monomer units, and combinations thereof, and wherein at least a portion are grafted to the copolymer backbone.

23. The latex coating composition of claim 22, wherein a weight percent of the acrylic monomer units, methacrylic monomer units, and combinations thereof is about 5 to about 55 weight percent.

24. The latex coating composition of claim 17, wherein the hybrid copolymer further includes methacrylic and/or acrylic acid and wherein a weight percent of the methacrylic and/or acrylic acid is about 1 to about 5 weight percent.

25. The latex coating composition of claim 17, wherein the hybrid copolymer includes about 40 to about 65 weight percent styrene monomers, about 2 to about 30 weight percent poly(alkene-vinyl alkanoate ketone), about 5 to about 55 weight percent acrylic monomers, and about 1 to about 5 weight percent methacrylic or acrylic acid.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/027089

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F255/02 C09D151/00
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, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 739 196 A (JENKINS RICHARD DUANE [US] ET AL) 14 April 1998 (1998-04-14) table J	1-25
A	----- WO 96/10615 A1 (DU PONT CANADA [CA]; ARTHURS TREVOR CURTIS [CA]) 11 April 1996 (1996-04-11) examples	1-25
A	----- JP S58 103547 A (TOKUYAMA SEKISUI IND CORP) 20 June 1983 (1983-06-20) the whole document	1-25
A	----- US 5 300 548 A (AKIMOTO HIDEO [JP] ET AL) 5 April 1994 (1994-04-05) table 1	1-25
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Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

20 June 2017

Date of mailing of the international search report

28/06/2017

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/027089

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	WO 96/25453 A1 (DOW CHEMICAL CO [US]) 22 August 1996 (1996-08-22) examples; tables -----	1-25
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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