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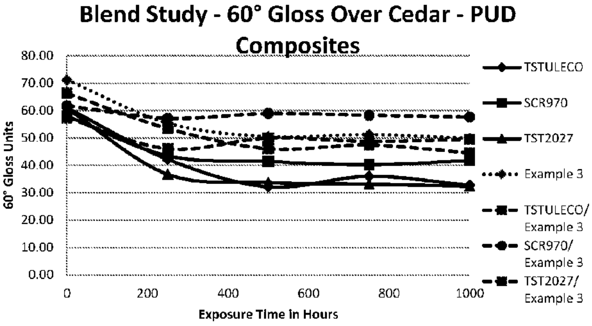
(54) Title: BLENDS OF WATER DISPERSIBLE POLYMER WITH DISPERSIONS OF POLYMERS FROM EPOXIDIZED TRIGLYCERIDES

FIG 3



(57) **Abstract**: The present invention provides an route to form a polymer blend from two polymers dispersed in aqueous media with enhanced characteristics, such as reduced amounts of coalescing solvents or lower minimum film formation temperature, etc. wherein one polymer is low Tg polymer derived from epoxidized triglyceride oil functionalized by reacting with carboxylic acid species carrying water dispersing groups, polymerizable unsaturation, and carbonyl groups capable of ketone-hydrazine crosslinking. The second polymer is desirably a conventional acrylate, urethane, or urethane-acrylate hybrid polymer dispersion.

BLENDS OF WATER DISPERSIBLE POLYMER WITH DISPERSIONS OF POLYMERS FROM EPOXIDIZED TRIGLYCERIDES

FIELD OF THE INVENTION

[0001] Blends of conventional polymer dispersions with a polymer derived from epoxidized triglycerides has useful properties for coatings or inks. Prepolymers from functionalized epoxidized triglyceride oils are disclosed that are free-radically co-polymerizable with other monomers. They can form polymers that are self-crosslinkable. Self-crosslinking can be achieved via a reaction sequence where a hydrazine containing moiety is added that can chemically react and bond to a carbon atom of a carbonyl group (e.g. reactive aldehyde or ketone type) attached to the prepolymer. The epoxidized triglyceride can be made copolymerizable with acrylate type monomers by reacting the epoxy group with acrylic or methacrylic acid, wherein the acid group opens the epoxy ring and leaves a residual hydroxyl group from the epoxy ring. The epoxidized triglyceride can be made water dispersible by chemically bonding an anhydride of a di or polycarboxylic acid molecule via an ester linkage with pendant hydroxyl groups on the prepolymer. The prepolymer can be modified with species such as levulinic acid to bond a reactive carbonyl (ketone) group to the triglyceride.

BACKGROUND OF THE INVENTION

[0002] Waterborne dispersions are utilized in the coatings industry to provide substrates with aesthetic beauty, solvent and chemical resistance, mar and scuff resistance, and abrasion resistance. Such waterborne dispersions are commonly used for coating wood, masonry, plastic, textile, and metal products and can also be used in ink jet ink compositions. In recent years, waterborne dispersions have come into favor from an environmental standpoint as replacements for oil based coating compositions because they can be formulated with a low level of volatile organic compounds (VOCs) and are preferably free of volatile organic compounds.

[0003] United States Patent 4,066,591 and United States Patent 4,147,679 disclose the preparation of waterborne polyurethane dispersions which contain unsaturated functional groups capable of undergoing auto-oxidative crosslinking.

[0004] United States Patent 4,598,121 discloses a method for preparing an aqueous polyurethane dispersion, comprising (a) preparing a prepolymer with free NCO groups by reacting an aliphatic or cycloaliphatic polyisocyanate with a polyol, and an anionic compound; (b) dispersing said prepolymer in water; (c) reacting said water-dispersed prepolymer with a diamino hydrazide as a chain lengthening agent; and (d) reacting the prepolymer of step (e) in said dispersion with formaldehyde to effect crosslinking.

[0005] United States Patent 4,983,662 discloses an aqueous self crosslinkable coating composition comprising an aqueous dispersion of at least one polyurethane and having hydrazine (or hydrazone) functional groups and carbonyl functional groups, disposed therein, to provide a self-crosslinking reaction in which the polyurethane polymer takes part via azomethine formation during and/or after film formation.

[0006] United States Patent 5,141,983 discloses a ketone-hydrazide crosslinking technology where the ketone, or carbonyl group resides on an acrylic polymer and a polyurethane polymer contains hydrazide functional groups. The composition is obtained by polymerizing the acrylic monomers in the presence of an aqueous polyurethane dispersion.

[0007] United States Patent 5,571,861 and United States Patent 5,623,016 disclose an aqueous, self-crosslinking polymer dispersion binder(s) comprising polyhydrazides and carbonyl-containing polyurethane-vinyl hybrid polymers and also, if desired, conventional additives useful in base coatings, aqueous coatings, adhesives and printing inks.

[0008] United States Patent 6,239,209 discloses waterborne urethane-acrylic compositions which are auto-oxidatively crosslinkable. In one embodiment, the composition also contains ketone hydrazide type self-crosslinking where the ketone/carbonyl is introduced via the acrylic and the hydrazide functionality is contained on the polyurethane along with the unsaturated oxidatively curable functional groups.

[0009] United States Patent 6,576,702 discloses waterborne polyurethane dispersions are prepared by reacting (1) at least one polyisocyanate; (2) at least one active hydrogen containing compound, such as a polyol or a polyamide; and (3) preferably also at least one water-dispersibility enhancing compound having water-dispersion enhancing groups, in order to form an isocyanate terminated prepolymer.

[0010] United States Patent Application Publication No. 2010/0330375 discloses aqueous polyurethane dispersions that are made from urethane prepolymers comprising one or more polyhydroxy compounds from ketone functional molecules derived from an epoxidized natural oil (triglycerides).

[0011] US2014/0378607 (WO2013/112530) discloses a water dispersible, self-crosslinkable prepolymer composition with a high content of raw materials from renewable resources. The prepolymers are based on epoxidized triglyceride oils reacted with acid containing molecules to generate pendant hydroxyl groups, pendant acid groups, pendant unsaturation, and pendant ketone or aldehyde groups. The prepolymers can be copolymerized with ethylenically unsaturated monomers to form polymer dispersions which form good coatings and are self-crosslinkable.

SUMMARY OF THE INVENTION

[0012] The present invention provides a new use for the copolymer with an adjustable content of raw materials from renewable resources and generally a lower volatile organic content disclosed in US2014/0378607. Those copolymers are copolymers of triglyceride oils, such as soybean oil, linseed oil, or some other natural oil, with a vinyl compound, such as an acrylate or methacrylate, and optionally a vinyl aromatic monomer, such as styrene.

[0013] Water based dispersions of conventional polymers used as dispersions in water struggle to meet two conflicting needs. Users of such polymers would like the final film to be hard, abrasion resistant, and resistant to water and organic solvents. But to form good films from the polymers, the polymers must be soft and flow at the film formation temperature (often room temperature 20-25 °C) selected by the end user. Formulators have used coalescing agents and plasticizers to soften the polymer and lower the film formation temperature. Coalescing agents tend to be considered as undesirable volatile organic contents after film formation. Plasticizers remain in the film and detract from final hardness, abrasion resistance and solvent resistance after film formation. It would be desirable to have a component that could lower film formation temperature but not be considered a coalescing agent or plasticizer.

[0014] The above described copolymers derived from functionalized epoxidized triglycerides copolymerized with various unsaturated monomers (desirably characterized as being less than 300 g/mole molecular weight before polymerization) including at least acrylate monomers can be used as an additive to conventional polymers for coatings to reduce the need for coalescing agents, plasticizers, etc. In that function they can lower the film formation temperature of the polymer, form a more fused polymer film, help flow and leveling of the coating, help the final gloss reading of the coating, etc. It has also been observed that the copolymers can modify the drying times (such as dry to the touch, dry enough to recoat, or dry enough to sand) of coatings derived from acrylate latexes or urethane dispersions. Using varying amounts of the copolymers from functionalized epoxidized triglycerides copolymerized with acrylates monomers allows formulators to create a variety of different coating blends customized to meet volatile organic content (VOC) requirements, film formation temperature requirements or drying characteristics.

[0015] The copolymers of functionalized epoxidized triglycerides can either be high in natural oil content, high in vinyl content, high in ionic species to help dispersibility, or high in crosslinking capability, or mixtures thereof depending on the intended end use. Moreover, a variety of functionality can be incorporated into the copolymer dispersions either through the natural oil and/or the vinyl component.

[0016] The present invention more specifically, discloses a physical blend of at two different water dispersible polymer compositions, wherein the first polymer is a copolymer comprised of a triglyceride oil having appended thereto (1) hydroxyl groups, (2) moieties which contain at least one aldehyde group or at least one ketone group, (3) moieties which contain at least one vinyl and/or substituted vinyl group, and (4) optionally, epoxy groups. In a preferred embodiment one, both, or all of the binder materials are crosslinkable with an external crosslinker or are self-crosslinkable.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Figure 1 illustrates the synthesis of a prepolymer (not functionalized yet for water-dispersibility) or macromonomer which utilizes an epoxidized triglyceride oil, such as epoxidized soybean oil, as the starting material. This reaction is carried out by reacting the epoxidized triglyceride oil with (1) a ketone functionalized carboxylic acid or an aldehyde functionalized carboxylic acid, and (2) optionally, a vinyl functionalized carboxylic acid.

[0018] Figure 2 illustrates the synthesis of a water dispersible self-crosslinkable polymer which utilizes the non-dispersible prepolymer of this invention, as described in Figure 1, as a starting material. In this reaction, the non-dispersible prepolymer is reacted with an anhydride of a di or polycarboxylic acid to prepare a water dispersible prepolymer.

[0019] Figure 3 illustrates the 60°gloss of polymer films over cedar board of various blends of Example 3 polymer with urethane and acrylic polymers after exposure for 200 to 1000 hours under UV340 lamp light.

DETAILED DESCRIPTION OF THE INVENTION

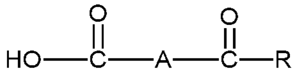
[0020] The water dispersible, self-crosslinkable copolymer compositions of this invention are comprised of a polymerization (e.g. free radical) product of triglyceride oil having appended thereto (1) hydroxyl groups, (2) moieties, which contain at least one carbonyl groups such as an aldehyde group or a ketone group, (3) moieties, which contain at least one vinyl and/or substituted vinyl group, and (4) optionally epoxy groups and water dispersibility enhancing groups. This monomer from epoxidized triglyceride which is generally above 300 g/mole molecular weight is copolymerized with vinyl or substituted vinyl monomers as described below (desirably characterized as being less than 300 g/mole molecular weight before polymerization) to form a copolymer. The term vinyl group is typically used to define a group with alpha-beta unsaturation wherein the two carbons of the alpha-beta unsaturation have jointly appended to them three hydrogen atoms. Applicant is defining substituted vinyl groups to include groups derived from unsaturated aliphatic anhydrides of di or polycarboxylic acids such as maleic anhydride or itaconic anhydride and/or C_{1-4}- alkyl substituted acrylic acids. In one embodiment, the substituted vinyl groups are derived from reacting the unsaturated aliphatic anhydrides or di or polycarboxylic acid directly with a hydroxyl group attached directly to a carbon of the triglyceride oil or to an epoxy functionality that comprises an oxygen atom and two carbon atoms of the triglyceride oil. In this embodiment, there are no polyether linkages between the triglyceride oil and the vinyl groups. In this context Applicant is defining substituted vinyl as being free radically copolymerizable with vinyl monomers such as where one of more of the three hydrogens are replaced by C_{1-4}-alkyl groups (such as derived from methacrylic acid) and/or carboxylic or C_{1-4}-alkyl carboxylic groups such as derived from maleic anhydride or itaconic anhydride. This prepolymer composition is made by reacting an epoxidized triglyceride oil with a ketone or aldehyde functionalized carboxylic acid and vinyl group containing carboxylic acid. This reaction is illustrated in Figure 1 and is normally carried out in the presence of a catalyst at an elevated temperature which is typically within the range of about 100 °C to about 150 °C. In most cases, it is preferred for this reaction to be conducted at a temperature which is within the range of 120 °C to about 135 °C. Zinc, zirconium, chromium, and iron catalysts can be used advantageously in carrying out this reaction. Some additional examples of catalysts that can be used include trialkylamines, phosphines such as triphenylphosphine, and imidiazoles, such as N-methylimidazole, and the like.

[0021] The triglyceride oils that can be utilized as a starting material are unsaturated vegetable oils, animal fats, or synthetic triglycerides, which are generally considered to be derived from condensation reactions of various fatty acids and glycerol. While the triglycerides are often described as oils, they may be solids at room temperature. The higher the amount of unsaturation present, the higher the degree of epoxidation possible under similar reaction conditions. Reactions of these unsaturated oils with strong oxidizers can convert the carbon to carbon double bond in the fatty acids to epoxides. Peracetic acid is a strong oxidizer that can be used for this purpose. The peracetic acid can be obtained from the reaction of acetic acid with hydrogen peroxide. Acetic acid can be obtained from the well-known process of bacterial fermentation.

[0022] Epoxidized vegetable oils are commercially available from a number of sources, including companies such as Dow Chemical and Chemtura. The oxirane oxygen content is generally within the range of about 2 to 14 weight percent and is typically within the range of 5 to 12 weight percent before reaction with the ketone or aldehyde functionalized carboxylic acid. It is, typically, preferred to employ an epoxidized triglyceride oil having an oxirane oxygen content which is within the range of 6 to 10 weight percent.

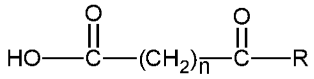
[0023] While the content of the various groups in the functionalized epoxidized triglyceride prepolymer (functionalized triglyceride) can vary widely, in one embodiment the amount of epoxidized triglyceride is from about 64 to 96 wt.%, more desirably 68-87 wt.% and preferably 72-83 wt.% of the functionalized triglyceride. In one embodiment, the amount of carbonyl functional carboxylic acid component in the functionalized triglyceride is from about 2 to about 25 wt.%, more desirably from about 8 to 20 wt.%, and preferably from about 10 to 15 wt.%. In one embodiment, the amount of di or poly carboxylic acids or anhydrides thereof incorporated into the functionalized triglyceride is from about 1 to about 15 wt.%, more desirably from about 3 to 10 wt.%, and preferably from about 4 to 8 wt.% of the functionalized triglyceride. In one embodiment, the amount of vinyl group and/or substituted vinyl group containing carboxylic acid in the functionalized triglyceride is from about 1 to about 10 wt.%, more desirably from about 2 to 6 wt.% and preferably from about 2.5 to 5 wt.% wherein all weights are based on the weight of the functionalized triglyceride.

[0024] The carbonyl, e.g. ketone or aldehyde, functionalized carboxylic acid utilized will normally be of the formula:



$$HO-\overset{O}{\overset{\|}{C}}-A-\overset{O}{\overset{\|}{C}}-R$$

wherein A represents a hydrocarbyl moiety containing from 1 to 20 carbon atoms and wherein R represents a hydrogen atom or an alkyl group containing from 1 to 8 carbon atoms. The ketone or aldehyde functionalized carboxylic acid will typically be of the formula:

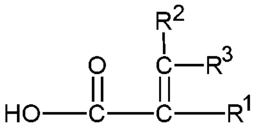


$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_n-\overset{O}{\overset{\|}{C}}-R$$

wherein n represents an integer from 1 to 8 and wherein R represents a hydrogen atom or a methyl group. In most cases, n will represent an integer from 2 to 4 with n typically representing 2.

[0025] A preferred carbonyl, e.g. ketone or aldehyde, containing carboxylic acid is levulinic acid (γ-ketovaleric acid; acetylpropionic acid, 4-oxopentanoic acid) or pyruvic acid (α-ketopropionic acid; acetylformic acid). The proportion of carbonyl functional groups in the free radically polymerized polymer (if such is present) is preferably 3 to 200 milliequivalents per 100g polymer (more preferably 6 to 100 milliequivalents per 100g polymer). It is possible to use ketone functional diols or polyols from synthetic sources in combination with those obtained from mainly renewable raw materials.

[0026] In cases where vinyl group containing carboxylic acids are utilized in making the prepolymer of this invention, they will normally be of the structural formula:



$$HO-\overset{O}{\overset{\|}{C}}-\overset{\overset{R^2}{|}\atop{C-R^3}}{\overset{\|}{C}}-R^1$$

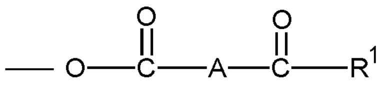
wherein R^1, R^2, and R^3 can be the same or different and represent hydrogen atoms or alkyl groups containing from 1 to 8 carbon atoms. Preferred vinyl group containing carboxylic acids include acrylic acid, methacrylic acid, ethacrylic acid, and the like.

[0027] In one embodiment, the synthesis of the water dispersible, self-crosslinkable prepolymer composition involves the reaction of the epoxidized vegetable oil with a ketone or aldehyde functionalized carboxylic acid and then reaction with an anhydride of a polycarboxylic acid, such as maleic anhydride, to produce an aqueous self-crosslinkable copolymer dispersion, optionally in the presence of a catalyst. A diluent, such as acetone, methyl ethyl ketone, or preferably a vinyl monomer, is normally added to keep the viscosity within a commercially acceptable range. This reaction is depicted in Figure 2 and is normally conducted at an elevated temperature in the presence of a catalyst. The catalyst can be a tertiary amine (such as a trialkylamine), a phosphonium compound, an inorganic metal salt, a metal alkoxide or a metal chelate. Some representative examples of catalysts that can be used include trimethylamine, triethylamine, tri-n-propylamine, tri-iso-propylamine, tri-n-butylamine, tri-t-butylamine, pyridine, isoquinoline, quinoline, N,N-dimethylcyclohexylamine, N-ethylmorpholine, dimethylaniline, dimethylbenzylamine, alkoxides, chelates, or halides of Al, B, Be, Fe(III), Sb(V), Sn, Ti, Zr, and Zn, and the like. It is typically preferred to utilize a trialkylamine, such as triethylamine, as the catalyst since they act both as a catalyst and as an ionizing base.

[0028] The anhydrides of di or polycarboxylic acids that can be utilized in preparing the water dispersible prepolymer can be aliphatic or aromatic. Some representative examples of such anhydrides include maleic anhydride, itaconic anhydride, succinic anhydride, phthalic anhydride, pyromellitic anhydride, mellitic anhydride, trimellitic anhydride, and the like. The preferred anhydrides for this use are maleic anhydride, itaconic anhydride, succinic anhydride, trimellitic anhydride, and phthalic anhydride. The most preferred anhydrides are maleic anhydride and itaconic anhydride. These anhydrides, after a ring opening reaction, as depicted in Figure 2, can function as a dispersing agent for the water dispersible prepolymer after being ionized. In an alternative embodiment of this invention, an external surfactant is utilized as a dispersing agent.

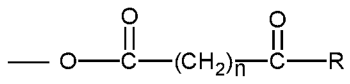
[0029] The water dispersible, self-crosslinkable prepolymer composition will generally have a number average molecular weight which is within the range of about 1,500 to about 19,000. The said prepolymer will typically have a number average molecular weight which is within the range of about 2,000 to 9,000, and will more typically have a number average molecular weight which is within the range of about 2,500 to about 5,000. The higher molecular weight can result from coupling multiple epoxidized oils (e.g., though ester linkages from the carboxylic acid groups of the maleic anhydride) into a prepolymer.

[0030] The moieties, which contain at least one carbonyl, e.g. aldehyde group or ketone group, are of the formula:



$$-O-\overset{O}{\overset{\|}{C}}-A-\overset{O}{\overset{\|}{C}}-R^1$$

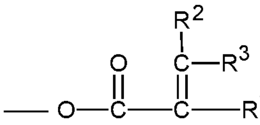
wherein A represents a hydrocarbyl moiety containing from 1 to 20 carbon atoms and wherein R^1 represents a hydrogen atom or an alkyl group containing from 1 to 8 carbon atoms. In many cases these moieties are of the formula:



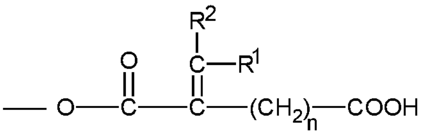
$$-O-\overset{O}{\overset{\|}{C}}-(CH_2)_n-\overset{O}{\overset{\|}{C}}-R$$

wherein n represents an integer from 1 to 8 and wherein R represents a hydrogen atom or a methyl group. In most cases, n will represent an integer from 2 to 4 with n typically representing 2.

[0031] The moieties, which contain at least one vinyl and/or substituted vinyl group, are of a formula selected from the group consisting of:

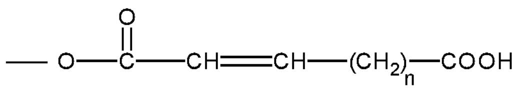


$$-O-\overset{O}{\overset{\|}{C}}-\overset{\overset{\overset{R^2}{|}}{C}-R^3}{\overset{\|}{C}}-R^1$$



$$-O-\overset{O}{\overset{\|}{C}}-\overset{\overset{\overset{R^2}{|}}{C}-R^1}{\overset{\|}{C}}-(CH_2)_n-COOH$$

and



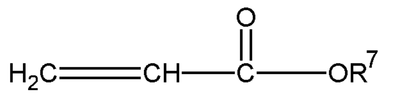
$$-O-\overset{O}{\overset{\|}{C}}-CH=CH-(CH_2)_n-COOH$$

or are a mixture of such moieties, wherein n represents an integer from 0 to 8, and wherein R^1, R^2, and R^3 can be the same or different and represents hydrogen atoms or alkyl groups containing from 1 to 8 carbon atoms. In most cases, n will represent in integer from 0 to 4 with n typically being 0. Normally, on average from 1 to about 4 functional groups will be appended to each molecule of triglyceride oil with it being more typical for 2 or 3 functional groups to be appended to each molecule of triglyceride oil. In one embodiment of this invention, the prepolymer is neutralized by reaction with at least one neutralizing agent and dispersed in aqueous medium.

[0032] Various additional monomers can optionally be copolymerized with the prepolymer. For instance, the acrylic polymer or copolymer can be derived from a variety of unsaturated monomers such as from acrylate, alkyl (alk)acrylate, vinyl chloride, vinylidene chloride, vinyl esters such as vinyl acetate, styrene, butadiene, acrylonitrile, and unsaturated acid containing monomers.

[0033] The copolymer from copolymerizing the functionalized triglyceride with acrylates and other monomers will in one embodiment desirably comprise from about 20 to about 65 or 75 wt.% of functionalized epoxidized oil residue, more desirably from about 30 to 55 wt.% and preferably from about 35 to 50 wt.% based on the weight of the copolymer. In one embodiment, the amount of acrylates, alkacrylates, and/or vinyl esters (the total for two or three is present and the conjunction "and" is used) is from about 5 to 40 wt.%, more desirably from about 10 to 30 wt.% and preferably from about 12 to 25 wt.%. In one embodiment, the amount of styrene or C_{1-4} alkyl substituted styrene is desirably from about 0 or 5 to 20, 25, or 30 wt.%, more desirably from about 5 to 25 wt.%. In one embodiment, the amount of polyfunctional crosslinkers (such as di, tri, or tetra-acrylate of a polyol or divinyl benzene) is from about 0 to about 5 wt.%, and more desirably from about 0.5 to 3 wt.% of the copolymer. In one embodiment, other unsaturated free radically polymerizable monomers (defined as other than acrylate, alkacrylate, vinyl ester, styrene, and polyfunctional monomers) can be used in amounts from about 0 to about 20 or 30 wt.% of the copolymer. Of course the above compositional ranges for each monomer component can be combined with ranges for other monomer components to create desirable copolymer compositions.

[0034] The various alkyl acrylates (or esters of acrylic acid) are of the formula:

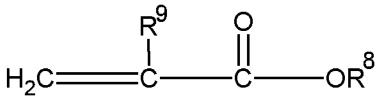


$$H_2C{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OR^7$$

wherein R^7 is an alkyl group containing 1 to about 15 carbon atoms, an alkoxyalkyl group containing a total of 1 to about 10 carbon atoms, a cyanoalkyl group containing 1 to about 10 carbon atoms, or a hydroxy alkyl group containing from 1 to about 18 carbon atoms.

The alkyl structure can contain primary, secondary, or tertiary carbon configurations and normally contains 1 to about 10 carbon atoms with 2 to 8 carbon atoms being preferred. Examples of such acrylic esters include methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-pentyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-methylpentyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, n-decyl acrylate, n-dodecyl acrylate, n-octadecyl acrylate, and the like. Preferred examples include ethylacrylate, butyl acrylate, 2-ethyl hexyl acrylate, and the like.

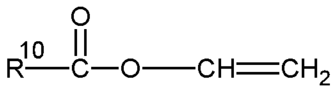
[0035] The various alkyl alkacrylates (or esters of alkacrylic acid) are of the formula:



$$H_2C{=}\overset{\overset{\displaystyle R^9}{|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR^8$$

wherein R^8 is an alkyl group containing 1 to about 15 carbon atoms, an alkoxyalkyl group containing a total of 1 to about 10 carbon atoms, a cyanoalkyl group containing 1 to about 10 carbon atoms, or a hydroxy alkyl group containing from 1 to about 18 carbon atoms (as described above) and wherein R^9 is an alkyl containing from 1 to about 4 carbon atoms, desirably, 1 or 2 carbon atoms with methyl being especially preferred. Examples of various alkyl (alk)acrylates include methyl methacrylate, ethyl methacrylate, methoxymethyl acrylate, methoxyethyl acrylate, ethoxyethyl acrylate, butoxy ethyl acrylate, ethoxypropyl acrylate, and the like. Derivatives include hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, and the like. Mixtures of two or more of the above monomers can also be utilized.

[0036] The vinyl esters can generally be represented by the formula:



$$R^{10}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH{=}CH_2$$

wherein R^{10} is an alkyl group generally having from 1 to about 10 or 12 carbon atoms with from about 1 to about 6 carbon atoms being preferred. Accordingly, suitable vinyl esters include vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, and the like. Vinyl esters with larger R^{10} groups include the vinyl versatate monomers, such as Veo VA-P, Veo Va-10, and Veo Va-11.

[0037] Considering the styrenic monomers (as both a primary monomer in styrene-butadiene polymers or a co-monomer in acrylate polymers), they are often referred to as vinyl substituted aromatic compounds (styrenic monomers) and include styrene, alkyl substituted styrene 1-vinylnaphthalene, 2-vinylnaphthalene, and the alkyl, cycloalkyl, aryl, alkaryl and aralkyl derivatives thereof, in which the total number of carbon atoms, in the combined, substituents is generally from 8 to about 12. Examples of such compounds include 3-methylstyrene vinyltoluene; alpha-methylstyrene; 4-n-propylstyrene, 4-t-butylstyrene, 4-dodecyl- styrene, 4-cyclohexylstyrene; 2-ethyl-4-benzylstyrene; 4-methoxy- styrene; 4-dimethylaminostyrene; 3,5-diphenoxystyrene; 4-p-tolylstyrene; 4-phenylstyrene; 4,5-dimethyl-1-vinylnaphthalene; 3-n-propyl-2-vinyl- naphthalene, and the like. Styrene is typically preferred.

[0038] Unsaturated acid containing monomers include acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, 2-carboxyethyl acrylate and the like. Acrylic acid is preferred. Half esters of the above di-carboxylic acids can also be used as monomers wherein the ester portion is desirably an alkyl having from 1 to about 10 carbon atoms and specific examples include mono methyl maleate, mono methyl fumerate, mono methyl itaconate, and the like.

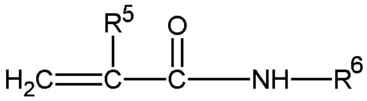
[0039] Other co-polymerizable (ethylenically unsaturated) monomers may be utilized to make copolymers including styrenic monomers (as a co-monomer in the acrylate latex), vinyl chloride type monomers, acrylonitrile type monomers, various vinyl ester monomers, various acrylamides monomers, various alkynol acrylamides and the like. The vinyl chloride type monomers include vinyl chloride, vinylidene chloride, and the like.

[0040] The various vinyl ethers can be represented by the formula:

$$H_2C{=}CH{-}O{-}R^4$$

wherein R^4 is desirably an alkyl having from 1 to about 10 carbon atoms. Specific examples include methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, and the like with methyl vinyl ether being preferred.

[0041] The acrylonitrile type monomers that can be utilized include acrylonitrile, or methacrylonitrile, or ethacrylonitrile, and the like. The acrylamide monomers which can be polymerized to form a copolymer generally have the following formula:



$$H_2C{=}\overset{\overset{\large R^5}{|}}{C}{-}\overset{\overset{\large O}{\|}}{C}{-}NH{-}R^6$$

wherein R^5 represents a hydrogen atom or a methyl group and wherein R^6 is represents a hydrogen atom or an alkyl group (straight chained or branched) containing from 1 to about 18 carbon atoms. Specific examples include acrylamide, ethyl acrylamide, butyl acrylamide, tert-octyl acrylamide, tert-butyl methacrylamide, and the like. Unlike the other optional monomers the one or more acrylamides can be utilized in large amounts such as up to about 20 percent by weight of the copolymer and desirably from about 0.5 to about 10 percent by weight.

[0042] Functionalized acrylamides can also be utilized. Examples of such acrylamides include AMPS, i.e., 2-acrylamido-2-methylpropanesulfonic acid, DMAPMA, i.e., dimethylaminopropyl methacryamide, and the like.

[0043] Carbonyl containing unsaturated comonomers may be copolymerized with the above monomers to make acrylic or vinyl polymers. Examples of carbonyl-containing monomers, which may be mentioned, include acrolein, methacrolein, diacetone-acrylamide, crotonaldehyde, 4-vinylbenzaldehyde, vinyl alkyl ketones of 4 to 7 carbon atoms such as vinyl methyl ketone, and acryloxy- and methacryloxy-alkyl propanols of formula $H_2C=C(R^3)-C(O)-O-C(R^{11})H-C(R^{12})(R^9)-C(O)H$ where R represents a hydrogen atom or a methyl group, R^{11} is H or alkyl of 1 to 3 carbon atoms, R^{12} is alkyl of 1 to 3 carbon atoms, and R^9 is alkyl of 1 to 4 carbon atoms. Further examples include acrylamidopivalaldehyde, methacrylamidopivalaldehyde, 3-acrylamidomethyl-anisaldehyde, diacetone acrylate, acetonyl acrylate, diacetone methacrylate, acetoacetoxyethylmethacrylate, 2-hydroxypropylacrylate acetylacetate, and butanediolacrylate acetylacetate. More details on using these monomers are provided in United States Patent 4,983,662. The teachings of United States Patent 4,983,662 are incorporated herein by reference for the purpose of describing the use of such monomers in greater detail.

[0044] In one embodiment, the vinyl monomers, described above, can be intentionally grafted or copolymerized with the water dispersible prepolymer component of this invention by using active hydrogen containing vinyl monomers in the formation of the prepolymer or the vinyl polymers. Examples of such active hydrogen containing vinyl monomers include 2-hydroxyethyl acrylate (2HEA) and 2-hydroxyethyl methacrylate (2HEMA).

[0045] Conventionally free radical initiators, known to the art and to the literature, can be utilized to initiate polymerization of the various above-noted monomers or co-monomers to form a polymer or copolymer. Such free radical initiators, generally, include the persulfates, the peroxides, and azo compounds, as well as redox combinations and radiation sources. Examples of preferred persulfate initiators include potassium persulfate, sodium persulfate, or ammonium persulfate, and the like. The free radical polymerization can be an emulsion, bulk, solution, or dispersion polymerization.

[0046] Generally, any type of peroxide, azo, redox system, or related initiator system can be utilized. Peroxide systems include dicumyl peroxide, cumene hydroperoxide, t-butyl perbenzoate, bis(t-butylperoxy) diisopropyl benzene, diisopropyl benzene hydroperoxide and n-butyl 4,4-bis(t-butylperoxy) valerate, as well as benzoyl peroxide, and t-butyl hydroperoxide, and the like. Cumene hydroperoxide, t-butyl hydroperoxide and diisopropyl benzene hydroperoxide are preferred. Azo initiators include 2,2'-azobis(isobutyronitrile)(AIBN) and related azo initiators.

[0047] Polymers or copolymers, can be made by utilizing chain-transfer agents/polymer physical property modifiers. Conventional chain-transfer agents can be utilized, such as, various mercaptans, for example, thioethanol mercaptan, hydroxyl ethyl mercaptan, various reaction products of alkyl esters of mercaptan with acidic acid or with thiogylcolic acid, and the like wherein the alkyl group has from about 2 to about 20 carbon atoms. Another suitable chain transfer agent is beta mercapto propionic acid and its esters such as butyl-3-mercaptoproprinate. Examples of chain transfer agents can include dithiocarbamates or di or trithiocarbonates.

[0048] Once the prepolymer is formed, it is dispersed in an aqueous medium to form a dispersion. Dispersing the prepolymer in aqueous medium can be done by any conventional technique, in the same way that polyurethane prepolymers made by bulk or solution polymerization are dispersed in water as described in United States Patent Application Publication No. 2010/0330375 A1. The teachings of United States Patent Application Publication No. 2010/0330375 A1 are incorporated herein by reference. Normally, this will be done by combining the prepolymer blend, with water with mixing. Where solvent polymerization is employed, the solvent and other volatile components can optionally be distilled off from the final dispersion, if desired. The hydrazine functional moiety, for crosslinking with the ketone group, can be added at this stage or later.

[0049] Two essential components to the current invention are the copolymer from functionalized triglyceride and a second more conventional polymer, both separately made or dispersed in water and then combined. It is desirable that the polymers be separately dispersed such that separate polymer compositions exist in separate particles that are then blended together. The conventional polymer dispersions may be acrylate type polymer dispersions (such as those made by emulsion polymerization), urethane dispersions in water made from processes where a urethane or prepolymer is first made and then dispersed in water and then chain extended, or hybrids of acrylate and urethane polymers dispersed in water. In one embodiment, the second (more conventional polymer dispersion) is crosslinkable either with an external crosslinker added shortly before using the coating or an internal crosslinker that can be added during formulations of a coating or ink from the polymers. In one embodiment, both the copolymer from acrylates and functionalized triglycerides and the conventional polymer dispersion are crosslinkable with an internal crosslinker (added at time of formulation of polymers into final formulation). In one embodiment on the copolymer from acrylates and the functionalized triglyceride is crosslinkable (either with internal crosslinker or external crosslinker). We use the term internal crosslinking to refer to crosslinkers that are incorporated into the polymer during polymerization (such as polyacrylates or ketone and hydrazine/hydrazide functionality). We use the term external crosslinkers for additives (such a polyisocyanates) that can be added to the coating shortly before application. External crosslinkers tend to be too reactive to be mixed with the binder at the binder manufacture or coating formulation stage.

[0050] An advantage of the current disclosure is that two separate polymer dispersions are made and can be stored and then at a later time they can be blended in a variety of weight ratios to get optimal performance as a coating or an ink. In one embodiment, the first copolymer of acrylate monomers and functionalized triglyeride (dispersed in water) is utilized in a polymer amounts from about 10 to about 90 weight percent (more desirably 20 to 80 weight percent) (based on the total polymers in the blend). In a more desirable embodiment, the copolymer of acrylates and functionalized triglycerides is used in polymer amounts from about 30 to about 60, 65, or 70 wt.%, and more preferably in an amount from about 35 to about 55, 60 or 65 wt.%. In a related embodiment, the conventional polymer (that is dispersed in water) is used in a polymer amount from about

10 to about 90 wt.% (more desirably from about 20 to 80 wt.%) of the blend, and in more desirable embodiments from about 30, 35 or 40 to about 70 wt.%, and preferably from about 40 or 45 to about 65 wt.% of the polymer blend in the two dispersions (based on the combined amounts of polymers plus any optional added polymers).

[0051] The conventional polymer as a dispersion in water can be any polymer but it is preferred to be an acrylate polymer, a urethane polymer or an acrylate-urethane hybrid polymer. The acrylate polymers in general are made by polymerizing the acrylate monomers in an emulsion polymerization or can be made by other processes (other than emulsion polymerization) and then dispersed in water similar to a urethane dispersion forming process. The urethane polymers are well known to the art and are typically made by a variety of processes where urethane forming monomers (polyisocyanates, polyols, optionally polyamines, etc.) are mixed and reacted (optionally using catalysts) to form prepolymers or polyurethanes. These prepolymers or polyurethanes are functionalized to make them water dispersible and then are dispersed in water. After dispersion in water the prepolymers can be chain extended with polyols or polyamines to former higher molecular weight polyurethanes. The hybrids of acrylate and urethane polymers are also well known to the art and are formed similarly to the polyurethane dispersion with the added step of adding acrylate monomers at some stage during or after the preparation of the urethane dispersion and thereafter polymerizing the acrylate monomers into a polyacrylate.

[0052] The conventional polymers often are formulated into coatings. In the coating formulation process it is common to add solvents or plasticizers to lower the minimum film formation temperature of the coating. These solvents and/or plasticizers are considered volatile organic components by regulatory agencies, such as the US Environmental Protection Agency (EPA). Generally different governmental and regulatory agencies define volatile organic compounds (VOC) slightly differently, depending on the perceived hazards associated with the volatile organic compounds intended for use in the coating. The US EPA defines volatile organic compounds for regulatory purposes as any compound of carbon (excluding carbon monoxide, carbon dioxide, carbonic acid, etc. along with named compounds with low environmental risk and high commercial benefit to society) which participates in atmospheric photochemical reactions. Other countries/regions define VOCs differently but start with the same volatile and organic definition but add or subtract compounds from the list for reasons known to the particular country/region. For the purpose of this specification, we will use the US EPA definition for VOC with the understanding that the exact VOC value in any particular country will vary depending on which compounds are included or excluded from the regulatory definition of volatile organic compounds in that country/region. USA EPA Method 24 for VOC determinations in coatings is a commonly accepted method in the USA for quantifying VOC.

[0053] In the USA it is common to formulate coatings (binder polymer, continuous phase, pigments, optional fillers, etc.) to have a volatile organic content (VOC) by USA EPA Method 24 of less than 300g/liter of coating, more desirably less than 150 g/liter, and preferably less than 50 or 25 g/liter to meet the current regulatory requirements or to reach to exceed anticipated future regulatory requirements. Often meeting these VOC limits means using less solvent or plasticizer, using solvents or plasticizers that are excluded from the regulatory definition of VOC, or otherwise modifying the formulation or polymer to meet VOC requirements. It is one intent of this specification to teach how the copolymer of acrylate monomers and functionalized triglyceride (dispersed in water) can function to help meet the minimum film formation temperature requirements for the coating (allowing the coating to form a continuous film at the desired temperature where the coating is applied to the substrate (e.g. 20-25 °C)) along with meeting various other performance requirements of the coating while keeping the calculated VOC value, as determined by USA EPA Method 24, of the coating under the previously disclosed limits of less than 300 g/liter, more desirably less than 150, and preferably less than 50 or 25 g/liter, based on liters of coating material.

[0054] In an embodiment where both the copolymer from acrylates and the functionalized triglyceride and the conventional polymer dispersion are crosslinkable, both polymers use the same chemical type of crosslinking mechanism. In another embodiment, the copolymer and the conventional polymer use different types of crosslinking mechanisms.

[0055] Crosslinking mechanism for polymer dispersions in water are taught in the prior art. Ketone-hydrazine crosslinking (also known as azomethine crosslinking) uses a combination of reactive carbonyl groups (aldehyde or ketone groups) and hydrazine or hydrazide groups to form a covalent chemical bond. This type of crosslinking is often used in the copolymer of acrylate and functionalized triglyceride. Another crosslinking mechanism is urethane or urea linkage which can be formed from reactive isocyanate groups and hydroxyl groups or primary or secondary amine groups. The isocyanate containing species can be added just before use or the isocyanate groups can be blocked with an isocyanate blocking groups. If the isocyanate groups are blocked, the isocyanate containing species can be added prior to use. Ketoxime type crosslinking is also available where a ketoxime group reacts with hydroxyl groups on the polymer to form a covalent bond. If one desires, conjugated unsaturated groups can be incorporated into a composition and these conjugated unsaturated groups can oxidatively crosslinked (often accelerated by a metal drier) to provided crosslinking. All of these crosslinking systems can be used with the copolymer and conventional polymers of this composition.

[0056] The preferred hydrazine functional moiety refers to a low molecular weight molecule or oligomers having one or more hydrazine or hydrazone groups. By a hydrazine functional group is meant the functional group of formula $-NHNH_2$. In the practice of this invention, the hydrazone functional group is a group derived from such a hydrazine group by reaction with a monoketone or monaldehyde containing at least 2 carbon atoms. Hydrazine functional moieties can also be dihydrazides and other polyhydrazides, as expressed below, in that these molecules have the specified $-NHNH_2$ group.

[0057] While hydrazine itself (H_2N-NH_2) at elevated concentrations, raises concerns about worker exposure, hydrazide ($-NHNH_2$) containing molecules are less of an exposure issue and offer the opportunity to build molecular weight and/or crosslink molecules/oligomers/polymers after polyurethane dispersion coagulation/film formation at or around room temperature. Volatile amines can play a significant role in the reactions using hydrazine functional moieties as the amines are/can be used in polyurethane dispersions to adjust the pH to the basic side before coalescence and allow the pH to shift to the acid side as the water and volatile amines evaporate. This pH shift and water evaporation promotes the reaction of hydrazine or hydrazide groups with available ketone or aldehyde groups (providing molecular weight buildup and or crosslinking).

[0058] In one embodiment of the invention, where the prepolymer includes enough water-dispersibility enhancing compound to form a stable dispersion without added emulsifiers (surfactants), the dispersion can be made without such compounds, i.e., substantially free of surfactants, if desired. In one embodiment of this invention, a surface active agent, such as a sulfate or a phosphate, can beneficially be included in the prepolymer composition.

[0059] In those instances in which the prepolymer includes water-dispersibility enhancing compounds which produce pendant carboxyl groups, these carboxyl groups can be converted to carboxylate anions for further enhancing the water-dispersibility of the prepolymer. A typical way the dispersions of the present invention can be made is by forming a prepolymer blend in the substantial absence of water and then dispersing the blend in an aqueous medium with mixing. Other ways of making aqueous dispersions can also be used to make the dispersions of this invention, including shear mixing, the acetone process, the continuous process polymerization, and the reverse feed process.

[0060] It is frequently desirable to include a bisulfite or sulfite to improve the stability of the dispersion. For instance, sodium sulfite, potassium sulfite, ammonium sulfite, calcium sulfite, magnesium sulfite, zinc sulfite, sodium bisulfite, potassium bisulfite, ammonium bisulfite, calcium bisulfite, magnesium bisulfite, or zinc bisulfite can be included in the dispersion. The sulfite or bisulfite will typically be added to the dispersion in a post polymerization step because it can interfere with the polymerization by acting as a chain transfer agent. In any case, the sulfite or bisulfite will typically not be added in more than a stoichiometric amount, based upon the number of ketone groups in the polymer. The sulfite or bisulfite will typically be added at a level which is within the range of 0.1 weight percent to 0.5 weight percent, based upon the solids content of the dispersion.

[0061] In shear mixing the prepolymer is dispersed by shear forces with emulsifiers (external emulsifiers, such as surfactants, or internal emulsifiers having nonionic, anionic, cationic and/or zwitterionic groups as part of or pendant to the polymer backbone, and/or as end groups on the polymer backbone).

[0062] In the acetone process a prepolymer is formed with or without the presence of acetone, MEK, and/or other polar solvents that are non-reactive and easily distilled. The prepolymer is further diluted in said solvents as necessary, and optionally chain extended with an active hydrogen-containing compound. Water is added and then the solvents are distilled off.

[0063] In the continuous process polymerization procedure a prepolymer is formed and then pumped through high shear mixing head(s) and dispersed into water. This is accomplished by multiple streams consisting of prepolymer (or neutralized prepolymer), optional neutralizing agent, water, and/or surfactant.

[0064] In the reverse feed process water and optional neutralizing agent(s) and/or extender amine(s) are charged to the prepolymer under agitation. The prepolymer can be neutralized before water is added.

[0065] The aqueous self-crosslinkable copolymer dispersion can then optionally be diluted with additional water to any concentration (solids content) that is desired. The aqueous self-crosslinkable copolymer dispersion can then be used in the preparation of water based coatings and inks, such as paints, varnishes, clear-coats, ink jet inks, and paper coatings, employing techniques that are well-known to those skilled in the art. Desired pigments, plasticizers, coalescing solvents, fillers, wetting agents, stabilizers, defoamers, dryers, antibacterial agents, fungicides, insecticides, antifouling agents, and anticorrosive agents can be mixed directly into the aqueous self-crosslinkable copolymer dispersion.

[0066] Pigments are normally added to paint formulations to impart color and hiding to the coating. Titanium dioxide is an example of a widely used pigment which imparts hiding and a white color. Mineral pigments (such as oxides of iron and chromium), organic pigments (such as phthalocyanine) and active anticorrosive pigments (such as zinc phosphate) are representative examples of other widely used pigments.

[0067] The fillers employed in making water based coating formulations are normally inexpensive materials which are added to attain the desired consistency and non-settling characteristics. Fillers can also improve a coating's physical properties, such as resistance to cracking and abrasion. Some representative examples of widely utilized fillers include chalks, clays, micas, barites, talcs, and silica.

[0068] Fungicides and algaecides are commonly added to interior and exterior house paints and are of particular value in coating formulations that will be used in warm climates. Antifouling compounds are commonly added to marine paints to inhibit marine growth.

[0069] A film forming, water based composition can be prepared utilizing a mixture of the aqueous self-crosslinkable copolymer dispersion, optionally with a suitable coalescing solvent and plasticizer. It is preferred for the coalescing solvent to be at least water immiscible and, even more preferably, for it to be water insoluble. Of the various solvents which can be used, generally, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol monobutyl ether, propylene glycol monoethyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, and/or dipropylene glycol monobutyl ether are preferred. It should be noted that the solvent and plasticizer can be mixed directly with the resin in its water emulsion.

[0070] Plasticizers are used to control the hardness of the coating and/or to impart flexibility. Poor adhesion can be encountered when water based coatings are applied to some substrates. Adhesion can frequently be improved by the addition of one or more plasticizers to the water based coating formulation.

[0071] Of the various plasticizers, it is desired that one be selected which is liquid at room temperature such as 25 °C and have a sufficiently high boiling point, preferably at least 100 °C, and even more preferably, at least 150 °C, so that they do not volatilize from the coating composition when applied to a substrate. The plasticizer should enhance the water insolubility of a dried coating of the coalesced resin. It is important for the plasticizer, or mixture of plasticizers, to be compatible with the resin itself.

[0072] A wide variety of plasticizers can be used in the practice of this invention. They can, for example, be of the type listed in the Federation Series on Coatings Technology, Unit Twenty-two, entitled "Plasticizers," published April, 1974, so long as they fulfill the melting point, boiling point and compatibility requirements. Some representative examples of plasticizers that can be used include propylene glycol methyl ether, dipropylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol methyl ether acetate, dipropylene glycol methyl ether acetate, propylene glycol n-propyl ether, dipropylene glycol n-propyl ether, propylene glycol n-butyl ether, dipropylene glycol n-butyl ether, tripropylene glycol n-butyl ether, propylene glycol phenyl ether, propylene glycol diacetate, dipropylene glycol dimethyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, diethylene glycol n-butyl ether, diethylene glycol hexyl ether, diethylene glycol n-butyl ether acetate, ethylene glycol propyl ether, ethylene glycol n-butyl ether, ethylene glycol hexyl ether, ethylene glycol n-butyl ether acetate, triethylene glycol methyl ether, triethylene glycol ethyl ether, triethylene glycol n-butyl ether, ethylene glycol phenyl ether, ethylene glycol n-butyl ether mixture, polyethylene glycol dibenzoate, ortho and/or para-toluene sulfonamide, trimethylpentanediol dibenzoate and trimethylpentanediol monoisobutyrate monobenzoate.

[0073] Desirably, the reaction between the ketone group of the prepolymer and hydrazine functional moiety is delayed until after particle coagulation and coalescence, but the technology is not limited thereby. Desirably, the ketone group and the hydrazine functional moiety react to form azomethine linkages as taught in United States Patent 4,210,565 and United States Patent 4,983,662, the teachings of which are incorporated herein by reference. Desirably, this reaction between the ketone groups of the prepolymer and the hydrazine functional moiety proceeds at a reasonable rate at 20 °C to 25 °C such that lower molecular weight species associated with these moieties are converted at 20 °C to 25 °C (ambient drying temperature) to higher molecular weight and/or crosslinked species that aid rather than detract from polymer hardness, strength, solvent resistance, and related properties of wear resistance.

[0074] This invention is illustrated by the following examples that are merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it can be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

[0075] <u>Example 1 of Ketone/Methacrylate Functional Epoxidized Soy Oil Polyol (Functionalized Triglyceride)</u>:

A poly-ketone functional triglyceride was prepared by combining items 1-5 of the ingredients below in a 4 neck flask equipped with a thermometer, overhead stirrer and dry air inlet. The Epoxidized Soybean Oil (ESO) can be sourced as Jenkinol^{TM} 680 from Acme Hardesty or Plasthall^{TM} ESO from Hallstar. With stirring and under a nitrogen blanket, the temperature of the reaction mixture was raised to 110 to 114 °C and held at this temperature for 1 hour. The temperature was then raised to 121 – 125 °C and held at this temperature for 2 hours or until the acid number was <1.0 (mg/g). The final material was clear with an amber tint and a viscosity of ~1,510 cps at 70 °C at an acid number of 0.9mg/g.

TABLE 1 for forming Functionalized Triglyceride

Item #	Material	Parts by wt.	moles
1	Epoxidized Soybean Oil (ESO)	317.5	
2	Levulinic Acid (LA)	52.9	
3	Methacrylic Acid (MAA)	13.1	
4	BHT (butylated hydroxytoluene)	0.2	-
5	Zirconium Propionate (as a 20% solution in levulinic acid)	2.0	-

[0076] Example 2 of functionalizing a ketone and acrylate functionalized triglyceride with an ionic dispersing group.

A dispersible functionalized triglyceride was prepared by first homogenizing a ketone/acrylate functionalized triglyceride prepared as described in above example (Item 1) with maleic anhydride and methyl methacrylate (MMA) (items 1-3) by heating to 60-70 °C until the solid maleic anhydride is homogenized (melted). This is followed by the addition of triethanol amine (TEA) (item 4) and the mixture held at 70 °C for 60 minutes. At this point most if not all of the anhydride has been consumed as evident in the FTIR spectrum not showing any significant peaks at 1779 and 1849 cm^{-1} (However, some anhydride peak might be buried under other absorption peaks such as those for ester groups). After which the mixture was allowed to cool to 25 – 30 °C and item 5 is added and homogenized in. This resulted in a prepolymer with a dark amber color of modest viscosity at the prepolymer dispersion temperature of 25 - 30 °C.

TABLE 2 Functionalizing with Ionic Group

Item #	Material	Parts by wt.
1	ESO-LA-MAA reaction product from preceding example	236.1
2	Maleic Anhydride	24.4
3	Methyl Methacrylate (MMA)	65.1
4	Triethylamine (TEA)	10.1
5	Ammonium Hydroxide (~29% in water)	4.4

[0077] Example 3 of Copolymerizing Acrylates with Ionic group/Ketone/Acrylate Functionalized Triglyceride. The resulting ionic group/ketone/acrylate functionalized triglyceride (180 parts of which) at ~25 °C was dispersed in 373 parts of water having an initial temperature of ~20 °C that provides a dispersion of a low particle size with a translucent appearance. To the resulting dispersion 58.6 parts of styrene, 12.3 parts methyl methacrylate and 5.8 parts of di-vinyl benzene (DVB 80) was added and allowed to homogenize into the dispersion; this resulted in an increase in particle size as evident by the dispersion having an opaque appearance. The resulting dispersion was free radical polymerized by adding 0.03 parts of a 1% Fe-EDTA and 8.0 parts of 3.5% t-butyl hydrogen peroxide which was allowed to mix into the dispersion prior to slowly adding 10.0 parts of 2.0% erythorbic acid at an initial temperature of 21 °C. This resulted in an initiation and polymerization of the vinyl functional monomers with an observed exotherm from 21 to 42 °C. The particle size was found to drop and the viscosity rise as the vinyl polymerization progressed. The vinyl polymerization was followed by the slow addition of 1.6 parts of sodium bisulfite versus 100 parts polymer solids as a 25 wt.% aqueous solution. Afterwards 7.7 parts of adipic dihydrazide was added to the dispersion to provide a polymer with the potential to self-crosslink through a condensation of the hydrazide with ketones on the polymer; the effect of which was observed in a significant increase in hardness, and very good mar and black heel mark resistance for the dried coating. The final dispersion (copolymer of acrylate and functionalized triglyceride dispersion) had a sediment level of <0.1%, with a solids level of 40.2 wt.%, a viscosity of 38 cps (at 25 °C at a pH of 7.0 with a particle size of 52.3 nm.

TABLE 3 Dispersing and Copolymerizing

Item #	Material	Parts by wt.
1	Ionic group/ketone/acrylate functionalized triglyceride from Table 2	180
2	Water	373
3	Methyl methacrylate	12.3
4	Di-vinyl benzene	5.8
5	1% Fe-EDTA in water	0.03
6	T-butyl hydroperoxide 3.5%	8.0
7	Erythorbic acid 2.0%	10.0
8	Sodium Bisulfite	3.2

9	Adipic dihydrazide	7.7

[0078] A variety of tests including minimum film formation temperature, chemical resistance, Dry Time using Recorder, Chemical Resistance ASTM D1308, Sandability, 1000 Hour QUV Exposure, and Dynamic Mechanical Analysis were run on commercial polymer dispersions in water, Example 3, and blends of the dispersions with Example 3.

[0079] Conventional polymer dispersions were selected from: Carboset® 2968 (CST 2968) an acrylic copolymer emulsion with 42 wt.% solids, pH 8.1, and a MffT of 57 °C; Turboset® 2027 (TST 2027) a polyurethane-acrylic hybrid dispersion with a MffT of about 2 °C; Turboset® Ultra Eco (TSTULECO) a self-crosslinking polyurethane-acrylic hybrid dispersion with about 36 wt.% solids, pH 8-9, and MffT 4 °C; Santocure^{TM} 970 (SCR 970) a thermoplastic polyurethane dispersion; and Carboset® CR-765 (CR-765) a styrene-acrylic copolymer with 42 wt.% solids, pH 8.2, and MffT 34 °C.

[0080] The minimum film formation temperature test (MffT) is performed on the neat resins and blends of resins, not formulated finishes. Measured Mfft comes out lower than theoretical Mfft for blend of CST2968 and Example 3, and blend of SCR970 with Example 3.

TABLE 4 Effect of Blends on Mfft as determined by ASTM D2354

		Mfft - °C	
Resin Used	Blend Ratio	Theoretical Mfft Resin Blends Only	Measured Mfft Resins Only
CST2968	100%		70
TSTULECO	100%		<5
TST2027	100%		40
CST2968/EXAMPLE 3	1:1	42	36
TSTULECO/EXAMPLE 3	1:1	9.5	6
TST2027/EXAMPLE 3	1:1	27	32

[0081] The data in Table 4 illustrates that for high MffT polymers blending with the Example 3 copolymer from acrylates and functionalized triglyceride provides a MffT closer to room temperature without requiring large amounts of plasticizer or coalescent.

[0082] **Low Temperature (film formation at 4.4C/50% Relative Humidity) and Ambient Film Formation:** Blending Example 3 with TSTULECO gives better low temperature film formation than either resin by itself. Coatings we applied to unsealed chart paper, sealed chart paper and sealed black chart paper.

TABLE 5 Film Forming Ability on Paper by ASTM D7306

	Formulation Data					**Film Formation: LTC & Ambient**					
Resin Used	Blend Ratio	Cosolvent	Wt Solids %	US VOC, G/L	EU VOC, G/L	Unsealed Chart Paper - Pass/Fail	Unsealed Chart Paper - Rating	Sealed Chart Paper =- Pass/Fail	Sealed Chart Paper - Rating	Ambient Sealed Black Chart Paper - Pass/Fail	Ambient Sealed Black Chart Paper - Rating
CST2968	100%	DPnB	30.7	230.3	86.6	Pass	5	Pass	5	Pass	5
TSTULECO	100%	DPnB	30.5	48.3	14.3	Fail	4	Fail	4	Pass	5
SCR970	100%	DPnB	30.4	274.9	106.2	Pass	5	Pass	5	Pass	5
TST2027	100%	DPnB	30.3	273.4	103.9	Pass	5	Pass	5	Pass	5
Example 3	100%	DPnB	30. 5	48.4	14.2	Fail	1	Fail	2	Pass	5
CST2968/ Example 3	1:1	DPnB	30.6	150.27	50.34	Pass	5	Pass	5	Pass	5
TSTULECO/ Example 3	1:1	DPnB	30.5	48.25	14.23	Fail	4	Pass	5	Pass	5
SCR 970/Example 3	1:1	DPnB	30.5	177.1	60.3	Fail	3	Fail	4	Pass	5
TST2027/ Example 3	1:1	DPnB	30.4	175.25	59.11	Pass	5	Pass	5	Pass	5

[0083] In Table 5 some of the polymers (TSTULECO and Example 3) had difficulty forming films over both unsealed and sealed chart paper. Blending TSTULECO and Example 3 resulted in better film formation over chart paper.

[0084] **Chemical Resistance – 1 Hour Exposures, 1 Hour Recovery Time:** Chemical resistance testing is for 1 hour exposure and 1 hour recovery by ASTM D1308. The ratings below are for recovery.

TABLE 6 Chemical Resistance of Coatings

	Recovery Chemical Resistance to Solutions Ratings - 1 Hr. Exposure												
Resin Used	Water	Hot Coffee	1% Spic N Span	Windex	1.4% Ammonia	Vinegar	Grape Juice	25% Clorox Ultra Bleach	French's Mustard	50% Ethanol/Water	Red Wine	70% Isopropanol/Water	**Total Recovery Score Max = 240**
CST2968	20	20	18	18	14	20	20	18	17	18	20	17	220
TSTULE-CO	20	14	20	17	14	20	17	6	12	18	9	18	185
TST2027	20	20	20	20	19	20	20	20	14	18	20	18	229
Exam. 3	18	16	18	16	14	20	20	20	12	19	11	19	203
CST2968/ Exam. 3	20	16	17	16	12	20	18	15	14	18	13	16	195
TSTULE-CO/ Exam. 3	18	14	19	15	12	20	19	17	12	19	12	15	192
TST2027/ Example 3	18	18	18	16	13	20	20	16	12	20	17	19	207

[0085] Two of the blends show improvements in resistance to specific chemicals which in turn improves the overall score for resistance properties. Ratings are from 0 to20 with 20 being the best chemical resistance. TSTULECO is self-crosslinking and benefits in Total Score from adding Example 3. Example 3 blends with the acrylic emulsion CST29688 show the exact opposite effect on performance and degrades the chemical resistance performance of CST2968.

TABLE 7

	Sandability - 5 = No Issues						
Resin Used	Application Method	Substrate	Curing Method	Curing Time	Sand Paper used for Evaluation	Powder generated (1-5) 5 = Lots	Cobbs on Sandpaper or Wood (1-5) 5 = None
CST2968	foam brush 1 coat	maple	ambient	1 hr	320 open coat	3	5
TSTULECO	foam brush 1 coat	maple	ambient	1 hr	320 open coat	2	5
TST2027	foam brush 1 coat	maple	ambient	1 hr	320 open coat	1	5
Example 3	foam brush 1 coat	maple	ambient	1 hr	320 open coat	4	5
CST2968/ Example 3	foam brush 1 coat	maple	ambient	1 hr	320 open coat	4	5
TSTULECO/ Example 3	foam brush 1 coat	maple	ambient	1 hr	320 open coat	2	5
TST2027/ Example 3	foam brush 1 coat	maple	ambient	1 hr	320 open coat	4	5

[0086] **Sandability:** Blended formulas show improvements in powder generation during sanding without clogging the sandpaper (cobbing is a measurement of sandpaper clogging). People sanding wood finishes like seeing the generation of dust or powder – this shows them that they are actually removing a small amount of the surface and smoothing it out. Example 3 does a good job of improving the development of powder generation of finishes that had poor powder generation. None of the finishes developed cobs on the sand paper – sometimes when more dust/powder is generated the dust agglomerates on the surface of the sand paper and clogs it up – the balls of agglomerates are called cobs.

[0087] **Dry Time Using a Recorder:** The recorder measures the different stages of drying which are interpreted as set to touch, surface dry, and through dry. Wet films are cast on glass and the recorder is placed in the film to determine the amount of time the film takes to achieve each step in the drying process according to ASTM D5895.

TABLE 8

	Dry Time of Formulations		
Resin Used	Set to Touch in Minutes	Surface Dry in Minutes	Thru-Dry in Minutes
CST2968	10	15	25
TSTULECO	8	15	33
TST2027	5	12	18
Example 3	10	17	19
CST2968/Example 3	15	20	28
TSTULECO/Example 3	14	20	27
TST2027/Example 3	5	7	15

[0088] Blends of CST2968 and TSTULECO both show better open time without significantly altering the through dry properties – this is desirable because it gives more time for the finish to flow out or be manipulated during application without increasing the amount of time needed to proceed to the next step for the article being finished. The next step can be sanding a sealer, applying another coat of finish, or packaging the final product.

[0089] The **QUV:** 1000 hours exposure to UV340 lamp light – done in four hour cycles – 4 hours light exposure and 4hours darkness with moisture. The gloss readings were made with a Byk-Gardner tri-gloss meter according to the supplier instructions. Solid cedar was used as the substrate for the results in Figure 3.

[0090] The Figure 3 results show that blends of polyurethane dispersions and Example 3 result in higher gloss retention than the individual polyurethanes by themselves. SCR970 is thermoplastic and TSTULECO and TST2027 are self-crosslinking polyurethane dispersions – both types show improvements in gloss retention. Acrylic emulsions – both thermoplastic and self-crosslinking were also tested in blends in this study but did not exhibit the same improvements in gloss retention. The same exposure using mahogany as the substrate shows results similar the data in the graph above.

[0091] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent, to those skilled in this art, that various changes and modifications can be made therein without departing from the scope of the subject invention.

WHAT IS CLAIMED IS:

1. A blend of two compositionally different polymer dispersions comprising,
   a) 10-90 wt.% of a colloidally dispersed self-crosslinkable copolymer in water comprising from 25 to 80 wt.% of polymerized unsaturated monomers (desirably characterized as being less than 300 g/mole molecular weight before polymerization) and 20 wt.% to 75 wt.% of monomers characterized as acrylate and ketone functionalized epoxidized triglyceride oil wherein the functionalizing groups are one or more carboxylic acid containing components having either carboxylic acid functionality or carbonyl functionality to impart crosslinking ability to the acrylate polymer;
   b) 10-90 wt% of a separately colloidally dispersed acrylate, urethane, or urethane-acrylate hybrid polymer in water, wherein said weight percent a) and b) is based upon the combined weight of the dispersed solids in a) and b) and any optional additional dispersed solid polymer dispersions.

2. The blend of two compositionally different polymer dispersions according to claim 1, wherein said a) is present from 20 to 80 wt.% and said b) is present from 20 to 80 wt.%.

3. The blend of two compositionally different polymer dispersions according to claim 1 or 2, further comprising an internal or external crosslinking agent capable of crosslinking said separately colloidally dispersed acrylate and/or urethane polymer in water.

4. The blend of two compositionally different polymer dispersions according to any of the preceding claims, wherein said a) is present from 30 to 70 wt.% and said b) is present from 30 to 70 wt.%.

5. The blend of two compositionally different polymer dispersions according to any of the preceding claims, wherein said b) separately colloidally dispersed acrylate and/or urethane polymer in water comprises a reactive carbonyl group in the form of ketone or aldehyde group such that it is crosslinkable through ketone-hydrazide or ketone-hydrazine type crosslinking reactions.

6. The blend of two compositionally different polymer dispersions according to any of the preceding claims, wherein said b) separately colloidally dispersed acrylate and/or urethane polymer in water comprises an acrylate polymer.

7. The blend of two compositionally different polymer dispersions according to any of claims 1-5, wherein said separately colloidally dispersed acrylate, urethane, or acrylate-urethane hybrid polymer in water comprises a urethane polymer dispersed in water.

8. The blend of two compositionally different polymer dispersions according to any of claims 1-5, wherein said separately colloidally dispersed acrylate, urethane, or acrylate-urethane hybrid polymer dispersed in water comprises an acrylate-urethane hybrid polymer.

9. The blend of two compositionally different polymer dispersions according to any of claims 1-8, wherein said blend is further comprised of at least one salt of sulfite or bisulfite selected from the group consisting of sodium sulfite, potassium sulfite, ammonium sulfite, calcium sulfite, magnesium sulfite, zinc sulfite, sodium bisulfite, potassium bisulfite, ammonium bisulfite, calcium bisulfite, magnesium bisulfite, and zinc bisulfite.

10. The blend of two compositionally different polymer dispersions according to claim 9, wherein the salt of sulfite or bisulfite is present at a level which is within the range of 0.1 weight percent to 5.0 weight percent, based upon the polymer solids content of the dispersion.

11. A method of modifying the film formation process of a conventional polymer dispersion in water comprising providing an acrylate, urethane, or acrylate-urethane hybrid polymer dispersion and diluting said conventional polymer dispersion with a first polymer dispersion, wherein said first polymer dispersion is derived from polymerizing acrylate and carbonyl functionalized epoxidized triglyceride oil with carboxylic acid functional molecules providing dispersing groups, unsaturated polymerizable groups, and carbonyl crosslinking groups, where the carboxylic acid functional molecules also comprise at least one functional group selected from ionic water dispersing groups, unsaturated

polymerizable groups, and carbonyl crosslinking groups that can form ketone-hydrazine type crosslinks.

12. The method of modifying the film formation process of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion according to claim 11, wherein said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion comprises an acrylate emulsion.

13. The method of modifying the film formation process of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion according to claim 11, wherein said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion comprises a urethane dispersion or acrylate-urethane hybrid dispersion.

14. The method of modifying the film formation process of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion according to claim 11, 12, or 13 wherein said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion modified with said first polymer dispersion is formulated into a coating or ink composition having a volatile organic content of less than 300 g/liter of coating or ink measured according to USA EPA Method 24.

15. The method of modifying the film formation process of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion according to claim 11, 12, or 13 wherein said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion modified with said first polymer dispersion is formulated into a coating or ink composition having a volatile organic content of less than 150 g/liter of coating or ink measured according to USA EPA Method 24.

16. The method of modifying the film formation process of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion according to claim 11, 12, or 13 wherein said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion modified with said first polymer dispersion is formulated into a coating or ink composition having a volatile organic content of less than 50 g/liter of coating or ink measured according to USA EPA Method 24 (more desirably less than 25 g/liter.

17. The method of modifying the film formation process of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion according to any of claims 11-16, wherein said the solids of said first polymer dispersion comprises from about 10 to about 90 wt.% of the solids of said modified polymer dispersion and the solids of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion comprises from about 10 to about 90 wt.% of the solids of said modified polymer dispersion.

18. The method of modifying the film formation process of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion according to any of claims 11-16, wherein said the solids of said first polymer dispersion comprises from about 20 to about 80 wt.% of the solids of said modified polymer dispersion and the solids of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion comprises from about 20 to about 80 wt.% of the solids of said modified polymer dispersion.

19. The method of modifying the film formation process of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion according to any of claims 11-16, wherein said the solids of said first polymer dispersion comprises from about 30 to about 70 wt.% of the solids of said modified polymer dispersion and the solids of said acrylate, urethane, or acrylate-urethane hybrid polymer dispersion comprises from about 30 to about 70 wt.% of the solids of said modified polymer dispersion.

FIG. 1

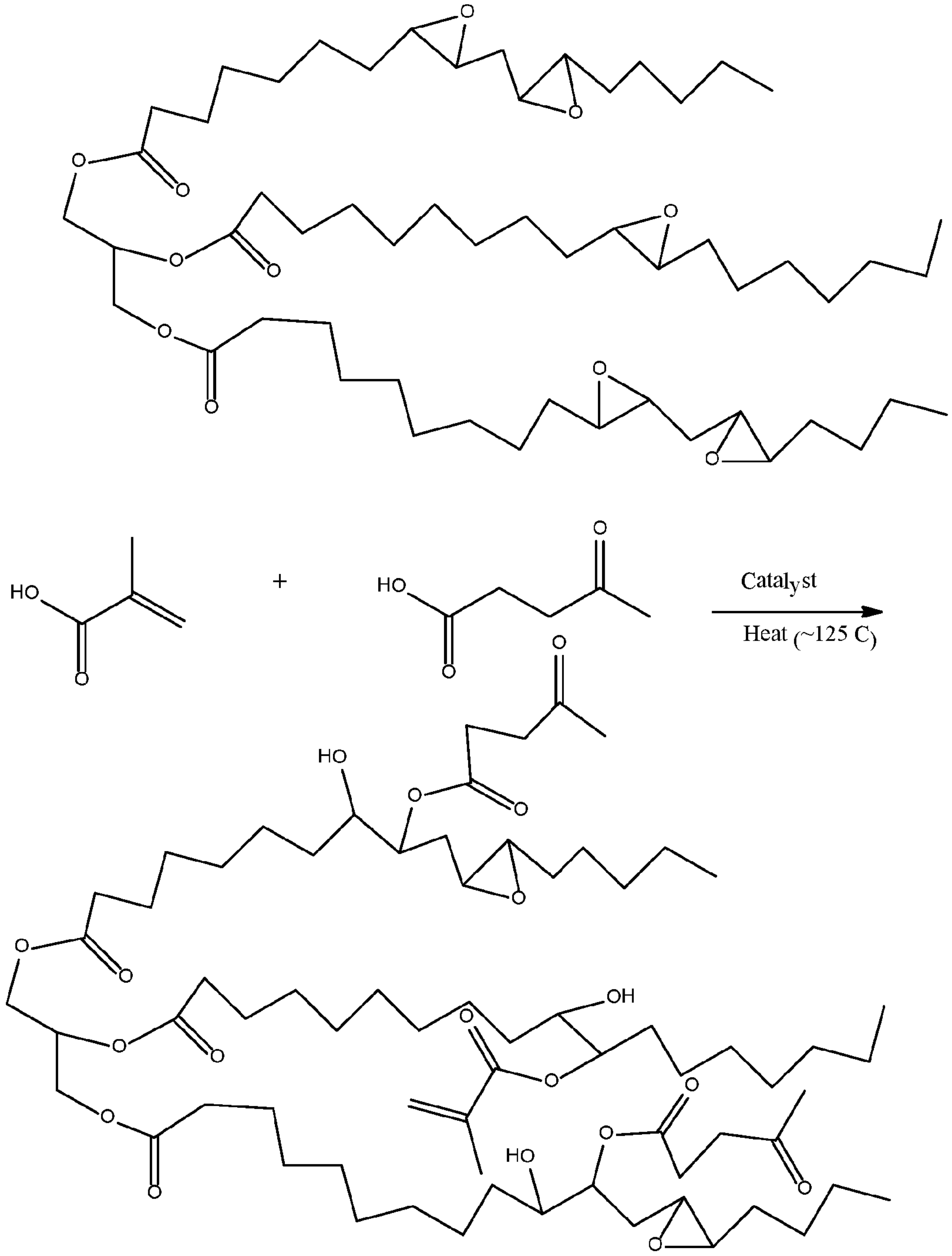
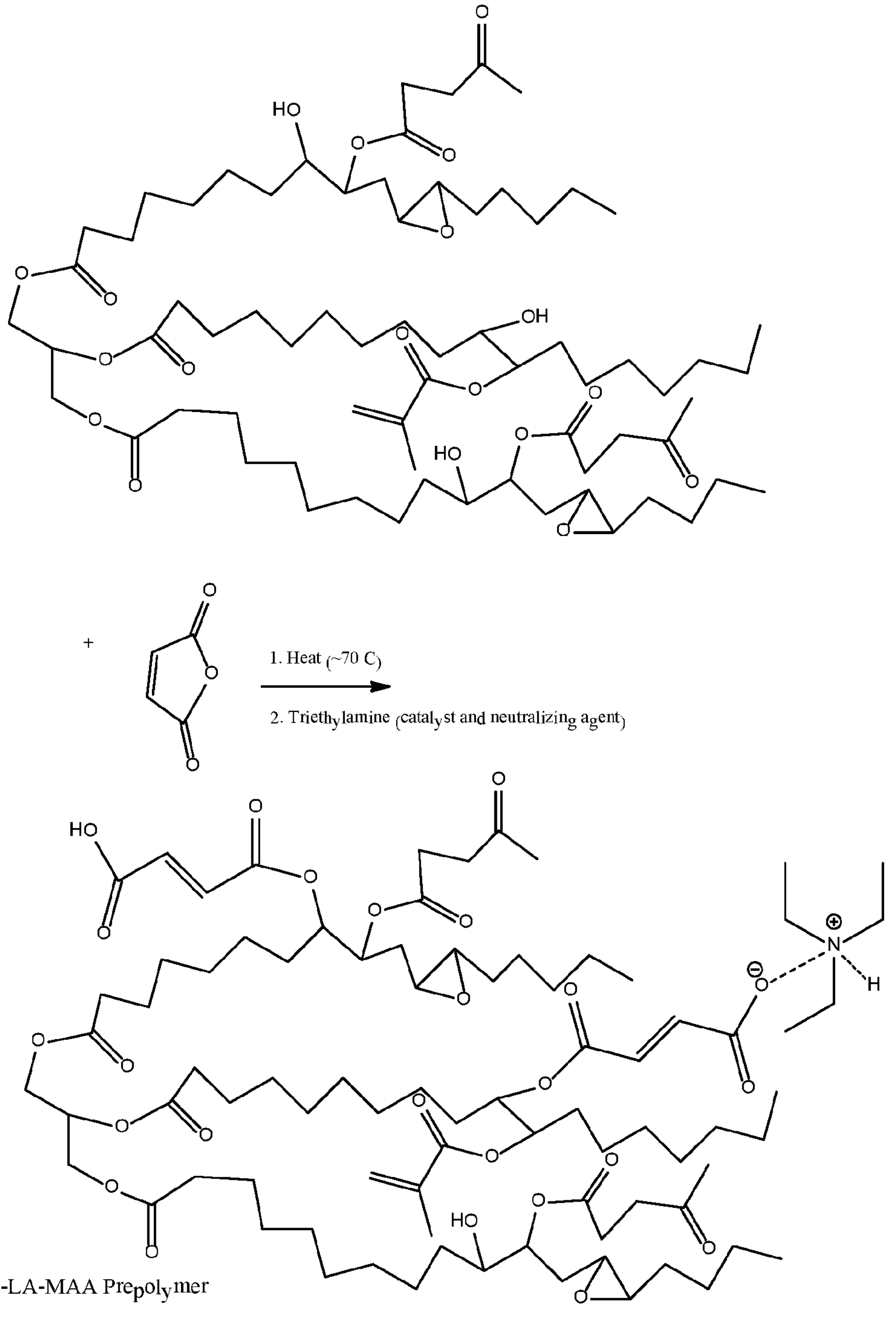
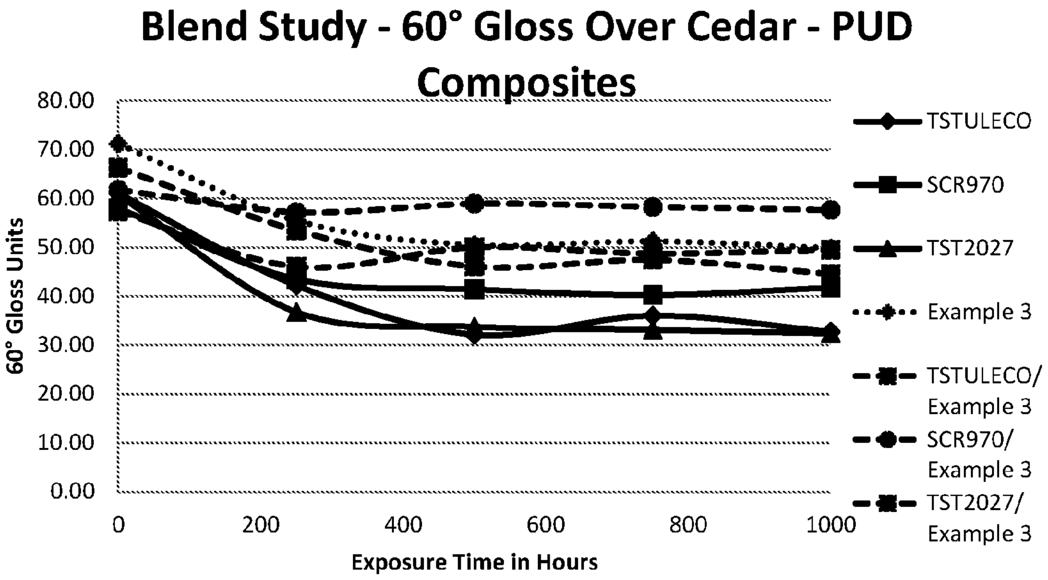


FIG. 2



ESO-LA-MAA Prepolymer

FIG 3


Blend Study - 60° Gloss Over Cedar - PUD Composites
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
60° Gloss Units
0
200
400
600
800
1000
Exposure Time in Hours
TSTULECO
SCR970
TST2027
Example 3
TSTULECO/ Example 3
SCR970/ Example 3
TST2027/ Example 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/022049

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/02
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/047369 A2 (ARCHER DANIELS MIDLAND CO [US]; LAROCK RICHARD C [US]; LU YONGSHANG [U) 21 April 2011 (2011-04-21) paragraph [0012] - paragraph [0013] abstract; claims 1, 2, 6-8; figures 1-16; tables 1-5 -----	1-19
X	WO 2008/016843 A1 (LUBRIZOL ADVANCED MAT INC [US]; PAJERSKI ANTHONY D [US]) 7 February 2008 (2008-02-07) paragraph [0016] - paragraph [0018] abstract; claims 1-5, 7, 8, 13, 14, 20; examples 1-9 -----	1-19
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 2 May 2016	Date of mailing of the international search report 11/05/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Glomm, Bernhard

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2016/022049

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/022049

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