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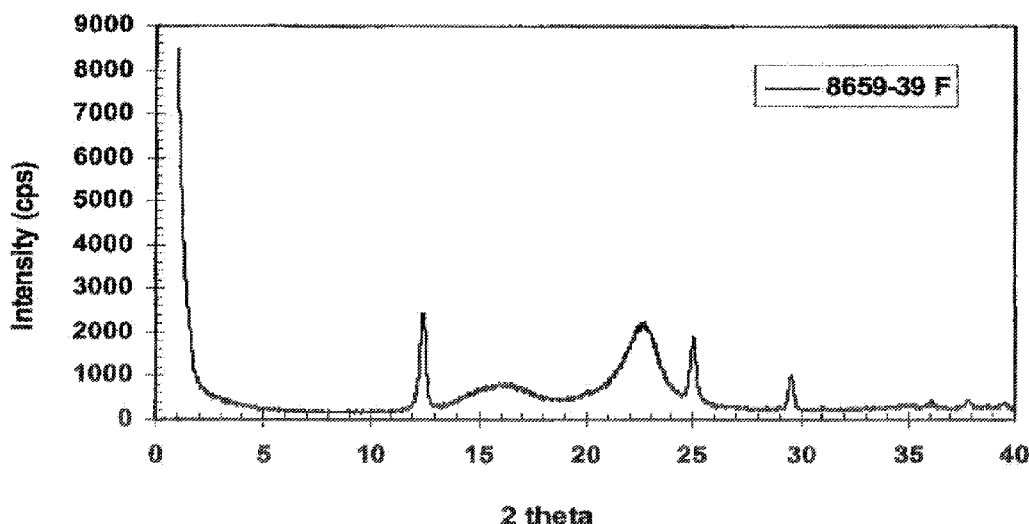
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(54) Title: WEAR RESISTANT COATING COMPOSITION

XRD



(57) Abstract: This invention relates to wear resistant coating compositions containing exfoliated clay-polymer emulsion obtained by emulsion polymerization of monomers in the presence of layered clay, also known as in situ emulsion polymerization. The layered clay may be added to the aqueous phase of the polymerization or introduced to the polymerization along with monomers through monomer feed.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

WEAR RESISTANT COATING COMPOSITION

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This non-provisional application relies on the filing date of provisional U.S. Application Serial No. 60/787,569, filed on March 30, 2006, having been filed within twelve (12) months thereof, which is incorporated herein by reference, and priority thereto is
10 claimed under 35 USC § 1.19(e).

BACKGROUND OF THE INVENTION

[0001] Wear resistant coating compositions for flooring have been explored. Silica particulates are often incorporated into the coating compositions to enhance wear resistance.
15 A film of an aqueous or non-aqueous composition containing silica particles, one or more polymerizable acrylic monomers, photoinitiator and optionally one or more silanes, is applied to the substrate and photopolymerized to generate a polymeric wear resistant coating on the surface thereof. European Patent Application No. 317,858 describes a wear resistant coating composition produced by photopolymerization of a mixture containing partial condensate of
20 colloidal silica with vinyl silane, a multi-functional (meth)acrylate-type monomer, and a lower alkanol in solvent medium. The coating composition contains relatively large quantities of solvent that must be evaporated after application. U.S. Patent No. 5,232,964 teaches a method of preparing wear resistant coating compositions including photopolymerization of a mixture containing one multi-functional acrylate monomer, one
25 silane, and colloidal silica dispersed in a solvent. Again, the coating compositions contain volatile organic solvent that must be evaporated after application.

[0002] Polymer-clay composites have been explored for their resistance properties in various applications (U.S. Patent Nos. 5,883,173 and 6,838,507). When layered silicates
30 (clays) and polymers are combined, three types of composites can be obtained, depending on the nature of each component and the preparation method. A phase separated composite demonstrating properties similar to a traditional microcomposite is attained, if the polymer chains are unable to intercalate between the silicate sheets. The other two types of polymer-

clay composite constitute the realm of possible nanocomposite structures. An intercalated structure is obtained when the polymer chains intercalate between host silicate sheets giving a well-ordered, stacked multilayers morphology. An exfoliated structure is obtained when the silicate layers are fully and uniformly dispersed in a continuous polymer matrix, but there is random and disordered in the nature of the silicate sheets. The exfoliated clay-polymer nanocomposites are known to demonstrate higher degrees of strength, stiffness and barrier properties with much lower clay content than those of conventional clay-polymer microcomposites.

[0003] There is still a need for coating compositions capable of imparting to the coated substrate excellent wear resistant and other optimizes properties desirable for surface coverings, such as increased abrasion and scuff resistance, enhanced water resistance, superior adhesion to the substrate, and improved chemical/stain/grease/UV resistance.

[0004] It is an object of the present invention to provide coating compositions that impart desirable surface covering properties to the surface treated thereof, such as excellent wear resistant, increased abrasion and scuff resistance, enhanced water resistance, superior adhesion to the substrate, and improved chemical/stain/grease/UV resistance.

[0005] It is another object of the present invention to provide coating compositions containing exfoliated clay-polymer emulsion obtained from *in-situ* polymerization process.

[0006] It is yet another object of the present invention to provide novel water-based, wear resistant coating compositions that contain no volatile organic solvents, thereby eliminating the need for evaporation of solvents after application, as well as improving the compliance with governmental regulation towards lower volatile organic content (VOC).

[0007] It is a further object of the present invention to provide a method of preparing exfoliated clay-polymer compositions through *in-situ* polymerization.

[0008] It is yet a further object of the present invention to provide substrates treated with the aforementioned wear resistant coating compositions containing exfoliated clay-

polymer emulsions.

[0009] Other objects and advantages of the present invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The advantages and purposes of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

SUMMARY OF THE INVENTION

[0010] This invention relates to wear resistant coating compositions containing exfoliated clay-polymer emulsion obtained by emulsion polymerization of monomers in the presence of layered clay, also known as *in situ* emulsion polymerization. The layered clay may be added to the aqueous phase of the polymerization or introduced to the polymerization along with monomers through monomer feed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] FIG.1 is a schematic X-ray diffraction patterns of clay-polymer composites having different structures (immiscible, intercalated and exfoliated) as published in *Macromolecules* (1997), volume 30, page 8000-8009;

[0012] FIG 2 is an X-ray diffraction of Sample 1 of the present invention;

[0013] FIG 3 is an X-ray diffraction of Sample 2 of the present invention;

[0014] FIG 4 is an X-ray diffraction of Sample 3 of the present invention;

[0015] FIG 5 is an X-ray diffraction of a post-blend of surface-treated montmorillonite clay and polymer.

DESCRIPTION OF THE INVENTION

[0016] The following detailed description illustrates embodiments of the present invention; however, it is not intended to limit the scope of the appended claims in any manner. It is to be understood that changes and modifications may be made therein as will be apparent to those skilled in the art. Such variations are to be considered within the scope of the invention as defined in the claims.

[0017] The advantages and purposes of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention.

5

[0018] The emulsion used in the wear resistant coating composition of the present invention is an exfoliated clay-polymer emulsion obtained by emulsion polymerization of monomers in the presence of layered clay, also known as *in situ* emulsion polymerization. In one embodiment, the clay is added into an aqueous phase of the polymerization. In another
10 embodiment, the clay is introduced to the polymerization along with monomer(s) through monomer feed, also known as "monomer co-feed."

[0019] The emulsions used in the wear resistant coating compositions of the present invention comprise:

15

- (a) polymerization product of a mixture comprising at least one free radical polymerizable monomer;
- (b) emulsifier; and
- (c) layered clay completely exfoliated with the polymer in an amount range of about 0.1% to about 20% weight based on dry weight of the polymer.

20

[0020] Suitable silicate clays for use in the present invention include, but are not limited to, smectite, phyllosilicate, montmorillonite, saponite, beidellite, montronite, hectorite, stevensite, vermiculite, kaolinite, hallosite, and synthetic phyllosilicate. The clay may be surface treated or non-surface treated.

25

[0021] Suitable polymers for use in the present invention are polymerization products of a mixture comprising at least one free radical polymerizable monomer such as acrylic-based monomer, styrenic-based monomer, vinylic-based monomer, and α,β -unsaturated monomer.

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[0022] Examples of acrylic-based monomers include, but are not limited to, acrylic acid; methacrylic acid; itaconic acid; maleic acid; fumaric acid; acryloxypropionic acid;

(meth)acryloxypropionic acid; sulphonic acid-bearing monomers such as styrene sulfonic acid, sodium vinyl sulfonate, sulfoethyl acrylate, sulfoethyl methacrylate, ethylmethacrylate-2-sulphonic acid, and 2-acrylamido-2-methylpropane sulphonic acid; phosphoethylmethacrylate; methacrylic anhydride; maleic anhydride; itaconic anhydride; succinic anhydride; acrylate; and methacrylate. Acrylate monomers include, but are not limited to, C₁–C₃₀ alkyl ester of acrylic acid monomers such as methyl acrylate, ethyl acrylate, n-propyl acrylate, butyl acrylate, allyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, octyl acrylate, nonyl acrylate, n-lauryl acrylate, stearyl acrylate, n-decyl acrylate, isodecyl acrylate, isobornyl acrylate; phenoxyethyl acrylate; 2-phenoxy acrylate; 2-methoxyethyl acrylate; lactone modified esters of acrylic acid; tetrahydrofuryl acrylate; 2-(2-ethoxyethoxy)ethyl acrylate; 2-phenoxyethyl acrylate; acrylated methylolmelamine; 2-(N,N-diethylamino)-ethyl acrylate; glycidyl acrylate; neopentyl glycol diacrylate; alkoxyated neopentyl glycol diacrylate; ethylene glycol diacrylate; hexylene glycol diacrylate; diethylene glycol diacrylate; dipropylene glycol diacrylate; tripropylene glycol diacrylate; tetraethylene glycol diacrylate; pentaerythritol di-, tri-, tetra-, or penta-acrylate; trimethylolpropane triacrylate; alkoxyated trimethylol-propane triacrylate containing from 2 to 14 moles of either ethylene or propylene oxide; triethylene glycol diacrylate; tetraethylene glycol diacrylate; alkoxyated neopentyl glycol diacrylate having from 2 to 14 moles of ethoxy or propoxy units; polyethylene glycol diacrylate; 1,3-butylene glycol diacrylate; 1,4-butanediol diacrylate; 1,6-hexanediol diacrylate; polyethylene glycol diacrylate; and a mixture thereof. Methacrylate monomers include, but are not limited to, methyl methacrylate; ethyl methacrylate; n-propyl methacrylate; n-butyl methacrylate; isopropyl methacrylate; isobutyl methacrylate; n-amyl methacrylate; n-hexyl methacrylate; isoamyl methacrylate; 2-hydroxyethyl methacrylate; 2-hydroxypropyl methacrylate; lactone modified esters of methacrylic acid; N,N-dimethylaminoethyl methacrylate; N,N-diethylaminoethyl methacrylate; t-butylaminoethyl methacrylate; 2-sulfoethyl methacrylate; trifluoroethyl methacrylate; glycidyl methacrylate; benzyl methacrylate; allyl methacrylate; 2-n-butoxyethyl methacrylate; 2-chloroethyl methacrylate; sec-butyl-methacrylate, tert-butyl methacrylate; 2-ethylbutyl methacrylate; cinnamyl methacrylate; crotyl methacrylate; cyclohexyl methacrylate; cyclopentyl methacrylate; 2-ethoxyethyl methacrylate; furfuryl methacrylate; hexafluoroisopropyl methacrylate; methallyl methacrylate; 3-methoxybutyl methacrylate; 2-methoxybutyl

methacrylate; 2-nitro-2-methylpropyl methacrylate; n-octylmethacrylate; 2-ethylhexyl methacrylate; 2-phenoxyethyl methacrylate; 2-phenylethyl methacrylate; phenyl methacrylate; methacrylamide; propargyl methacrylate; tetrahydrofurfuryl methacrylate; and tetrahydropyranyl methacrylate.

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[0023] The styrenic-based monomers suitable for use in the present invention may be substituted or unsubstituted. Representative examples of styrene monomers include, but are not limited to, styrene, α -methyl styrene, p-methyl styrene, α -ethyl styrene and α -isopropyl styrene.

10

[0024] Examples of vinylic-based monomers include, but are not limited to, ethylene, propylene, vinyl chloride, vinyl acetate, acrylonitrile, butene, hexene, heptene, isobutylene, and octane.

15

[0025] Examples of α,β -unsaturated monomers include, but are not limited to, butadiene, isoprene, chloroprene, and other dienes.

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[0026] Any emulsifier known for its use in an emulsion polymerization may be employed in the present invention. These include nonionic emulsifiers, anionic emulsifiers, and combinations thereof. Suitable anionic emulsifiers include, but are not limited to, alkyl sulfates, ether sulfates, phosphate esters, sulfonates, and the like. Suitable nonionic emulsifiers include, but are not limited to, fatty acids, alcohol ethoxylates, alkylphenol ethoxylate, phenol ethoxylate, block copolymers, and the like. Anionic and non-ionic emulsifiers containing polymerizable groups (known in the art as "polymerizable surfactants") are also suitable for use in the present invention. Furthermore, gemini surfactant may be used in the present invention.

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[0027] In one embodiment of the present invention, water-dispersible stabilized polymer is used as an emulsifier. The water-dispersible stabilized polymer is added to the initial aqueous phase prior to an addition of monomers and/or clay. Suitable water-dispersible stabilized polymers for use in the present invention have an average molecular weight in the range of about 2,000 to about 12,000. In some embodiments, the water-

dispersible stabilized polymers have an average molecular weight in the range of about 5,000 to about 11,000.

[0028] The water-dispersible stabilized polymers suitable for use in the present invention have an acid number of about 200 to about 290. In some embodiments, the acid number is about 200 to about 280. In some other embodiments, the acid number is about 200 to about 275. Polar, non-ionic water-dispersible polymers may also be employed in the present invention.

[0029] In some embodiments, the water-dispersible stabilized polymers are low molecular weight styrene acrylic copolymer. In some other embodiments, the water-dispersible stabilized polymers are low molecular weight hybrid resin of acrylic monomers, rosins and fatty acids. Examples of water-dispersible stabilized polymers include, but are not limited to, any hybrid resin of acrylic monomers, rosins and fatty acids, styrene-acrylic copolymers or acrylic hard resins known for their dispersion capabilities in emulsion polymerization reactions.

[0030] A catalytic amount of at least one polymerization initiator is used in the polymerization reaction. Traditional polymerization initiators such as thermal initiators, redox initiators, and combinations thereof are suitable for use in the emulsion polymerization of the present invention. The type of polymerization initiator is known in the art to depend upon the desired temperature for the reaction. Thermal initiators which are suitable for use include, but are not limited to, hydrogen peroxide, t-butyl hydroperoxide, di-t-butyl peroxide, benzoyl peroxide, benzoyl hydroperoxide, 2,4-dichlorobenzoyl peroxide, t-butyl peracetate, azobisisobutyronitrile, ammonium persulfate, sodium persulfate, potassium persulfate, isopropyl peroxy carbonate, and combinations thereof. Suitable redox initiators include, but are not limited to, sodium persulfate-sodium formaldehyde sulfoxylate, cumene hydroperoxide-sodium metabisulfite, potassium persulfate-sodium metabisulfite, potassium persulfate-sodium bisulfite, cumene hydroperoxide-iron (II) sulfate, and combinations thereof.

[0031] Optionally, at least one chain transfer agent may be incorporated during

polymerization to control the molecular weight of the polymer. Examples of chain transfer agents include, but are not limited to, mercaptans, polymercaptans, and polyhalogen compounds. Further, non-limiting examples of chain transfer agents include alkyl mercaptans such as ethyl mercaptan, n-propyl mercaptan, n-butyl mercaptan, isobutyl mercaptan, t-butyl
5 mercaptan, n-amyl mercaptan, isoamyl mercaptan, t-amyl mercaptan, n-hexyl mercaptan, cyclohexyl mercaptan, n-octyl mercaptan, n-decyl mercaptan, n-dodecyl mercaptan; mercapto carboxylic acids and their esters, such as methyl mercaptopropionate and 3-mercaptopropionic acid; alcohols such as isopropanol, isobutanol, lauryl alcohol and t-octyl alcohol; and halogenated compounds such as carbon tetrachloride, tetrachloroethylene, and
10 trichloro-bromoethane.

[0032] Where desired, crosslinkers may be added to the polymerization reaction mixture. Examples of suitable crosslinkers include, but are not limited to, divinyl benzene, butylene glycol dimethacrylate, alkanepolyol-polyacrylates, alkanepolyol-polymethacrylates,
15 ethylene glycol di(meth)acrylate, butylene glycol diacrylate, oligoethylene glycol diacrylate, oligoethylene glycol dimeth-acrylate, trimethylol-propane diacrylate, trimethylolpropane dimeth-acrylate, trimethylol-propane triacrylate, trimethylolpropane trimethacrylate, and unsaturated carboxylic acid allyl.

20 [0033] In one embodiment of the present invention, the emulsion containing polymer and clay completely exfoliated within the polymer matrix is produced using an *in-situ* polymerization process comprising the steps of:

- (i) providing an initial aqueous phase containing emulsifier;
- 25 (ii) adding dispersed clay to the aqueous phase;
- (iii) adding to the aqueous phase, a mixture comprising at least one free radical polymerizable monomer; and
- (iii) polymerizing the reaction mixture.

30 [0034] In one embodiment of the present invention, the emulsion containing polymer and clay completely exfoliated within the polymer matrix is produced using an *in-situ* polymerization process comprising the steps of:

- (i) providing an initial aqueous phase containing emulsifier;
- (ii) mixing clay with at least one monomer;
- (iii) adding to the aqueous phase, a monomer mixture comprising at least one free radical polymerizable monomer; and
- 5 (iv) polymerizing the mixture.

[0035] It is to be understood that various emulsion polymerization procedures may be used in preparing the invention emulsions. Examples of emulsion polymerization procedures include, but are not limited to, core-shell, single stage, multi-stage, mini-emulsion, and grad-
10 add polymerizations.

[0036] Montmorillonite clay is an aluminosilicate smectite clay. It is a cation-poor layered silicate; therefore, its layers can be easily separated. X-ray diffraction (XRD) is commonly used to analyze clay, since it allows for the measurement of the distance between
15 basal layers (d-spacing) of the clays or any other layered materials. First, the X-ray diffraction is taken for the clay. Then, the clay-polymer composite is formed and an X-ray diffraction is taken for the composite. The change in the d-spacing between the clay itself and the d-spacing of the clay-polymer composite is used to determine the morphology of the clay-polymer composite. An increase of d-spacing in the clay-polymer composite, compared
20 to the d-spacing of the clay itself, indicates that some polymer chains enter the galleries of the clay material and increase the space between the clay layers. The three main types of clay-polymer composites (immiscible, intercalated and exfoliated) can be characterized using XRD as shown in FIG.1.

25 [0037] No change in the d-spacing between the clay itself and the d-spacing of the clay-polymer mixture is described as **Immiscible**. In this case, no polymer enters the gallery of the clay; therefore, the distance between basal layers (d-spacing) of the clays remains the same.

30 [0038] An increase between the d-spacing of the clay itself and the d-spacing of the clay-polymer mixture is described as **Intercalated**. In this case, some polymer chains enter the gallery of the clay, expanding the layers apart. However, the clay layers are still close

enough to each other in an ordered state that the diffraction is still observed.

[0039] No XRD peak observed is described as **Exfoliated**. In this case, more polymer chains enter the clay galleries, expanding the layers so far apart that diffraction cannot be observed with wide-angle X-ray (XRD) technique. Moreover, the layers are sufficiently disordered such that they no longer give a coherent XRD signal.

[0040] The structure of the clay-polymer emulsions of the present invention was analyzed using X-ray diffraction (XRD) and compared to that of the clay-polymer composition obtained from known preparation process. Sample 1 of the present invention was prepared by an *in-situ* emulsion polymerization of styrene and acrylic monomers in the presence of surface treated montmorillonite clay, wherein the clay was added to the aqueous phase of the polymerization. The X-ray diffraction of montmorillonite clay itself shows a d-spacing peak of 1.86 nm. The X-ray diffraction of Sample 1 showed no XRD peak at the 2θ of about 4-6 degree, demonstrating that the *in-situ* clay-polymer emulsion of Sample 1 has an exfoliated clay structure. (FIG. 2) Sample 2 was prepared using the same *in-situ* emulsion polymerization process as Sample 1, except non-surface treated montmorillonite clay was used. The X-ray diffraction of Sample 2 also showed no XRD peak at the 2θ of about 4-6 degree, confirming that the *in-situ* clay-polymer emulsion of Sample 2 also has an exfoliated clay structure. (FIG. 3) Sample 3 was prepared by an *in-situ* emulsion polymerization of styrene and acrylic monomers in the presence of surface treated montmorillonite clay, wherein the clay was mixed with monomer and added to the reaction mixture through monomer feed. The X-ray diffraction of Sample 3 showed no XRD peak at the 2θ of about 4-6 degree, indicating that the *in-situ* clay-polymer emulsion of Sample 3 has an exfoliated clay structure. (FIG. 4) When preformed polymer was blended with surface-treated montmorillonite clay, also known as "post-blend," the x-ray diffraction of such system showed, at a small intensity, d-spacing peak of 2.8 nm at the 2θ of about 4-6 degree. (FIG. 5) This indicated that the post-blend of clay and polymer provided immiscible or intercalated clay-polymer system, or mixture thereof.

[0041] The wear resistant coating composition of the present invention comprises the aforementioned emulsions containing polymer and clay completely exfoliated in the polymer matrix.

5 [0042] When desired, the invention wear resistant compositions may contain one or more crosslinkers capable of crosslinking at room temperature or elevated temperature. Some of these crosslinkers include, but are not limited to, polycarbodiimide, functional silane, and melamine resin.

10 [0043] Where desired, a film-forming aid such as coalescence agents, plasticizers, and the like may be added to the coating composition. It is well within the ability of one skilled in the art to determine the appropriate pH range, solids level, and film-forming characteristics for such applications.

15 [0044] The invention coating compositions may further include additives such as buffers, neutralizers, thickeners or rheology modifiers, humectants, wetting agents, biocides, plasticizers, antifoaming agents, colorants, fillers, waxes, water repellants, slip or mar aids, anti-oxidants, and the like.

20 [0045] The invention coating composition may be applied by any conventional application methods. Examples of these include, but are not limited to, brushing, spraying, roll coating, doctor-blade application, air knife coating, trailing blade coating, curtain coating, and extrusion.

25 [0046] The invention coating compositions may be applied to any flooring materials. Examples of flooring include, but are not limited to, wood, vinyl, slate, concrete, and stone.

 [0047] The foregoing description and the following examples represent embodiments of the present invention. It is to be understood that changes and modifications may be made
30 therein as will be apparent to those skilled in the art. Such variations are to be considered within the scope of the invention as defined in the following claims.

EXPERIMENTAL

[0048] Sample 1

5 [0049] To a round-bottomed flask fitted with a mechanical stirrer, a heating mantle and inlet tubes for monomer feed, was charged, with stirring, 380.2 g of deionized water, 82 g of a low molecular weight alkali-soluble, water-dispersible styrene acrylic polymer and 20.5 g of a 28-30 % ammonium hydroxide solution. The mixture was heated to 71°C until complete dissolution. Then oleic acid (37.4 g), ammonium hydroxide (7.1 g) and 3 wt %
10 (based on monomers) of Cloisite® 25A (surface treated montmorillonite provided by Southern Clay Products Inc.) were added to the initial charge, followed by an increase in temperature to 80°C. A solution of 2.46 g of ammonium persulfate in 11.1 mL of deionized water was added to the flask. The monomer feed was then prepared, composed of a mixture of 136.8 g of 2-ethylhexyl acrylate, 143.3 g of methyl methacrylate, and 5.5 g of glycidyl
15 methacrylate. The monomer feed was added to the flask over a period of two hours. At the end of the addition period, the mixture was held at 80°C for an additional half hour. Thereafter, a solution of 0.5 g of ammonium persulfate in 21.4 mL of deionized water was added to the flask, the temperature of the mixture was held at 80°C for an additional hour. Following a cooling period, a solution of 0.6 g of biocide (Proxel GXL manufactured by
20 Avecia) in 1.2 mL of deionized water was added to the mixture.

[0050] The resulting latex composition had a solids content of 49.4%, Brookfield viscosity of 500 cps at 25°C, and an average particle size of 78.3 nm.

25 [0051] Sample 2

[0052] Same process as Example 1, but non-surface treated montmorillonite clay was used instead of surface treated montmorillonite clay.

[0053] Sample 3

30 [0054] To a round-bottomed flask fitted with a mechanical stirrer, a heating mantle and inlet tubes for monomer feed, was charged, with stirring, 380.2 g of deionized water, 82 g of a low molecular weight alkali-soluble, water-dispersible styrene acrylic polymer and

20.5 g of a 28-30 % ammonium hydroxide solution. The mixture was heated to 71°C until the low molecular weight polymer was completely dissolved. Oleic acid (37.4 g) and ammonium hydroxide (7.1 g) were added to the initial charge, followed by an increase in temperature to 80°C. A solution of 2.46 g of ammonium persulfate in 11.1 mL of deionized water was added to the flask. The monomer feed was then prepared, composed of a mixture of 136.8 g of 2-ethylhexyl acrylate, 143.3 g of methyl methacrylate, and 5.5 g of glycidyl methacrylate. Prior to mixing all the monomers together, 3 wt % (based on monomers) of Cloisite® 25A (surface treated montmorillonite provided by Southern Clay Products Inc.) was mixed with 2-ethylhexyl acrylate under high shear. The monomer feed was added to the flask over a period of two hours. At the end of the addition period, the mixture was held at 80°C for an additional half hour. Thereafter, a solution of 0.5 g of ammonium persulfate in 21.4 mL of deionized water was added to the flask, and the temperature of the mixture was held at 80°C for an additional hour. Following a cooling period, a solution of 0.6 g of biocide (Proxel GXL manufactured by Avecia) in 1.2 mL of deionized water was added to the mixture.

[0055] The resulting latex composition had a solids content of 49.4%, Brookfield viscosity of 3350 cps at 25°C, and an average particle size of 74.3 nm.

What Is Claimed Is:

1. An emulsion comprising:
 - (a) polymerization product of a mixture comprising at least one free radical polymerizable monomer;
 - (b) emulsifier; and
 - (c) layered clay exfoliated with the polymer, in an amount range of about 0.1% to about 20% weight based on dry weight of the polymer.
2. The emulsion of claim 1, wherein the clay comprises at least one member selected from the group consisting of smectite, phyllosilicate, synthetic phyllosilicates, montmorillonite, saponite, beidellite, montionite, hectorite, stevensite, vermiculite, kaolinite and hallosite.
3. The emulsion of claim 1, wherein the free radical polymerizable monomer comprises at least one member selected from the group consisting of acrylic-based monomer, styrenic-based monomer, vinylic-based monomer, α,β -unsaturated monomer, and combinations thereof.
4. The emulsion of claim 3, wherein the acrylic-based monomer comprises at least one member selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acryloxypropionic acid, methacryloxypropionic acid, sulphonic acid-bearing monomers, phosphoethylmethacrylate, methacrylic anhydride, maleic anhydride, itaconic anhydride, succinic anhydride, glycidyl acrylate, glycidyl methacrylate, $C_1 - C_{30}$ alkyl ester of acrylic acid, phenoxyethyl acrylate, 2-phenoxy acrylate, 2-methoxyethyl acrylate, lactone modified esters of acrylic acid, butyl acrylate, allyl acrylate, tetrahydrofuryl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-phenoxyethyl acrylate, acrylated methylolmelamine, 2-(N,N-diethylamino)-ethyl acrylate, neopentyl glycol diacrylate, alkoxyated neopentyl glycol diacrylate, ethylene glycol diacrylate, hexylene glycol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, pentaerythritol acrylate, trimethylolpropane triacrylate, alkoxyated trimethylol-propane triacrylate containing from 2 to 14 moles of ethylene oxide, alkoxyated trimethylol-propane triacrylate

containing from 2 to 14 moles of propylene oxide, triethylene glycol diacrylate, tetraethylene glycol diacrylate, alkoxylated neopentyl glycol diacrylate having from 2 to 14 moles of ethoxy units, alkoxylated neopentyl glycol diacrylate having from 2 to 14 moles of propoxy units, polyethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, polyethylene glycol diacrylate, C₁ – C₃₀ alkyl ester of methacrylic acid, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, lactone modified esters of methacrylic acid, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, 2-sulfoethyl methacrylate, trifluoroethyl methacrylate, glycidyl methacrylate, benzyl methacrylate, allyl methacrylate, 2-n-butoxyethyl methacrylate, 2-chloroethyl methacrylate, sec-butyl-methacrylate, tert-butyl methacrylate, 2-ethylbutyl methacrylate, cinnamyl methacrylate, crotyl methacrylate, cyclohexyl methacrylate, cyclopentyl methacrylate, 2-ethoxyethyl methacrylate, furfuryl methacrylate, hexafluoroisopropyl methacrylate, methallyl methacrylate, 3-methoxybutyl methacrylate, 2-methoxybutyl methacrylate, 2-nitro-2-methylpropyl methacrylate, n-octylmethacrylate, 2-ethylhexyl methacrylate, 2-phenoxyethyl methacrylate, 2-phenylethyl methacrylate, phenyl methacrylate, methacrylamide, propargyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydropyranyl methacrylate, and combinations thereof.

5. The emulsion of claim 3, wherein the styrenic-based monomer is selected from the group consisting of unsubstituted styrene monomer, substituted styrene monomer, and combinations thereof.
6. The emulsion of claim 3, wherein the vinylic-based monomer comprises at least one member selected from the group consisting of ethylene, propylene, vinyl chloride, vinyl acetate, acrylonitrile, butene, hexene, heptane, isobutylene, octane, and combinations thereof.
7. The emulsion of claim 3, wherein the α,β -unsaturated monomer comprises at least one member selected from the group consisting of butadiene, isoprene, chloroprene, dienes, and combinations thereof.

8. The emulsion of claim 1, wherein the emulsifier comprises at least one member selected from the group consisting of nonionic emulsifiers, anionic emulsifiers, water-dispersible stabilized polymer, polymerizable surfactants, gemini surfactants, and combinations thereof.

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9. The emulsion of claim 8, wherein the water-dispersible stabilized polymer has an average molecular weight in the range of about 2,000 to about 12,000.

10. The emulsion of claim 8, wherein the water-dispersible stabilized polymer has an acid number in the range of about 200 to about 290.

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11. The emulsion of claim 1, wherein the mixture further comprises crosslinker.

12. A coating composition including exfoliated clay-polymer emulsion, wherein the emulsion comprises:

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- (a) polymerization product of a mixture comprising at least one free radical polymerizable monomer;
- (b) emulsifier; and
- (c) layered clay exfoliated with the polymer, in an amount range of about 0.1% to about 20% weight based on dry weight of the polymer.

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13. The coating composition of claim 12, wherein the clay comprises at least one member selected from the group consisting of smectite, phyllosilicate, synthetic phyllosilicates, montmorillonite, saponite, beidellite, montionite, hectorite, stevensite, vermiculite, kaolinite and hallosite.

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14. The coating composition of claim 12, wherein the free radical polymerizable monomer comprises at least one member selected from the group consisting of acrylic-based monomer, styrenic-based monomer, vinylic-based monomer, α,β -unsaturated monomer, and combinations thereof.

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15. The coating composition of claim 14, wherein the acrylic-based monomer comprises at least one member selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acryloxypropionic acid, (meth)acryloxypropionic acid, sulphonic acid-bearing monomers, phosphoethylmethacrylate, methacrylic anhydride, maleic anhydride, itaconic anhydride, succinic anhydride, glycidyl acrylate, glycidyl methacrylate, C₁–C₃₀ alkyl ester of acrylic acid, phenoxyethyl acrylate, 2-phenoxy acrylate, 2-methoxyethyl acrylate, lactone modified esters of acrylic acid, butyl acrylate, allyl acrylate, tetrahydrofuryl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-phenoxyethyl acrylate, acrylated methylolmelamine, 2-(N,N-diethylamino)-ethyl acrylate, neopentyl glycol diacrylate, alkoxylated neopentyl glycol diacrylate, ethylene glycol diacrylate, hexylene glycol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, pentaerythritol acrylate, trimethylolpropane triacrylate, alkoxylated trimethylol-propane triacrylate containing from 2 to 14 moles of ethylene oxide, alkoxylated trimethylol-propane triacrylate containing from 2 to 14 moles of propylene oxide, triethylene glycol diacrylate, tetraethylene glycol diacrylate, alkoxylated neopentyl glycol diacrylate having from 2 to 14 moles of ethoxy units, alkoxylated neopentyl glycol diacrylate having from 2 to 14 moles of propoxy units, polyethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, polyethylene glycol diacrylate, C₁–C₃₀ alkyl ester of methacrylic acid, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, lactone modified esters of methacrylic acid, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, 2-sulfoethyl methacrylate, trifluoroethyl methacrylate, glycidyl methacrylate, benzyl methacrylate, allyl methacrylate, 2-n-butoxyethyl methacrylate, 2-chloroethyl methacrylate, sec-butyl-methacrylate, tert-butyl methacrylate, 2-ethylbutyl methacrylate, cinnamyl methacrylate, crotyl methacrylate, cyclohexyl methacrylate, cyclopentyl methacrylate, 2-ethoxyethyl methacrylate, furfuryl methacrylate, hexafluoroisopropyl methacrylate, methallyl methacrylate, 3-methoxybutyl methacrylate, 2-methoxybutyl methacrylate, 2-nitro-2-methylpropyl methacrylate, n-octylmethacrylate, 2-ethylhexyl methacrylate, 2-phenoxyethyl methacrylate, 2-phenylethyl methacrylate, phenyl methacrylate, methacrylamide,

propargyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydropyranyl methacrylate, and combinations thereof.

16. The coating composition of claim 14, wherein the styrenic-based monomer is selected
5 from the group consisting of unsubstituted styrene monomer, substituted styrene monomer, and combinations thereof.
17. The coating composition of claim 14, wherein the vinylic-based monomer comprises at
10 least one member selected from the group consisting of ethylene, propylene, vinyl chloride, vinyl acetate, acrylonitrile, butene, hexene, heptane, isobutylene, octane, and combinations thereof.
18. The coating composition of claim 14, wherein the α,β -unsaturated monomer comprises
15 at least one member selected from the group consisting of butadiene, isoprene, chloroprene, dienes, and combinations thereof.
19. The coating composition of claim 12, wherein the emulsifier comprises at least one
20 member selected from the group consisting of nonionic emulsifiers, anionic emulsifiers, water-dispersible stabilized polymer, polymerizable surfactants, gemini surfactants, and combinations thereof.
20. The coating composition of claim 19, wherein the water-dispersible stabilized polymer
has an average molecular weight in the range of about 2,000 to about 12,000.
- 25 21. The coating composition of claim 19, wherein the water-dispersible stabilized polymer has an acid number in the range of about 200 to about 290.
22. The coating composition of claim 12, wherein the mixture further comprises
30 crosslinker.
23. The coating composition of claim 12, further comprising at least one member selected from the group consisting of crosslinker, coalescence agent, plasticizer, buffers,

neutralizers, thickeners, rheology modifiers, humectants, wetting agents, biocides, plasticizers, antifoaming agents, colorants, fillers, waxes, water repellants, slip or mar aids, anti-oxidants, and combinations thereof.

- 5 24. A substrate treated with coating composition including exfoliated clay-polymer emulsion, wherein the emulsion comprises:
 - (a) polymerization product of a mixture comprising at least one free radical polymerizable monomer;
 - (b) emulsifier; and
 - 10 (c) layered clay exfoliated with the polymer, in an amount range of about 0.1% to about 20% weight based on dry weight of the polymer.
25. The substrate of claim 24, wherein the clay comprises at least one member selected from the group consisting of smectite, phyllosilicate, synthetic phyllosilicates,

15 montmorillonite, saponite, beidellite, montionite, hectorite, stevensite, vermiculite, kaolinite and hallosite.
26. The substrate of claim 24, wherein the free radical polymerizable monomer comprises at least one member selected from the group consisting of acrylic-based monomer,

20 styrenic-based monomer, vinylic-based monomer, α,β -unsaturated monomer, and combinations thereof.
27. The substrate of claim 26, wherein the acrylic-based monomer comprises at least one member selected from the group consisting of acrylic acid, methacrylic acid, itaconic

25 acid, maleic acid, fumaric acid, acryloxypropionic acid, (meth)acryloxypropionic acid, sulphonic acid-bearing monomers, phosphoethylmethacrylate, methacrylic anhydride, maleic anhydride, itaconic anhydride, succinic anhydride, glycidyl acrylate, glycidyl methacrylate, C_1-C_{30} alkyl ester of acrylic acid, phenoxyethyl acrylate, 2-phenoxy

30 acrylate, 2-methoxyethyl acrylate, lactone modified esters of acrylic acid, butyl acrylate, allyl acrylate, tetrahydrofuryl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-phenoxyethyl acrylate, acrylated methylolmelamine, 2-(N,N-diethylamino)-ethyl acrylate, neopentyl glycol diacrylate, alkoxyated neopentyl glycol diacrylate, ethylene

glycol diacrylate, hexylene glycol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, pentaerythritol acrylate, trimethylolpropane triacrylate, alkoxyated trimethylol-propane triacrylate containing from 2 to 14 moles of ethylene oxide, alkoxyated trimethylol-propane triacrylate containing from 2 to 14 moles of propylene oxide, triethylene glycol diacrylate, tetraethylene glycol diacrylate, alkoxyated neopentyl glycol diacrylate having from 2 to 14 moles of ethoxy units, alkoxyated neopentyl glycol diacrylate having from 2 to 14 moles of propoxy units, polyethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, polyethylene glycol diacrylate, C₁–C₃₀ alkyl ester of methacrylic acid, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, lactone modified esters of methacrylic acid, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, 2-sulfoethyl methacrylate, trifluoroethyl methacrylate, glycidyl methacrylate, benzyl methacrylate, allyl methacrylate, 2-n-butoxyethyl methacrylate, 2-chloroethyl methacrylate, sec-butyl-methacrylate, tert-butyl methacrylate, 2-ethylbutyl methacrylate, cinnamyl methacrylate, crotyl methacrylate, cyclohexyl methacrylate, cyclopentyl methacrylate, 2-ethoxyethyl methacrylate, furfuryl methacrylate, hexafluoroisopropyl methacrylate, methallyl methacrylate, 3-methoxybutyl methacrylate, 2-methoxybutyl methacrylate, 2-nitro-2-methylpropyl methacrylate, n-octylmethacrylate, 2-ethylhexyl methacrylate, 2-phenoxyethyl methacrylate, 2-phenylethyl methacrylate, phenyl methacrylate, methacrylamide, propargyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydropyranyl methacrylate, and combinations thereof.

28. The substrate of claim 26, wherein the styrenic-based monomer is selected from the group consisting of unsubstituted styrene monomer, substituted styrene monomer, and combinations thereof.
29. The substrate of claim 26, wherein the vinylic-based monomer comprises at least one member selected from the group consisting of ethylene, propylene, vinyl chloride, vinyl acetate, acrylonitrile, butene, hexene, heptane, isobutylene, octane, and combinations thereof.

30. The substrate of claim 26, wherein the α,β -unsaturated monomer comprises at least one member selected from the group consisting of butadiene, isoprene, chloroprene, dienes, and combinations thereof.

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31. The substrate of claim 24, wherein the emulsifier comprises at least one member selected from the group consisting of nonionic emulsifiers, anionic emulsifiers, water-dispersible stabilized polymer, polymerizable surfactants, gemini surfactants, and combinations thereof.

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32. The substrate of claim 31, wherein the water-dispersible stabilized polymer has an average molecular weight in the range of about 2,000 to about 12,000.

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33. The substrate of claim 31, wherein the water-dispersible stabilized polymer has an acid number in the range of about 200 to about 290.

34. The substrate of claim 24, wherein the mixture further comprises crosslinker.

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35. The substrate of claim 24, wherein the coating composition further comprises at least one member selected from the group consisting of crosslinker, coalescence agent, plasticizer, buffers, neutralizers, thickeners, rheology modifiers, humectants, wetting agents, biocides, plasticizers, antifoaming agents, colorants, fillers, waxes, water repellants, slip or mar aids, anti-oxidants, and combinations thereof.

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36. A process for preparing an emulsion including polymer and clay completely exfoliated within the polymer matrix, comprising the steps of:

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- (i) providing an initial aqueous phase containing emulsifier;
- (ii) adding dispersed clay to the aqueous phase;
- (ii) adding to the aqueous phase, a mixture comprising at least one free radical polymerizable monomer; and
- (iii) polymerizing the mixture.

37. The process of claim 36, wherein the clay comprises at least one member selected from the group consisting of smectite, phyllosilicate, synthetic phyllosilicates, montmorillonite, saponite, beidellite, montionite, hectorite, stevensite, vermiculite, kaolinite and hallosite.

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38. The process of claim 36, wherein the free radical polymerizable monomer comprises at least one member selected from the group consisting of acrylic-based monomer, styrenic-based monomer, vinylic-based monomer, α,β -unsaturated monomer, and combinations thereof.

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39. The process of claim 38, wherein the acrylic-based monomer comprises at least one member selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, acryloxypropionic acid, (meth)acryloxypropionic acid, sulphonic acid-bearing monomers, phosphoethylmethacrylate, methacrylic anhydride, maleic anhydride, itaconic anhydride, succinic anhydride, glycidyl acrylate, glycidyl methacrylate, C_1-C_{30} alkyl ester of acrylic acid, phenoxyethyl acrylate, 2-phenoxy acrylate, 2-methoxyethyl acrylate, lactone modified esters of acrylic acid, butyl acrylate, allyl acrylate, tetrahydrofuryl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-phenoxyethyl acrylate, acrylated methylolmelamine, 2-(N,N-diethylamino)-ethyl acrylate, neopentyl glycol diacrylate, alkoxyated neopentyl glycol diacrylate, ethylene glycol diacrylate, hexylene glycol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, pentaerythritol acrylate, trimethylolpropane triacrylate, alkoxyated trimethylol-propane triacrylate containing from 2 to 14 moles of ethylene oxide, alkoxyated trimethylol-propane triacrylate containing from 2 to 14 moles of propylene oxide, triethylene glycol diacrylate, tetraethylene glycol diacrylate, alkoxyated neopentyl glycol diacrylate having from 2 to 14 moles of ethoxy units, alkoxyated neopentyl glycol diacrylate having from 2 to 14 moles of propoxy units, polyethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, polyethylene glycol diacrylate, C_1-C_{30} alkyl ester of methacrylic acid, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, lactone modified esters of methacrylic acid, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, t-

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butylaminoethyl methacrylate, 2-sulfoethyl methacrylate, trifluoroethyl methacrylate, glycidyl methacrylate, benzyl methacrylate, allyl methacrylate, 2-n-butoxyethyl methacrylate, 2-chloroethyl methacrylate, sec-butyl-methacrylate, tert-butyl methacrylate, 2-ethylbutyl methacrylate, cinnamyl methacrylate, crotyl methacrylate, 5 cyclohexyl methacrylate, cyclopentyl methacrylate, 2-ethoxyethyl methacrylate, furfuryl methacrylate, hexafluoroisopropyl methacrylate, methallyl methacrylate, 3-methoxybutyl methacrylate, 2-methoxybutyl methacrylate, 2-nitro-2-methylpropyl methacrylate, n-octylmethacrylate, 2-ethylhexyl methacrylate, 2-phenoxyethyl methacrylate, 2-phenylethyl methacrylate, phenyl methacrylate, methacrylamide, 10 propargyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydropyranyl methacrylate, and combinations thereof.

40. The process of claim 38, wherein the styrenic-based monomer is selected from the group consisting of unsubstituted styrene monomer, substituted styrene monomer, and 15 combinations thereof.

41. The process of claim 38, wherein the vinylic-based monomer comprises at least one member selected from the group consisting of ethylene, propylene, vinyl chloride, vinyl acetate, acrylonitrile, butene, hexene, heptane, isobutylene, octane, and combinations 20 thereof.

42. The process of claim 38, wherein the α,β -unsaturated monomer comprises at least one member selected from the group consisting of butadiene, isoprene, chloroprene, dienes, and combinations thereof. 25

43. The process of claim 36, wherein the emulsifier comprises at least one member selected from the group consisting of nonionic emulsifiers, anionic emulsifiers, water-dispersible stabilized polymer, polymerizable surfactants, gemini surfactants, and combinations thereof. 30

44. The process of claim 43, wherein the water-dispersible stabilized polymer has an average molecular weight in the range of about 2,000 to about 12,000.

45. The process of claim 43, wherein the water-dispersible stabilized polymer has an acid number in the range of about 200 to about 290.

5 46. The process of claim 36, wherein the mixture further comprises at least one crosslinker.

47. The process of claim 36, wherein the mixture is added into the aqueous phase on a gradual basis during the polymerization step.

10 48. The process of claim 36, wherein the clay is in an amount range of about 0.1% to about 20% weight based on dry weight of the polymer.

49. A process for preparing an emulsion including polymer and clay completely exfoliated within the polymer matrix, comprising the steps of:

- 15 (i) providing an initial aqueous phase containing emulsifier;
(ii) mixing clay with at least one monomer;
(iii) adding to the aqueous phase, the mixture comprising at least one free radical polymerizable monomer; and
(iv) polymerizing the mixture.

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50. The process of claim 49, wherein the clay comprises at least one member selected from the group consisting of smectite, phyllosilicate, synthetic phyllosilicates, montmorillonite, saponite, beidellite, montionite, hectorite, stevensite, vermiculite, kaolinite and hallosite.

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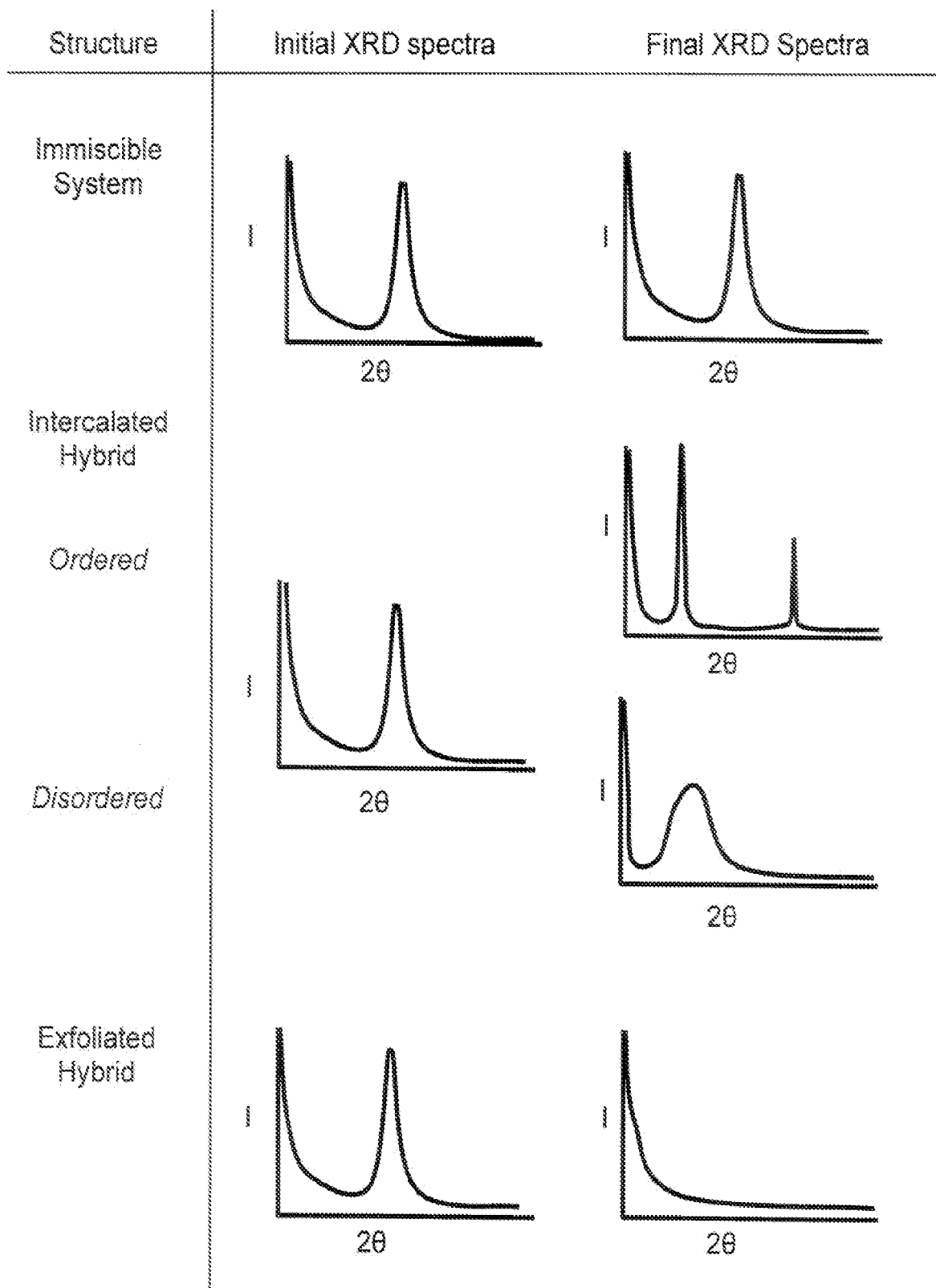
51. The process of claim 49, wherein the free radical polymerizable monomer comprises at least one member selected from the group consisting of acrylic-based monomer, styrenic-based monomer, vinylic-based monomer, α,β -unsaturated monomer, and combinations thereof.

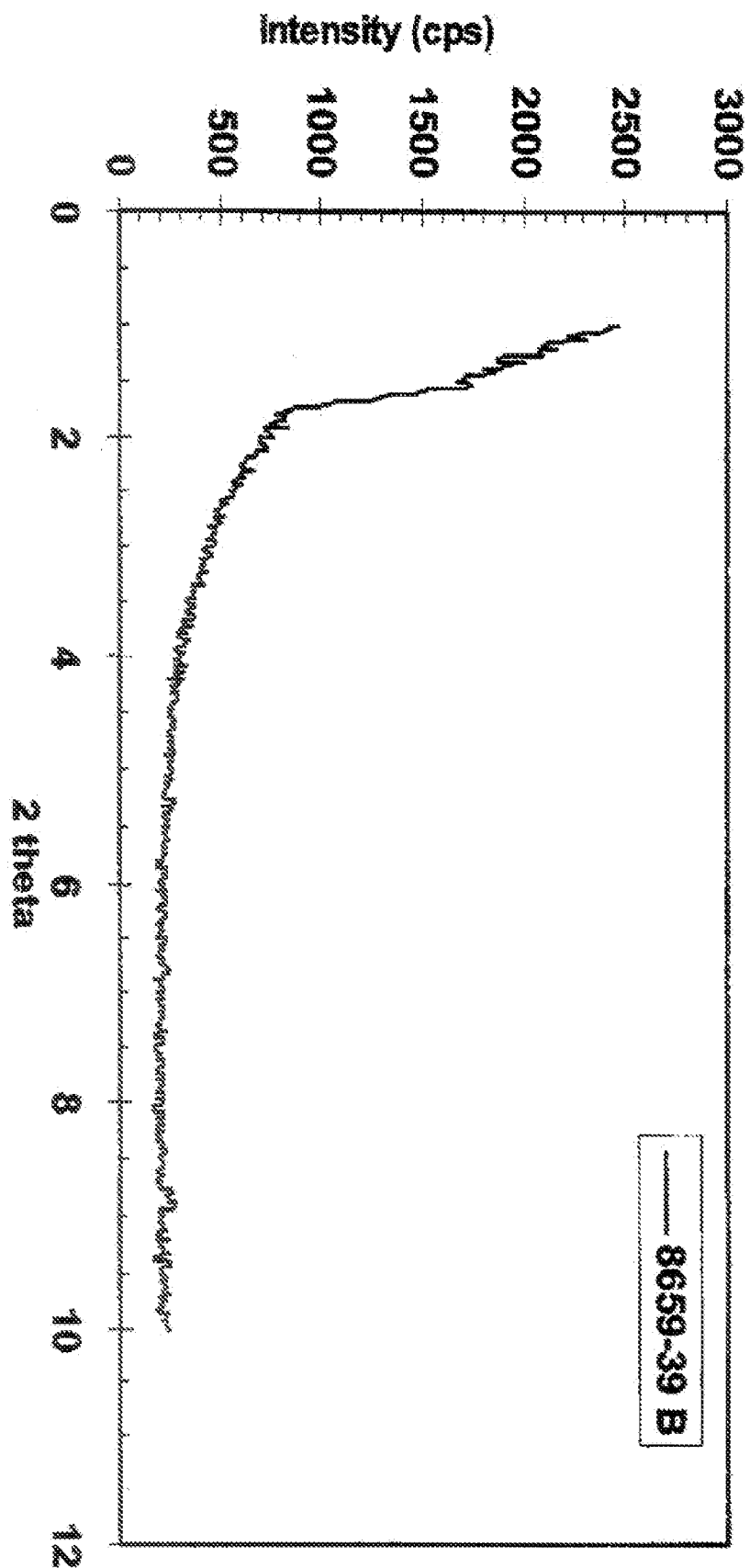
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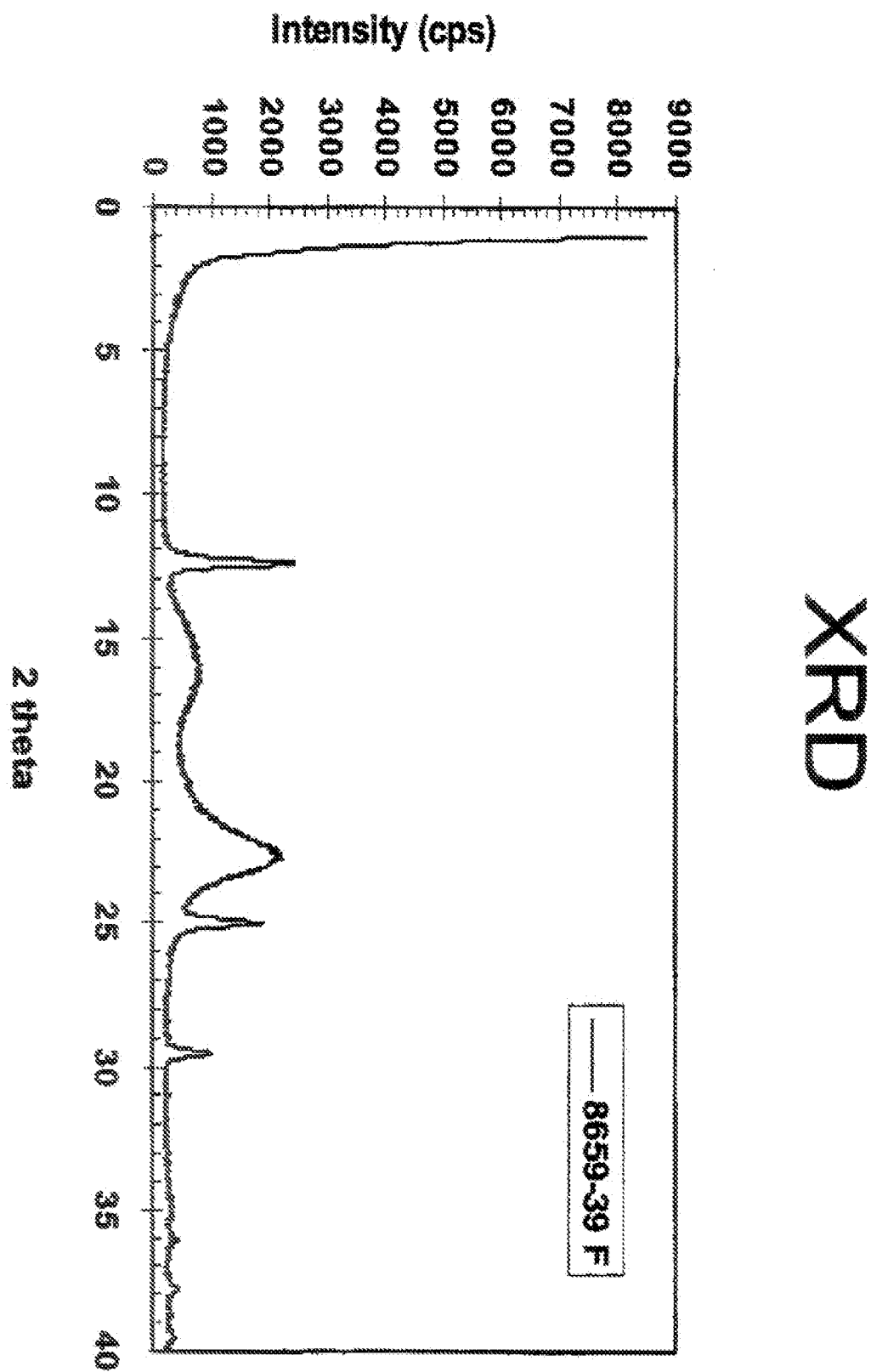
52. The process of claim 51, wherein the acrylic-based monomer comprises at least one member selected from the group consisting of acrylic acid, methacrylic acid, itaconic

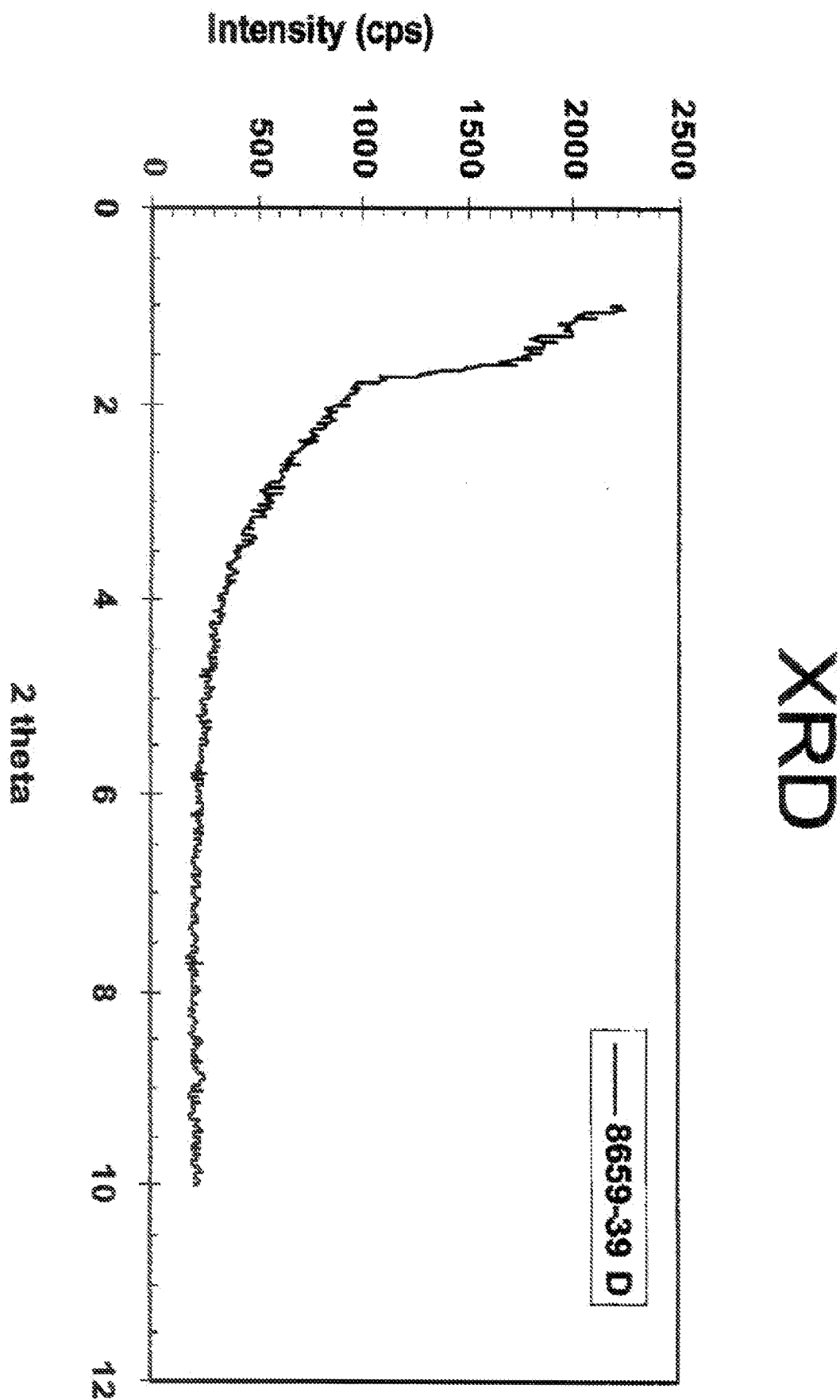
acid, maleic acid, fumaric acid, acryloxypropionic acid, (meth)acryloxypropionic acid, sulphonic acid-bearing monomers, phosphoethylmethacrylate, methacrylic anhydride, maleic anhydride, itaconic anhydride, succinic anhydride, glycidyl acrylate, glycidyl methacrylate, C₁–C₃₀ alkyl ester of acrylic acid, phenoxyethyl acrylate, 2-phenoxy acrylate, 2-methoxyethyl acrylate, lactone modified esters of acrylic acid, butyl acrylate, allyl acrylate, tetrahydrofuryl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-phenoxyethyl acrylate, acrylated methylolmelamine, 2-(N,N-diethylamino)-ethyl acrylate, neopentyl glycol diacrylate, alkoxyated neopentyl glycol diacrylate, ethylene glycol diacrylate, hexylene glycol diacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, tetraethylene glycol diacrylate, pentaerythritol acrylate, trimethylolpropane triacrylate, alkoxyated trimethylol-propane triacrylate containing from 2 to 14 moles of ethylene oxide, alkoxyated trimethylol-propane triacrylate containing from 2 to 14 moles of propylene oxide, triethylene glycol diacrylate, tetraethylene glycol diacrylate, alkoxyated neopentyl glycol diacrylate having from 2 to 14 moles of ethoxy units, alkoxyated neopentyl glycol diacrylate having from 2 to 14 moles of propoxy units, polyethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, polyethylene glycol diacrylate, C₁–C₃₀ alkyl ester of methacrylic acid, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, lactone modified esters of methacrylic acid, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, 2-sulfoethyl methacrylate, trifluoroethyl methacrylate, glycidyl methacrylate, benzyl methacrylate, allyl methacrylate, 2-n-butoxyethyl methacrylate, 2-chloroethyl methacrylate, sec-butyl-methacrylate, tert-butyl methacrylate, 2-ethylbutyl methacrylate, cinnamyl methacrylate, crotyl methacrylate, cyclohexyl methacrylate, cyclopentyl methacrylate, 2-ethoxyethyl methacrylate, furfuryl methacrylate, hexafluoroisopropyl methacrylate, methallyl methacrylate, 3-methoxybutyl methacrylate, 2-methoxybutyl methacrylate, 2-nitro-2-methylpropyl methacrylate, n-octylmethacrylate, 2-ethylhexyl methacrylate, 2-phenoxyethyl methacrylate, 2-phenylethyl methacrylate, phenyl methacrylate, methacrylamide, propargyl methacrylate, tetrahydrofurfuryl methacrylate, tetrahydropyranyl methacrylate, and combinations thereof.

53. The process of claim 51, wherein the styrenic-based monomer is selected from the group consisting of unsubstituted styrene monomer, substituted styrene monomer, and combinations thereof.
- 5 54. The process of claim 51, wherein the vinylic-based monomer comprises at least one member selected from the group consisting of ethylene, propylene, vinyl chloride, vinyl acetate, acrylonitrile, butene, hexene, heptane, isobutylene, octane, and combinations thereof.
- 10 55. The process of claim 51, wherein the α,β -unsaturated monomer comprises at least one member selected from the group consisting of butadiene, isoprene, chloroprene, dienes, and combinations thereof.
- 15 56. The process of claim 49, wherein the emulsifier comprises at least one member selected from the group consisting of nonionic emulsifiers, anionic emulsifiers, water-dispersible stabilized polymer, polymerizable surfactants, gemini surfactants, and combinations thereof.
- 20 57. The process of claim 56, wherein the water-dispersible stabilized polymer has an average molecular weight in the range of about 2,000 to about 12,000.
58. The process of claim 56, wherein the water-dispersible stabilized polymer has an acid number in the range of about 200 to about 290.
- 25 59. The process of claim 49, wherein the mixture further comprises crosslinker.
60. The process of claim 49, wherein the mixture is added into the aqueous phase on a gradual basis during the polymerization step.
- 30 61. The process of claim 49, wherein the clay is in an amount range of about 0.1% to about 20% weight based on dry weight of the polymer.

1 / 5
Figure 1

2 / 5
Figure 2**XRD**

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Figure 3

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Figure 4

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Figure 5

