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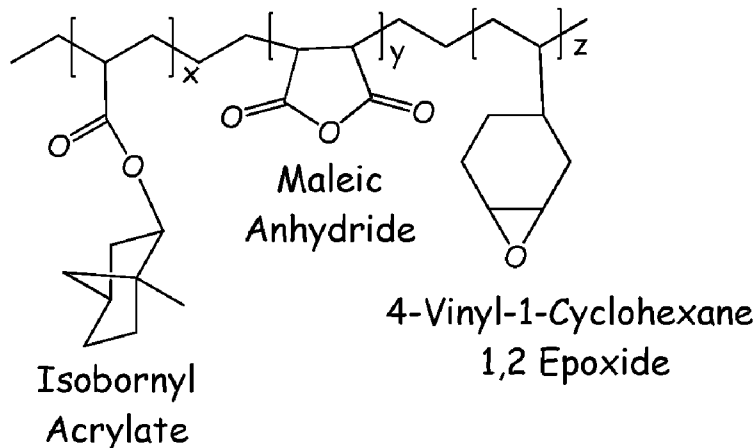
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(54) Title: HYDROPHOBIC COATING COMPOSITIONS FOR FORMING TONER RECEPTIVE COATINGS



(57) Abstract: This invention provides hydrophobic compositions for forming hydrophobic toner receptive coatings on a substrate. The hydrophobic coating compositions for forming toner receptive coatings on a substrate contain a hydrophobic polymer comprising: (a) a maleic anhydride monomer, (b) a non-reactive hydrophobic monomer moiety, and (c) a solvent. The coating compositions may further comprise (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof. The invention also provides compositions suitable for addition to toner to enhance adhesion and toner substrates coated with the hydrophobic coating compositions. A representative hydrophobic polymer structure is set out below, wherein x, y, and z are defined herein.

HYDROPHOBIC COATING COMPOSITIONS FOR FORMING TONER RECEPTIVE COATINGS

FIELD OF THE INVENTION

[001] This invention provides hydrophobic compositions for forming hydrophobic toner receptive coatings on a substrate. The hydrophobic coating compositions for forming toner receptive coatings on a substrate contain a hydrophobic polymer comprising: (a) a maleic anhydride monomer, (b) a non-reactive hydrophobic monomer moiety, and (c) a solvent. The coating compositions may further comprise (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof. The invention also provides compositions suitable for addition to toner to enhance adhesion and toner substrates coated with the hydrophobic coating compositions.

BACKGROUND OF THE INVENTION

[002] The use of coating compositions for forming toner receptor coatings is a successful method for forming images on different substrates such as paper, polyester, vinyl, and canvas. However, printing onto substrates such as plastics, such as vinyl, polyester, and polyolefin has not attained the print quality, integrity, and adhesion commonly observed for paper substrates.

[003] United States Patent Application Publications US 2007/0092666 and US 2007/0092668 disclose coating compositions for forming ink jet-receptive coatings on a substrate. United States Patent Application Publication US 8,198,353 B2 and United States Patent 5,789,123 disclose coating compositions for forming liquid toner receptor coatings on a substrate. International Publication Number WO 2005/115763 A1 discloses coating compositions for forming liquid toner receptor coatings on a substrate.

[004] United States Patent nos. 2,687,404, 7,507,451, and 8,242,224 disclose epoxy containing copolymers. United States Patent Application Publication US 2005/0245651 and European Patent Application EP1 114 734 disclose epoxy containing copolymers. International Publication Number WO 2009/023843 A1 discloses polyvinylamide polymers containing polymerizable functionalities. International Publication Number WO 2011/063171 A1 discloses a reactive solution of polymerizable polymer comprising

polymerizable functionality, processes and compositions thereof. The reactive functionality of a polyvinyl amide polymerizable polymer is disclosed in "Synthesis and Reactive Features of a Terpolymer: Poly(N-vinyl-2-pyrrolidone-co-vinyl acetate-co-glycidyl methacrylate)" by D.K. Hood et. al. (*J. Appl. Polym. Sci.* **128**: p1381-1389, 2013).

[005] Accordingly, there is a need for improved hydrophobic coating compositions for forming toner receptor coatings, which exhibit improved properties including the ability to absorb and retain the ink effectively in hydrophobic solvent-based ink printable forms. There is also a need to enhance adhesion through compositions suitable for addition to toners.

SUMMARY OF THE INVENTION

[006] This invention provides hydrophobic compositions for forming hydrophobic toner receptive coatings on a substrate. The hydrophobic coating compositions for forming toner receptive coatings on a substrate contain a hydrophobic polymer comprising: (a) a maleic anhydride monomer, (b) a non-reactive hydrophobic monomer moiety, and (c) a solvent. The coating compositions may further comprise (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof. The invention also provides compositions suitable for addition to toner to enhance adhesion and toner substrates coated with the hydrophobic coating compositions.

DETAILED DESCRIPTION OF THE INVENTION

[007] This invention provides hydrophobic coating compositions for forming toner receptive coatings on a substrate. This invention also provides substrates coated with the hydrophobic toner receptive coatings. The hydrophobic coating compositions include (a) a maleic anhydride monomer, (b) a non-reactive hydrophobic monomer moiety, and (c) a solvent; and may further comprise (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof.

[008] As used herein, the following terms have the meanings set out below.

[009] The term "acidic conditions" refers to conditions relating to the pH value of an aqueous solution. Pure water is considered to be neutral, with a pH close to 7.0 at 25°C. Solutions with a pH value less than 7 are considered to be acidic solutions.

[0010] The term "anion" refers to an "anionic" (adjective) ion, which has more electrons than protons, providing it with a net negative charge.

[0011] The term "anionic addition polymerization" refers to a form of chain-growth polymerization or addition polymerization that involves the polymerization of vinyl monomers with strong electronegative groups. The polymerization is carried out through a carbanion active species. Addition polymerizations take place in three steps: chain initiation, chain propagation, and chain termination.

[0012] The term "basic conditions" refers to conditions relating to the pH value. Pure water is considered to be neutral, with a pH close to 7.0 at 25°C. Solutions with a pH value greater than 7 are considered to be basic or alkaline.

[0013] The term "branched and unbranched alkyl groups" refers to alkyl groups, which may be straight chained or branched. For example, the alkyl groups have from 1 to about 30 carbon atoms, more particularly, from 1 to about 25 carbon atoms, and yet more particularly from 1 to about 20 carbon atoms. Branched groups include isopropyl, *sec*-butyl, *tert*-butyl, and the like.

[0014] The term "cation" refers to an "cationic" (adjective) ion, which has fewer electrons than protons, providing it with a net positive charge.

[0015] The term "copolymer" refers to chains comprising more than one type of monomer unit.

[0016] The term "cyclic" in chemistry refers to a compound in which a series of atoms is connected to form a loop or ring. The vast majority of cyclic compounds are organic. Cyclic compounds may or may not be aromatic. The term "polycyclic" is used when more than one ring is formed in a single molecule.

[0017] The term "ether" refers to a class of organic compounds that contain an ether group, an oxygen atom connected to two alkyl or aryl groups. An example is the solvent diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$). Ethers are common in organic chemistry and pervasive in biochemistry, as they are common linkages in carbohydrates and lignin.

[0018] The term "halogen" refers to chloro, bromo, iodo and fluoro, and in one embodiment is bromo and/or chloro.

[0019] The term "heteroatom" refers to atoms such as oxygen, nitrogen, sulfur, and phosphorous. When the heteroatom is a nitrogen atom, the nitrogen atom may be present in the form of a quaternary amine.

[0020] The term "hydrophilic" refers to a molecular entity that tends to be polarized and is attracted to, and tends to be dissolved by, water. A hydrophilic molecule or portion of a molecule is one that has a tendency to interact with or be dissolved by water and other polar substances. A hydrophilic molecule or portion of a molecule is one that is typically charge-polarized and capable of hydrogen bonding, enabling it to dissolve more readily in water than in oil or other hydrophobic solvents.

[0021] The term "hydrophobic" refers to a molecular entity that tends to be non-polar and, thus, prefers other neutral molecules and non-polar solvents. Examples of hydrophobic molecules include the alkanes, oils, fats, and greasy substances in general. Hydrophobic is often used interchangeably with lipophilic, "fat-loving"; however, the two terms are not synonymous.

[0022] The term "inert solvent" refers to a solvent that does not interfere chemically with the reaction.

[0023] The term "maleic anhydride" (butenedioic anhydride, 2,5-dioxafuran) refers to an organic compound with the formula $C_2H_2(CO)_2O$. Maleic anhydride is the acid anhydride of maleic acid.

[0024] The term "mineral acid" refers to an acid derived from one or more inorganic compounds. Mineral acids release hydrogen ions when dissolved in water. Commonly used mineral acids are sulfuric acid, hydrochloric acid, and nitric acid.

[0025] The term "monomer" refers to the repeat units comprising a polymer. A monomer is a small molecule that chemically bonds to other monomers to form a polymer.

[0026] The term "non-homopolymer" refers to a polymer formed from two or more monomers and includes essentially all polymers that are not homopolymers. Nonlimiting examples of non-homopolymers include copolymers, terpolymers, tetramers, and the like, wherein the non-homopolymer is a random, blocked, or alternating polymer.

[0027] The term "nonion" refers to an "nonionic" (adjective) ion, an ion that has no charge.

[0028] The term "pH" refers to a measure of the acidity or basicity of an aqueous solution. Pure water is considered to be neutral, with a pH close to 7.0 at 25°C. Solutions with a pH less than 7 are considered to be acidic and solutions with a pH greater than 7 are considered to be basic or alkaline.

[0029] The term "polymer" refers to a large molecule (macromolecule) composed of repeating structural units (monomers) connected by covalent chemical bonds.

[0030] The term "polymerization" refers to methods for chemically reacting monomer compounds to form polymer chains. The polymer chain may be alternating, branched, blocked, or random. The type of polymerization method may be selected from a wide variety of methods. Such methods include, but are not limited to, free radical polymerization methods, such as classical radical polymerization and controlled radical polymerization, Nitroxide Mediation Polymerization (NMP), Atom Transfer Radical Polymerization (ATRP), and Reversible Addition Fragmentation Chain-Transfer (RAFT).

[0031] The term "reactive solvent" refers to a solvent capable of transforming, particularly polymerizing or curing, upon suitable activation or initiation. Examples include monomers comprising at least one cyclic ether or vinyl ether functional groups capable of solvating an inventive polymer. Background on epoxy chemistry and technology can be found in the "Handbook of Epoxy Resins" by Lee and Neville (McGraw-Hill, New York, 1967). Blends of reactive solvents and polymerizable polymers may also be employed.

[0032] The present invention provides hydrophobic coating compositions for forming toner receptor coatings on substrates containing a hydrophobic polymer comprising: (a) a maleic anhydride monomer, (b) a non-reactive hydrophobic monomer moiety, and (c) a solvent.

[0033] The (a) maleic anhydride monomer is an organic compound with the formula $C_2H_2(CO)_2O$. Maleic anhydride is the acid anhydride of maleic acid. A monomer is a small molecule that chemically bonds to other monomers to form a polymer.

[0034] The (b) non-reactive hydrophobic monomer may comprise a non-reactive C_1 - C_{20} alkyl acrylate monomer. Preferably, the (b) non-reactive C_1 - C_{20} alkyl acrylate monomer is selected from the group consisting of isobornyl acrylate, octyl acrylate, decyl acrylate, and mixtures thereof.

[0035] Suitable (c) solvents in the coating compositions comprise aqueous and non-aqueous solvents. Illustrative non-limiting examples of solvents include water, ethanol, isopropanol, butanol, acetone, methyl ethyl ketone, ethyl acetate, reactive solvents and mixtures thereof. Other suitable solvents are described in the "Industrial Solvents Handbook, 4th Edition" edited by E.W. Flick (Noyes Data Corporation, Park Ridge, New Jersey, 1991) and in the "Polymer Handbook, 4th Edition," edited by J. Brandrup et. al. (J. Wiley and Sons, New York, 1999), which disclosures are incorporated by reference herein. A solvent is a substance that dissolves a solute resulting in a solution. In solution, all of the ingredients are uniformly distributed at a molecular level and no residue remains. The mixing is referred to as miscibility, whereas the ability to dissolve one compound into another is known as solubility. However, in addition to mixing, both substances in the solution interact with each other. Solvents can be broadly classified into two categories: polar and non-polar. The polarity, dipole moment, polarizability and hydrogen bonding of a solvent determines what type of compounds it is able to dissolve and with what other solvents or liquid compounds it is miscible. Polar solvents dissolve polar compounds best and non-polar solvents dissolve non-polar compounds best. Strongly polar compounds like sugars (e.g., sucrose) or ionic compounds, like inorganic salts (e.g., table salt) dissolve only in very polar solvents like water, while strongly non-polar compounds like oils or waxes dissolve only in very non-polar organic solvents like hexane. Similarly, water and hexane (or vinegar and vegetable oil) are not miscible with each other.

[0036] Examples of reactive solvents and co-solvents include, but are not limited to, 2-hydroxy methyl methacrylate (HEMA), 2-hydroxy ethyl acrylate (HEA), 2-phenoxy ethyl acrylate (PEA), 2-ethylhexyl-diglycol acrylate, 2-(2-ethoxyethoxy)ethyl acrylate (EOEOEA), lauryl acrylate (LA), stearyl acrylate (SA), isobornyl acrylate (IBOA), acrylic acid-2-ethylhexyl ester, isodecyl acrylate, diacetone acrylamide, acryloyl morpholine (ACMO), cyclic trimethylol-propane formal acrylate (CTFA), 3-(methacryloylamino)propyl]trimethylammonium chloride (MAPTAC), 4-hydroxybutyl acrylate, (3-Acrylamidopropyl)trimethylammonium chloride (APTAC), C8-C10 acrylate (ODA), isodecyl acrylate (ISODA), lauryl methacrylate (LM), stearyl methacrylate (SM), 2,2,2-trifluoroethyl methacrylate, 2-acrylamido-2-methyl-1-propanesulfonic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt, [2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide, [3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide inner salt, 1,6-

hexanediol diacrylate (HDDA), dipropylene glycol diacrylate (DPGDA), tripropylene glycol diacrylate (TPGDA), water, alcohol, hydro-alcohol mixtures, 1,4-butanediol diacrylate (BDDA), tripropylene glycol diacrylate (TPGDA), dipropylene glycol diacrylate (DPGDA), tripropylene glycol diacrylate (TRPGDA), 1,9-nonanediol diacrylate (NNDA), neopentyl glycol diacrylate (NPGDA), propoxylated neopentyl glycol diacrylate (NPG2PODA), polyethylene glycol (200) diacrylate (PEG(200)DA), polyethylene glycol (400) diacrylate (PEG(400)DA), polyethylene glycol (600) diacrylate (PEG(600)DA), ethoxylated bisphenol-A diacrylate (BPA2EODA), triethylene glycol diacrylate (TEGDA), triethylene glycol dimethacrylate (TEGDMA), glycerol propoxylated triacrylate (GPTA), diethylene glycol dimethacrylate (DEGDMA), ethoxylated bisphenol-A dimethacrylate (BPA10EODMA), trimethylolpropane triacrylate (TMPTA), pentaerythritol triacrylate (PET3A), ethoxylated trimethylolpropane triacrylate (TMP3EOTA), propoxylated tri-methylolpropane triacrylate (TMP3POTA), propoxylated glyceryl triacrylate (GPTA), trimethylolpropane trimethylacrylate (TMPTMA), ethoxylated trimethylolpropane trimethacrylate (TMP3EOTMA), 2,2-dionol diacrylate, pentaerythritol tetraacrylate (PETA), neopentylglycol diacrylate hydroxypivalate, 2-acryloyloxyethylphthalic acid, 2-acryloyloxyethyl-2-hydroxyethylphthalic acid, dimethyloltricyclodecane diacrylate, 2-acryloyloxyethylsuccinic acid, nonylphenol ethylene oxide adduct acrylate, phenol acrylates, methoxy-polyethylene glycol acrylate, tetramethylolmethane triacrylate, dipentaerythritol hexaacrylate (DPHA), isocyanate-functional unsaturated acrylic ester resin, urethane diacrylates oligomers, urethane acrylates, modified urethane acrylates, polyester acrylates, modified bisphenol A diacrylate, phenoxy-polyethylene glycol acrylate, bisphenol A propylene oxide modified diacrylate, bisphenol A ethylene oxide adduct diacrylate, pentaerythritol triacrylate hexamethylenediisocyanate, urethane prepolymer, isoamyl acrylate, isomyristyl acrylate, isostearyl acrylate, carbitol acrylate, cyclohexyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylates, acrylamides, polyfunctional acrylamides, polyfunctional (polyethylene glycol) acrylates, polyfunctional vinyl amides, 1,4-butane-diol-monoacrylate and/or diglycidyl ether of 1,4-butanediol, and the like, and mixtures thereof.

[0037] Additional examples of reactive solvents and co-solvents include, but are not limited to, methyl vinylether, ethyl vinylether, propyl vinylether, n-butyl vinylether, t-butyl vinylether, 2-ethylhexyl vinylether, n-nonyl vinylether, lauryl vinylether, cyclohexyl vinylether, cyclohexylmethyl vinylether, 4-methylcyclohexylmethyl vinylether, benzyl vinylether, dicyclopentenyl vinylether, 2-dicyclopentenoxyethyl vinyl ether, methoxyethyl

vinylether, ethoxyethyl vinylether, butoxyethyl vinyl ether, methoxyethoxy vinylether, ethoxyethoxyethyl vinylether, methoxypolyethylene glycol vinylether, tetrahydrofurfuryl vinylether, dodecyl vinylether, diethylene glycol monovinylether, 2-hydroxyethyl vinylether, 2-hydroxypropyl vinylether, 4-hydroxybutyl vinylether, 4-hydroxymethylcyclohexylmethyl vinylether, polyethylene glycol vinylether, chloroethyl vinylether, chlorobutyl vinylether, phenylethyl vinylether, phenoxypolyethylene glycol vinylether, ethylene glycol divinylether, butylenes glycol divinylether, hexandiol divinylether, bisphenol A alkyleneoxide divinylethers, bisphenol F alkyleneoxide divinylethers, propyleneoxide adducts of trimethylolpropane trivinylether, triethylene glycol divinylether, cyclohexane dimethanol divinylether, N-vinyl-2-pyrrolidone (VP), N-vinyl caprolactam (VCap), N-vinyl imidazole (VI), n-vinyl amides, 4-vinyl pyridine, 2-vinyl pyridine, styrene, 5-vinyl-2-norbornene and the like, and mixtures thereof.

[0038] Preferably, (a) is 0.1-80%, (b) is 1-80%, and (c) is to 100%, by weight. More preferably, (a) is 1-70%, (b) is 1-60%, and (c) is to 100%, by weight. Most preferably, (a) is 1-60%, (b) is 1-50%, and (c) is to 100%, by weight.

[0039] In another aspect, the polymer further comprises (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof.

[0040] Preferably, the substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures, thereof is selected from the group consisting of substituted or unsubstituted monomer comprising a cyclic ether is selected from the group consisting of allyl glycidyl ether ([2-propenyloxy)methyl]-oxirane), butadiene monoxide, glycidyl acrylate, glycidyl methacrylate, vinyl cyclohexene monoxide, 4-vinyl-1-cyclohexene-1,2-epoxide, 3-N-(6-propyl vinyl ether) benzoxazine, 3,4-epoxycyclohexylmethyl methacrylate, (3-ethyl-3-oxetanyl) methyl acrylate, (3-ethyl-3-oxetanyl) methyl methacrylate, 2-(3-methyl-3-oxetanemethoxy)ethyl vinyl ether, acetoacetoxyethyl (meth)acrylate, acetoacetoxyethyl acrylate, allyl acetoacetate, and mixtures thereof.

[0041] The substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof may a monofunctional or a multifunctional epoxy compound. Non-limiting examples of monofunctional epoxy compounds include phenyl glycidylether, p-tert-butylphenyl glycidylether, butyl glycidylether, 2-ethylhexyl glycidylether, allyl glycidylether, 1,2-butyleneoxide, 1,3-butadienemonooxide, 1,2-

epoxydodecane, epichlorohydrin, 1,2-epoxydecane, styreneoxide, cyclohexeneoxide, 3-methacryloyloxymethylcyclohexeneoxide, 3-acryloyloxymethylcyclohexeneoxide, 3-vinylcyclohexeneoxide, and the like, and mixtures thereof. Non-limiting examples of multifunctional epoxy compounds include 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 3-ethyl-3-((ethyloxetane-3-yl)methoxy) methyl)oxetane, bisphenol A diglycidylether, bisphenol F diglycidylether, bisphenol S diglycidylether, brominated bisphenol A diglycidylether, brominated bisphenol F diglycidylethers, brominated bisphenol S diglycidylether, epoxy novolak resins, hydrogenated bisphenol A diglycidylethers, hydrogenated bisphenol F diglycidylethers, hydrogenated bisphenol S diglycidylethers, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy) cyclohexane-meta-dioxane, bis(3,4-epoxycyclohexylmethyl) adipate, vinylcyclohexeneoxide, 4-vinylepoxycyclohexane, bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate, 3,4-epoxy-6-methylcyclohexyl-3',4'-epoxy-6'-methylcyclohexane carboxylate, methylene-bis(3,4-epoxycyclohexane), dicyclopentadiene diepoxide, ethylene glycol di(3,4-epoxycyclohexylmethyl)ether, ethylene bis(3,4-epoxycyclohexanecarboxylate), epoxyhexahydrodiethyl phthalate, epoxyhexahydrodi-2-ethylhexyl phthalate, 1,4-butanediol diglycidylether, 1,6-hexanediol diglycidylether, glycerol triglycidylether, trimethylolpropane triglycidylether, polyethylene glycol diglycidylether, polypropylene glycol diglycidylether, 1,1,3-tetradecadienedioxide, limonenedioxide, 1,2,7,8-diepoxyoctane, 1,2,5,6-diepoxyoctane, and the like, and mixtures thereof.

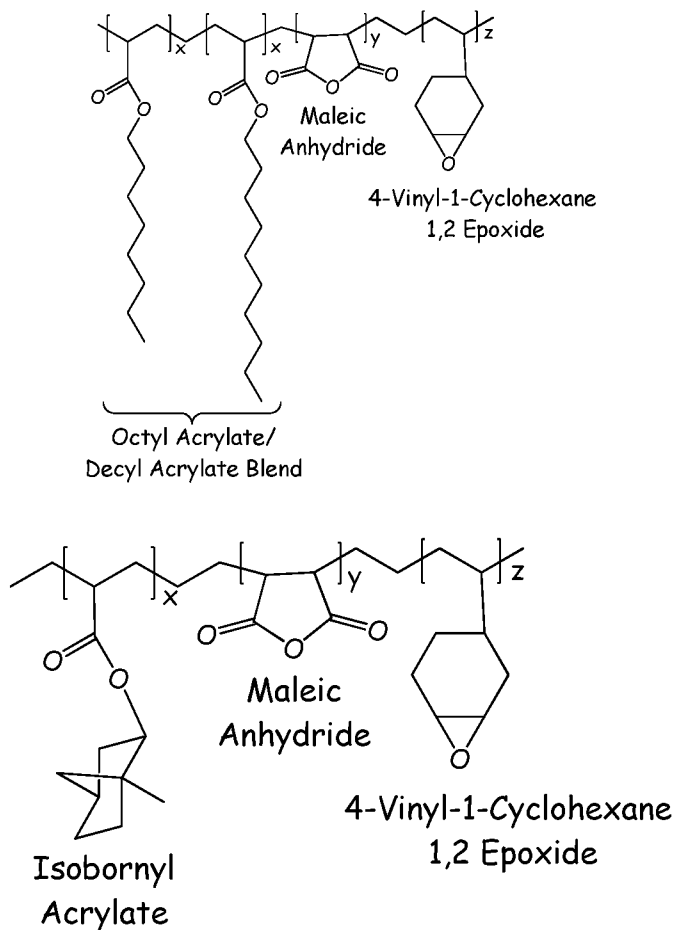
[0042] Preferably, the (d) substituted or unsubstituted monomer comprising a cyclic ether is selected from the group consisting of 4-vinyl-1-cyclohexene-1,2-epoxide, allyl glycidyl ether ([2-propenyloxy)methyl]-oxirane), butadiene monoxide, glycidyl acrylate, glycidyl methacrylate, vinyl cyclohexene monoxide, 3-N-(6-propyl vinyl ether) benzoxazine, 3,4-epoxycyclohexylmethyl methacrylate, (3-ethyl-3-oxetanyl) methyl acrylate, (3-ethyl-3-oxetanyl) methyl methacrylate, 2-(3-methyl-3-oxetanemethoxy)ethyl vinyl ether, and mixtures thereof. More preferably, the (d) substituted or unsubstituted monomer comprises a cyclic ether derived from 4-vinyl-1-cyclohexene-1,2-epoxide.

[0043] Preferably, the (d) acetoacetate is selected from the group consisting of acetoacetoxyethyl (meth)acrylate, acetoacetoxyethyl acrylate, and allyl acetoacetate, and mixtures thereof.

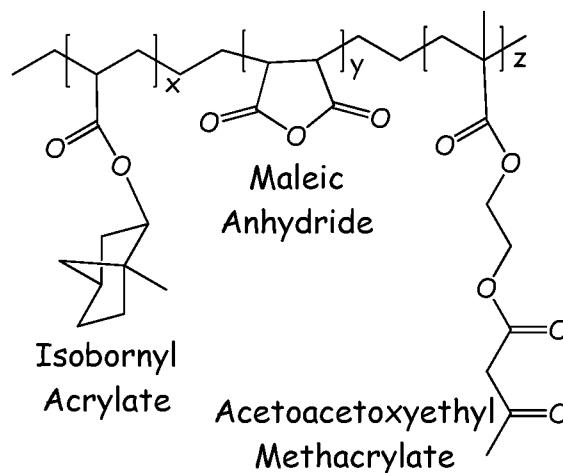
Preferably, the hydrophobic coating composition for forming a toner receptor coating on a

substrate containing a hydrophobic polymer is selected from the group consisting of octyl acrylate/decyl acrylate/maleic anhydride/4-vinyl-1-cyclohexene-1,2-epoxide, isobornyl acrylate/maleic anhydride/4-vinyl-1-cyclohexene-1,2-epoxide, and isobornyl acrylate/maleic anhydride/ acetoacetoxyethyl methacrylate.

[0044] In another aspect, the hydrophobic polymer is represented by the following structures:



and



wherein x, y, and z are molar amounts, the sum of which equals 100%.

[0045] The coating compositions set out above are suitable for addition to toners

[0046] Polymers in accordance with the present invention may be in the form of a powder, solid, liquid, or solution form. Compositions comprising the polymer may be curable via ultra violet (UV) radiation, thermal, electron beam, or gamma irradiation. The polymers may be utilized in the formulation of aqueous, UV curable coatings, or in 100% solid, UV curable coatings. Compositions comprising the polymer may be thermally and/or cationically curable or thermally and/or anionically curable. The polymers or compositions containing the polymers may be thermoplastic polymers that can be produced in either liquid or powder form.

[0047] Preferably, the polymer has a solids content of about 15-50% and a viscosity of about 200-15,000 cps. The composition may also be in the form of an aqueous dispersion. The coating composition has a polymer solids content of about 15-50% and a viscosity of about 200-3,000 cps.

[0048] The toner receptive coatings may be in the form of a liquid, solid, or wax. Preferably, the toner receptive coatings are in the form of a liquid. Toner additives may be in the form of a liquid, solid, or wax. Preferably, toner additives are in the form of a liquid.

[0049] In another aspect, the invention provides a toner substrate coated with a hydrophobic coating composition for forming a toner receptor coating on a substrate containing a hydrophobic polymer comprising: (a) a N-vinyl amide monomer, (b) a non-reactive hydrophobic monomer moiety, and (c) a solvent. The toner substrate coated with a

hydrophobic coating composition may further comprise (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof.

[0050] In another aspect, the invention provides a flexible food package substrate coated with a coating composition containing a polymer comprising: (a) a N-vinyl amide monomer, (b) a vinyl acetate monomer, (c) a reactive monomer comprising an acetoacetate moiety, and (e) an additional hydrophobic monomer moiety. The flexible food package substrate coated with a hydrophobic coating composition may further comprise (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof.

[0051] The present invention further provides toner substrates coated with the coating compositions.

[0052] Polymeric binders, also referred to as emulsions, latexes, adhesives, glues, dispersions, or resins, are versatile systems in the construction and design of polymers. Examples of suitable binder classes include styrene butadiene rubber (SBR) latex, styrene acrylate, polyvinyl alcohol and copolymers, polyvinyl acetate copolymers, vinyl acetate copolymers, carboxylated SBR latex, polyolefins and copolymer of polyolefins (i.e.; poly(ethylene-co-acrylic acid) and poly(ethylene-co-vinyl acetate)), styrene acrylate copolymers, styrene/butadiene/acrylonitrile, styrene/butadiene/acrylate/acrylonitrile, polyalkylene imines, polyvinyl pyrrolidone and copolymers, polyurethanes, polyamines, polyamides, cationic polyurethanes, polyethylene oxide, poly(2-ethyl-2-oxazoline), polyester resins, gelatins, casein, alginate, cellulose derivatives, hydroxyethyl cellulose, ethyl cellulose, hydroxypropyl cellulose, starches, ethoxylated, oxidized and enzyme converted starches, cationic starches, guar, cationic guar, water soluble gums, acrylic vinyl polymers, soy protein polymers as well as mixtures of water soluble and water-insoluble resins, latexes may be used. Latex binders are most commonly emulsions (polymer particles suspended in a liquid medium).

[0053] Preferably, a binder is present in the coating compositions of the invention. A preferred binder is a vinyl acetate-ethylene copolymer, such as Vinnapas® 465 Emulsion, available from Wacker Chemie, AG. Vinnapas® 465 Emulsion is a rapid-setting vinyl acetate-ethylene copolymer, which is a high-solids emulsion. This polymer adheres well to various substrates such as polyester, poly(ethylene terephthalate), tempered aluminum foil and polystyrene. This emulsion combines a high-solids content with a low viscosity, which is

a combination that permits the addition of high-filler loadings, resulting in adhesive formulations with solid contents of 80%, or more. Furthermore, this emulsion does not thicken excessively on the addition of plasticizers, which allows for the formulation of very high-solids adhesives. Vinnapas® 465 Emulsion also is shear stable, and can be applied on high-speed packaging machines using roll, extrusion, or spray equipment. The emulsion dries to a slightly tacky, clear, water-resistant film. Another preferred binder is Witcobond W-213 polyurethane dispersion, available from Uniroyal Chemical. Witcobond W-213 polyurethane dispersion is a waterborne, cationic dispersion from aliphatic urethanes. Strong, cohesive films can be produced simply by the evaporation of its water content. Witcobond W-213 polyurethane dispersion is used with cationic additives as a protective coating or surface treatment, where the properties of a light stable, waterborne urethane are suitable, primarily for textiles, nonwovens, fiberglass, paper, wood, urethane foam, or other porous substrates.

[0054] Preferably a pigment or pigments (colorant or colorants) are used in the coating compositions of the invention. Suitable pigment materials are described in Hunger's "Industrial Organic Pigments," Itoh's "Dictionary of Pigments," and Leach and Pierce's "Printing Ink Manual." Pigment can be added by mixing components. Pigment or pigments may be added with a plasticizer and/or a filler. The exact choice and amount of pigment will depend upon the final desired coating composition and such information is well known in the art.

[0055] The electrophotographic process is disclosed in "Effect of Toner Fixing Temperature on Print Properties in the Electrophotographic Process" by T. Hartus (*TAGA Journal*, **4**, 2008, 165-177). The adhesion science of toner is disclosed in "Adhesion of Electrophotographic Toner on Paper" by T. Hartus (*Graphic Arts in Finland* **30**, 2001, 3). Information related to the electrophotographic process as well as liquid and dry toner materials can be found in "Handbook of Imaging Materials" by A.S. Diamond and D.S. Weiss (ed.) (Marcel Dekker, 2002). Preferably, the toner receptive coating is suitable for fusing to toner at temperatures between 50°C and 175°C.

[0056] Preferably a surfactant is used in the coating compositions of the invention. Surfactants (wetting agents, are compounds that lower the surface tension of a liquid, the interfacial tension between two liquids, or that between a liquid and a solid. Surfactants may act as detergents, emulsifiers, foaming agents, and dispersants. Surfactants are usually

organic compounds that are amphiphilic, meaning they contain both hydrophobic groups and hydrophilic groups. Therefore, a surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble component. Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. The insoluble hydrophobic group may extend out of the bulk water phase, into the air or into the oil phase, while the water-soluble head group remains in the water phase. This alignment of surfactants at the surface modifies the surface properties of water at the water/air or water/oil interface. The exact choice and amount of surfactant will depend upon the final desired coating composition and such information is well known in the art.

[0057] Other suitable components for aqueous based coatings of this invention include silicates and silica gels, free radical initiators, aluminates and aluminas, N-vinyl-2-pyrrolidone, N-vinyl-caprolactam, other N-vinyl amides, 1-vinyl imidazole, 4-acryloyl morpholine, polyvinyl pyrrolidone, polyvinyl alcohol, acetoacetylated polyvinyl alcohol, oxygen scavengers, styrene/acrylate latexes, acrylic latexes, polyalkylene glycols, maleic anhydride-co-methyl vinyl ether polymers, polyalkylene imines, oxetanes, oxazolines, benzoxazines, polydi allyldialkylammonium chloride materials, starch, acrylated epoxides, glycidyl acrylate monomers, polyurethanes, acrylated oligomers of polyurethanes, acrylated glycidyl oligomers, polyfunctional acrylates, polyfunctional aziridines, clays, calcium carbonates, talcs, cellulose, cycloaliphatic epoxides, vinyl ethers, epoxy based dispersions, anionic surfactants (i.e., sodium lauryl sulfate), non-ionic surfactants, cationic surfactants, silanes or silicone based polymers, and anionic polyacrylates, such as polyacrylic acid. Optional components in the composition for optimization of the coating composition when coated on different substrates include pigments, clays, e.g. organoclays and water-swelling clays, acrylic polymers, acrylic copolymers, alginates, carrageenan, microcrystalline cellulose, gelatin, carboxymethylcellulose sodium, hydroxyethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, methylcellulose, guar and guar derivatives, locust bean gum, polyethylene oxide, polyvinylpyrrolidones, copolymers of polyvinylpyrrolidones, polyvinylalcohols, charge control agents, optical brighteners, other water soluble polymers, silicas, aluminates, zirconates, calcium carbonates, xanthan gums, polymers or copolymers of water soluble vinyl lactams optionally having in situ-formed particles of crosslinked vinyl lactam polymers or copolymers, crosslinked polyvinyl pyrrolidone, and crosslinkers to achieve advantageous printable surface coatings having light

stability (see US 6,872,787 B2). Preferred components and optimal amounts of these components will depend upon the specific support coating and application and can be readily determined by one of ordinary skill in the art.

[0058] The present invention relates to curing or cross-linking or polymerizing a polymerizable material carried out by any appropriate method known in the arts. Insight into curing and cross-linking technology is disclosed in “Thermosetting Polymers,” J.P. Pascault et. al. (Marcel Dekker, New York, 2002), which disclosure is incorporated by reference herein. The polymerization of reactive solution comprising polymerizable polymer may be carried out by employing any of the methods disclosed in “Principles of Polymerization 4th edition,” by George Odian (J. Wiley and Sons, Hoboken, New Jersey, 2004), which disclosure is incorporated by reference herein. The preferable techniques or methods employed by the present invention to polymerize the polymers would include UV-radiation, UV-LED, laser beam, electron beam, gamma irradiation, free-radical, cationic, anionic, thermal, exposure to e-beam and/or by employing a high-energy source in presence of suitable photo initiator for the initiation of polymerization. Suitable sources of radiation include, but are not limited to, mercury, xenon, halogen, carbon arc lamps, sunlight, and radioactive sources.

[0059] In order to induce polymerization *via* irradiation, photoinitiators are often incorporated to initiate the polymerization reaction system. Preferable photoinitiators are selected from the following non-limiting group or class of compounds such as 2-hydroxy-2-methyl-1-phenylpropane-1-one, 1-hydroxycyclohexyl phenyl ketone, and 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1-on; benzoin e.g. benzyl dimethyl ketal; benzophenones such as benzophenone, 4-phenylbenzophenone, and hydroxybenzophenone; thioxanthenes such as isopropylthioxanthone and 2,4-diethylthioxanthone; acylphosphine oxides; and other special initiators such as methyl phenyl glyoxylate; bis[4-(di(4-(2-hydroxyethyl)phenyl)sulfonio)phenyl sulfide], a mixture of bis[4-diphenylsulfonio]phenyl sulfide bis(hexafluoroantimonate and diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate, bis[4-(di(4-(2-hydroxyethyl)phenyl)sulfonio)phenyl sulfide], 5-2,4-cyclopentadiene-1-yl- [(1,2,3,4,5,6-eta.)-(1-methylethyl)-benzene]-iron (1+)-hexafluorophosphate(1-)), 4-(2-hydroxytetradecanyloxy) diphenyliodonium hexafluoroantimonate, (4-hydroxynaphthyl) dimethylsulfonium hexafluoroantimonate), photo latent bases such as photo latent

diazabicyclo nonene, triphenylsulfonium hexafluorophosphate, triphenylsulfonium hexafluoroantimonate, 4-methoxyphenyldiphenylsulfonium hexafluoroantimonate, 4-methoxyphenyliodonium hexafluoroantimonate, bis(4-tert-butylphenyl)iodonium tetrafluoroborate, (bis(4-tert-butylphenyl)iodonium hexafluorophosphate), (bis(4-tert-phenyl)iodonium hexafluoroantimonate), (bis[4-(diphenylsulfonio)phenyl]sulfide bis(hexafluorophosphate)), aryldiazonium salts, diaryliodonium salts, triarylsulfonium salts, triarylselenonium salts, dialkylphenacylsulfonium salts, triarylsulfoxonium salts, triethanol amine, aryloxydiarylsulfonium salts, and the like for example, triphenylsulfonium hexafluorophosphate, methyldiphenylsulfonium hexafluorophosphate, dimethylphenylsulfonium hexafluorophosphate, diphenylnaphthylsulfonium hexafluorophosphate, di(methoxynaphthyl)methylsulfonium hexafluorophosphate, (4-octyloxyphenyl) phenyl iodonium hexafluoro antimonate, (4-octyloxyphenyl) diphenyl sulfonium hexafluoro antimonate, (4-decyloxyphenyl) phenyl iodonium hexafluoro antimonite, (4-dodecyloxyphenyl)diphenyl sulfonium hexafluoroantimonate. Preferably, the photoinitiator includes 10-biphenyl-4-yl-2-isopropyl-9H-thioxanthene-10-ium hexafluorophosphate, 4,4'-dimethyl iodonium hexafluorophosphate, mixed triarylsulfonium hexafluorophosphate salts and reaction products of polyol and 10-(2-carboxymethoxy)-biphenyl-4yl-2-isopropyl-9-oxo-9H-thioxanthene-10-ium hexafluorophosphate. The photoinitiators may be used alone or in combinations thereof. Alternatively, the photoinitiator may be used by mixing it with one or more photopolymerization accelerator, such as a benzoic acid (e.g., 4-dimethylaminobenzoic acid) or a tertiary amine (e.g., diazabicyclo nonene (DBN)), in any appropriate ratio. The photoinitiator is preferably added to the photopolymerizable composition in the range of about 0.1% to about 20% by weight.

[0060] The coating compositions of the invention can provide a glossy, transparent to matte, opaque finish coating on synthetic films such as polyester, vinyl, polyolefins, and the like, as well as paper and canvas.

[0061] Generally, the coating composition has a solids content of about a solids content of about 15-50% and a viscosity of about 200-3000 cps.

[0062] The polymer in the coating composition suitably has a K-Value of about 5 to about 100, preferably about 10 to about 70.

[0063] Colloidal silica, amorphous colloidal silica particles may be included, e.g. 20-150 nm.

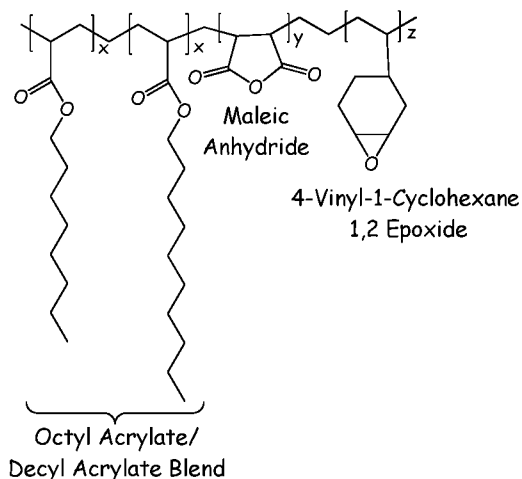
Preferred colloidal silicas are Silcron IJ-25 and IJ-50. Silica gels, amorphous colloidal silica particles, may also be included, e.g., 4-7 microns. A preferred silica gel is Silcron G 100.

[0064] The polymers of the present invention are suitable for use in industrial, personal care, household, and pharmaceutical applications. Industrial uses include, but are not limited to, formulating inks, flocculation agents, hydrogels, gel forming materials, surface modification agents, coatings, microporous print media, paper sizing additives, shale swell inhibitors, metal coatings, metal working fluids, ceramics, rheology modifiers, reactive biocides, decorated titanium, interlaminar adhesives, agricultural compositions, dispersants, batteries, products comprised of iodine, products comprised of silver, products comprised of carbon and graphene, products comprised of nano carbons, comb/branch polymer adducts, biocidal films, tackifiers, latex weather resistant modifiers, decorated pigments for inks and pastes, decorated cenospheres, decorated barium sulfate, cross-linkers, automotive products and protective films, super-absorbers (i.e., diapers) (see U.S. Pat. App. 2009/0043005A1, the contents of which are hereby incorporated by reference), printing plates, macro-initiating materials, products comprised of graphene, hydrophilic enhancement agents for membranes (see U.S. Pat. App. Ser. No. 61/242900 and PCT/US/2010/028852, the contents of which are hereby incorporated by reference), anti-fog coatings, polymer blocks, additives to extrudable compounds and films, protective colloidal agents, multi dimensional printing materials including pigments, polymers and inks (for example see WO/2008/077850A2, the contents of which are hereby incorporated by reference), refractive index modifiers, cross-linking agents, microencapsulation particles and additives (see US 5,811,121 and WO 2007/146722 A1), rheology control agents, grease resistant paper and films, fiber sizing agents, products comprised of alumina, conductive films, cementitious compositions, bioadhesives, tablet coatings, battery binders, resinous UV absorbers (U.S. Pat. App. Ser. No. 12/698,583, the contents of which are hereby incorporated by reference), iodine stabilizers, conductive coatings and gels, reactive rheology modifying agents, macro-initiators, coating flex agents, and non-migratory anti-static agents. Personal care and household applications include, but are not limited to, formulating cosmetics, hair care products, toiletries, hydrogels, laundry products and household cleaning products, and dye absorbent non-woven swatches. Pharmaceutical applications include, but are not limited to, processing aids, medical stents, lubricity modification agents, catheters and other medical device coatings, active ingredient solubilizers, adhesive patches, optical lenses, formulating drug delivery systems, and preparing tablet coatings.

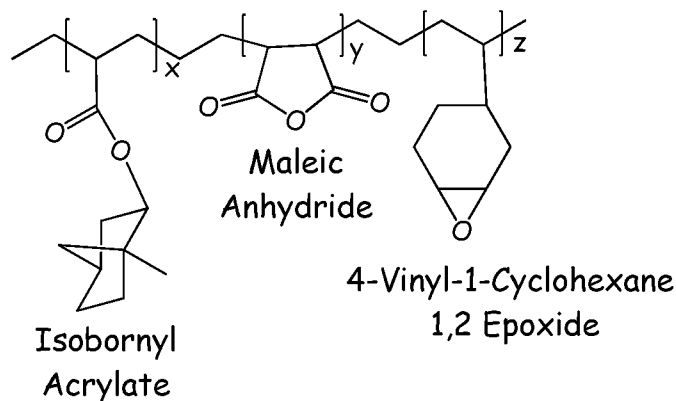
[0065] The coating compositions can be prepared according to the examples set out below. The examples are presented for purposes of demonstrating, but not limiting, the preparation of the coating compositions of this invention.

EXAMPLES

[0066] The following non-limiting examples are provided to illustrate a few of the methods for preparing novel coating compositions for forming toner receptive coatings. The examples are presented for purposes of demonstrating, but not limiting, the preparation of the compounds and compositions of this invention.

Example 1**Synthesis of ODA/MAN/VCHE (80/10/10)**

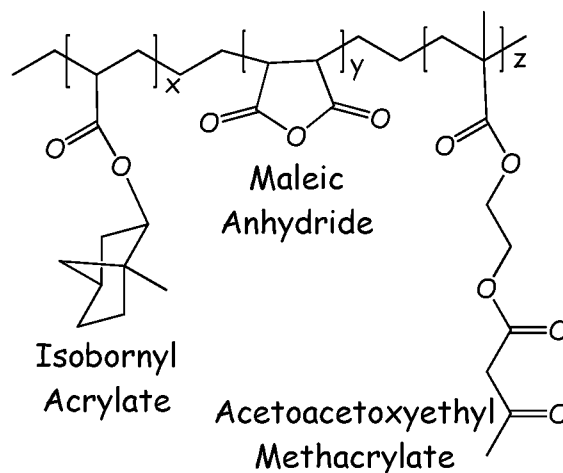
[0067] Feed one is prepared with 103.59g octyl acrylate/decyl acrylate (ODA), 6.25g maleic anhydride (MAN), 7.92g 4-vinyl-1-cyclohexene-1,2-epoxide (VCHE), and 32.7g methyl ethyl ketone) (MEK). Put 163.55g MEK into the reactor and commence purging of the reaction vessel with nitrogen. Heat the reaction flask containing MEK to reflux $\sim 78^{\circ}\text{C}$. In a separate vessel prepare a mixture of Triganox 25C 75 (15g) and MEK (15g). Label this vessel "Triganox Solution". When the reaction flask has reached reflux temperature, begin adding Feed 1, drop-wise, into the reaction vessel over a period of 180 minutes. After 15 minutes of monomer feed, add 3g of the Triganox Solution into the reactor. Continue the drop-wise addition of Feed 1 over a period of approximately 165 minutes. While the monomers are feeding into the reactor, charge 3.0g of the Triganox solution over 30 minutes. After 45, 60, 75, 90, 105 and 120 minutes, charge 3.0g Triganox solution into the reactor. After 150 minutes, charge 3.0g Triganox solution into the reactor. At the completion of the monomer feeds, charge the reaction vessel with the remainder of the Triganox solution. The reaction vessel is allowed to heat to reflux for an additional 180 minutes. Note: during the initiator shots, additional MEK was added to replace any that has volatilized. Cool the reaction vessel and leave the material in the reactor. This is the end of 'day one'. On 'day two', re-heat the vessel to reflux and charge with 2.0g Triganox 25C 75. Hold for 2 hours. Add an additional 2.0g Triganox 25C 75. Hold for 5 hours then cool reaction mixture.

Example 2**Synthesis of IBOA/MAN/VCHE (80/10/10)**

[0068] Feed one is prepared with 105.48g isobornyl acrylate (IBOA), 6.21g maleic anhydride (MAN), 7.86g 4-vinyl-1-cyclohexene-1,2-epoxide (VCHE), and 32.46g MEK. Put 162.29g MEK into the reactor and commence purging of the reaction vessel with nitrogen. Heat the reaction flask containing MEK to reflux $\sim 78^{\circ}\text{C}$. In a separate vessel prepare a mixture of Triganox 25C 75 (15g) and MEK (15g). Label this vessel "Triganox Solution". When the reaction flask has reached reflux temperature, begin adding Feed 1, drop-wise, in to the reaction vessel over a period of 180 minutes. After 15 minutes of monomer feed, add 3g of the Triganox Solution into the reactor. Continue the drop-wise addition of Feed 1 over a period of approximately 165 minutes. While the monomers are feeding into the reactor, after 30 minutes charge 3.0g of the Triganox solution. After 45, 60, 75, 90, 105 and 120 minutes, charge 3.0g Triganox solution into the reactor. After 150 minutes, charge 3.0g Triganox solution into the reactor. At the completion of the monomer feeds, charge the reaction vessel with the remainder of the Triganox solution. The reaction vessel is allowed to heat at reflux for an additional 180 minutes. Note: during the initiator shots, additional MEK was added to replace any that has volatilized. Cool the reaction vessel and leave the material in the reactor. This is the end of 'day one'. On 'day two', re-heat the vessel to reflux and charge with 2.0g Triganox 25C 75. Hold for 2 hours. Add an additional 2.0g Triganox 25C 75. Hold for 5 hours then cool reaction mixture.

Example 3

Synthesis of IBOA/MAN/AcAc (80/10/10)



[0069] Feed one is prepared with 103.79g isobornyl acrylate (IBOA), 6.11g maleic anhydride (MAN), 13.34g acetoacetoxyethyl methacrylate (AcAc), and 31.94g MEK. Put 159.69g MEK into the reactor and commence purging of the reaction vessel with nitrogen. Heat the reaction flask containing MEK to reflux $\sim 78^{\circ}\text{C}$. In a separate vessel prepare a mixture of Triganox 25C 75 (15g) and MEK (15g). Label this vessel "Triganox Solution". When the reaction flask has reached reflux temperature, begin adding Feed 1, drop-wise, in to the reaction vessel over a period of 180 minutes. After 15 minutes of monomer feed, add 3g of the Triganox Solution into the reactor. Continue the drop-wise addition of Feed 1 over a period of approximately 165 minutes. While the monomers are feeding into the reactor, after 30 minutes charge 3.0g of the Triganox solution. After 45, 60, 75, 90, 105 and 120 minutes, charge 3.0g Triganox solution into the reactor. After 150 minutes, charge 3.0g Triganox solution into the reactor. At the completion of the monomer feeds, charge the reaction vessel with the remainder of the Triganox solution. The reaction vessel is allowed to heat at reflux for an additional 180 minutes. Note: during the initiator shots, additional MEK was added to replace any that has volatilized. Cool the reaction vessel and leave the material in the reactor. This is the end of 'day one'. On 'day two', re-heat the vessel to reflux and charge with 2.0g Triganox 25C 75. Hold for 2 hours. Add an additional 2.0g Triganox 25C 75. Hold for 5 hours then cool reaction mixture.

Example 4
Solubility Test Results

| | Example # | Isopar H | Isopar K | Isopar L | Isopar M | Isopar V |
|--------------------------|-----------|---|---|---|--------------------------------------|--------------------------------------|
| Polymer | | Soluble? (Y, P, N) P = partial | Soluble? (Y, P, N) P = partial | Soluble? (Y, P, N) P = partial | Soluble? (Y, P, N) P = partial | Soluble? (Y, P, N) P = partial |
| ODA/MAN/VCHE (80/10/10) | 1 | Y | Y | Y | Y | Y |
| IBOA/MAN/VCHE (80/10/10) | 2 | Y- | Y- | Y- | Y | Y- |
| IBOA/MAN/ACAC (80/10/10) | 3 | P | P | P | P+ | N |

| | Example # | Linseed Oil | Mineral Oil | Isopar C | Isopar E | Isopar G |
|--------------------------|-----------|---|---|---|--------------------------------------|--------------------------------------|
| Polymer | | Soluble? (Y, P, N) P = partial | Soluble? (Y, P, N) P = partial | Soluble? (Y, P, N) P = partial | Soluble? (Y, P, N) P = partial | Soluble? (Y, P, N) P = partial |
| ODA/MAN/VCHE (80/10/10) | 1 | Y | Y | Y | Y | Y |
| IBOA/MAN/VCHE (80/10/10) | 2 | Y | Y | Y- | Y- | Y |
| IBOA/MAN/ACAC (80/10/10) | 3 | Y | P | P | Y | P |

[0070] While a number of embodiments of this invention have been represented, it was apparent that the basic construction can be altered to provide other embodiments that utilize the invention without departing from the spirit and scope of the invention. All such modifications and variations are intended to be included within the scope of the invention as defined in the appended claims rather than the specific embodiments that have been presented by way of example.

We claim:

1. A hydrophobic coating composition for forming a toner coating on a substrate containing a hydrophobic polymer comprising: (a) a maleic anhydride monomer, (b) a non-reactive hydrophobic monomer moiety, and (c) a solvent.

2. The coating composition according to claim 1, wherein the (b) non-reactive hydrophobic monomer moiety comprises a C₁-C₂₀ alkyl acrylate monomer.

3. The coating composition according to claim 2, wherein the C₁-C₂₀ alkyl acrylate monomer is selected from the group consisting of lauryl (meth)acrylate, isobutyl (meth)acrylate, isobornyl acrylate, octyl acrylate, decyl acrylate, and mixtures thereof.

4. The coating composition according to claim 3, wherein the C₁-C₂₀ alkyl acrylate monomer is selected from the group consisting of isobornyl acrylate, octyl acrylate, decyl acrylate, and mixtures thereof.

5. The coating composition according to claim 1, wherein (a) is 0.1-80%, (b) is 1-80%, and (c) is to 100%, by weight.

6. The coating composition according to claim 1, further comprising (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof.

7. The coating composition according to claim 6, wherein the (d) substituted or unsubstituted monomer comprising a cyclic ether is selected from the group consisting of allyl glycidyl ether ([2-propenyloxy)methyl]-oxirane), butadiene monoxide, glycidyl acrylate, glycidyl methacrylate, vinyl cyclohexene monoxide, 4-vinyl-1-cyclohexene-1,2-epoxide, 3-N-(6-propyl vinyl ether) benzoxazine, 3,4-epoxycyclohexylmethyl methacrylate, (3-ethyl-3-oxetanyl) methyl acrylate, (3-ethyl-3-oxetanyl) methyl methacrylate, 2-(3-methyl-3-oxetanemethoxy)ethyl vinyl ether, acetoacetoxyethyl (meth)acrylate, acetoacetoxyethyl acrylate, allyl acetoacetate, and mixtures thereof.

8. The coating composition according to claim 7, wherein the (d) substituted or unsubstituted monomer comprising a cyclic ether is derived from 4-vinyl-1-cyclohexene-1,2-epoxide.

9. The coating composition according to claim 6, wherein the (d) acetoacetate is

selected from the group consisting of acetoacetoxyethyl (meth)acrylate, acetoacetoxyethyl acrylate, and allyl acetoacetate, and mixtures thereof.

10. The coating composition according to claim 1, further comprising (e) a binder, (f) a pigment, and (g) a surfactant.

11. The coating composition according to claim 1, having a solids content of about 15-50% and a viscosity of about 200-3000 cps.

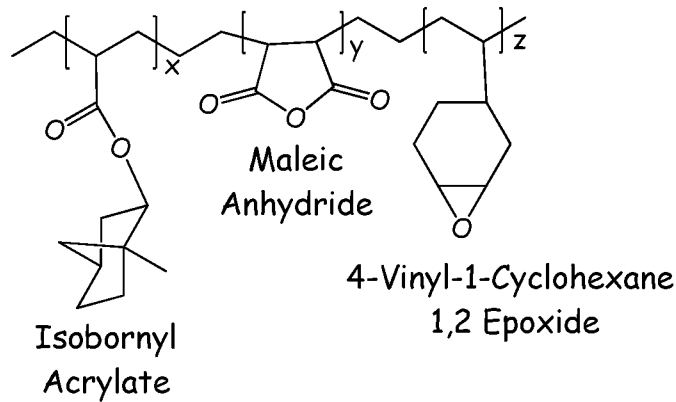
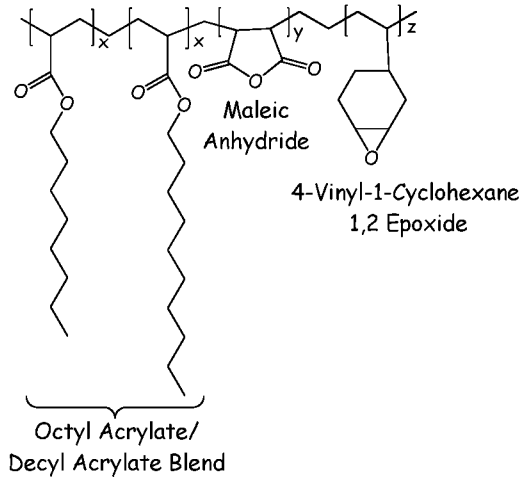
12. The coating composition according to claim 1, wherein the composition is in the form of an aqueous dispersion.

13. The coating composition according to claim 1, wherein the polymer further comprises an additive selected from the group consisting of adhesives, aerosols, agricultural agents, anti-soil redeposition agents, batteries agents, beverages, biocides, block copolymers, branch/comb copolymers, cementing agents, cleaning agents, coating agents, conductive materials, cosmetic agents, cross-linkers, dental agents, decorated pigments, detergents, dispersants, drugs, electronics, encapsulations, foods, hair sprays, household-industrial-institutional, inks and coatings, interlaminar adhesives, lithographic solutions, membrane additive agents, metal working fluids, oilfield agents, paints, paper, paper sizing agents, personal care agents, pharmaceuticals, pigment additives, plasters, plastics, printing, reactive biocides, reactive rheology modifiers, refractive index modifiers, sequestrants, soil release agents, static control agents, and wood-care agents.

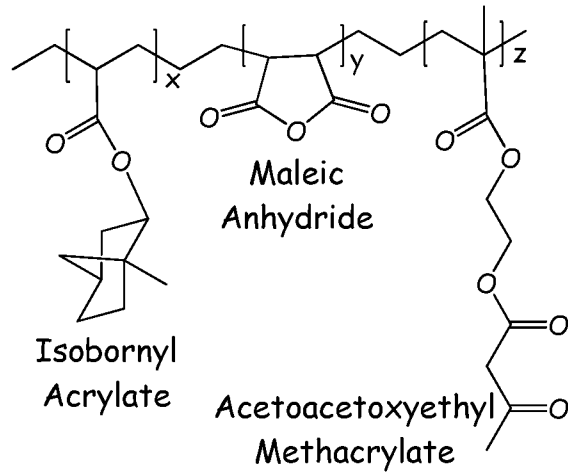
14. The coating composition according to claim 1, wherein the polymer is a film-forming polymer soluble in a hydrophobic solvent.

15. The coating composition according to claim 1, wherein the hydrophobic polymer is selected from the group consisting of octyl acrylate/decyl acrylate/maleic anhydride/4-vinyl-1-cyclohexene-1,2-epoxide; isobornyl acrylate/maleic anhydride/4-vinyl-1-cyclohexene-1,2-epoxide; and isobornyl acrylate/maleic anhydride/acetoacetoxyethyl (meth)acrylate.

16. The coating composition according to claim 15, wherein the hydrophobic polymer is represented by the following structures:



and



wherein x, y, and z are molar amounts, the sum of which equals 100%.

17. A toner substrate coated with a hydrophobic coating composition for forming a toner coating on a substrate containing a hydrophobic polymer comprising: (a) a maleic anhydride monomer, (b) a hydrophobic monomer moiety, and (c) a solvent.

18. The toner substrate toner substrate coating composition according to claim 17, further comprising (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof.

19. A flexible food package substrate coated with a hydrophobic coating composition for forming a toner coating on a substrate containing a hydrophobic polymer comprising: (a) a maleic anhydride monomer, (b) a hydrophobic monomer moiety, and (c) a solvent.

20. The toner substrate according to claim 19, further comprising (d) a substituted or unsubstituted monomer comprising a cyclic ether or an acetoacetate, or mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/31826

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B41M 5/50, 5/52; G03G 8/00 (2014.01)

USPC - 347/105; 428/195.1, 221

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)

IPC(8): B32B 9/00; B41M 5/00, 5/50, 5/52; G03G 7/00, 8/00 (2014.01)

USPC: 347/101, 105; 428/195.1, 221, 500

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)

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); Google Scholar; ProQuest; IP.com; hydrophobic, toner, receptor, coating, maleic anhydride, acrylate, cyclohexene, epoxide, solvent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|--------------|--|--|
| X -- Y | US 5,244,714 A (MALHOTRA, SL et al.) 14 September 1993; column 6, lines 27-45; column 10, lines 1-68; column 11, lines 27-48; column 12, lines 34-68 | 1-2, 14 -- 3-4 |
| X -- Y | US 3,494,783 A (KIMURA, TJ et al.) 10 February 1970; column 1, lines 10-15; column 2, lines 11-34; column 3, lines 1-15; column 4, lines 24-44; column 8, lines 8-13 | 1, 5, 10, 12-13, 17 -- 6-9, 11, 15-16, 18-20 |
| Y | WO 2012/051153 A2 (HOOD, DK et al.) 19 April 2012; paragraphs [0026], [0056] | 3-4, 16 |
| Y | US 6,433,097 B1 (NIXON, SA et al.) 13 August 2002; column 2, lines 20-73; column 3, lines 31-42; column 4, lines 30-64 | 6-9, 11, 15-16, 18, 20 |
| Y | US 5,094,863 A (VANDENBURG, DM) 10 March 1992; column 2, lines 49-53; column 5, lines 4-10; column 5, lines 40-68 | 19-20 |

 Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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Date of the actual completion of the international search

14 July 2014 (14.07.2014)

Date of mailing of the international search report

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