(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 June 2019 (27.06.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/120183 A1

(51) International Patent Classification:
C07C 43/20 (2006.01)

(21) International Application Number:
PCT/CN2018/121666

(22) International Filing Date:
18 December 2018 (18.12.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PCT/CN2017/117934
22 December 2017 (22.12.2017) CN

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2019/120183 A1

(54) Title: METHOD FOR IMPROVING SCRUB RESISTANCE OF COATINGS

(57) Abstract: A method for improving scrub resistance of a coating composition by adding an alkoxylated tristyrylphenol compound into said coating composition. In particular, the coating composition is an aqueous coating composition comprising a vinyl acetate-acrylic co-polymer or a vinyl acetate-ethylene-acrylic co-polymer.

Method for Improving Scrub Resistance of Coatings

[0001] This application claims priority to PCT international patent application no. PCT/CN2017/117934 filed on Dec 22, 2017, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

[0002] The present invention relates to a method for improving scrub resistance of a coating composition, comprising a step of adding an alkoxylated tristyrylphenol compound in the coating composition. In particular, the coating composition comprises a vinyl acetate-acrylic co-polymer or a vinyl acetate-ethylene-acrylic co-polymer.

Background Art

[0003] In the paint and coating industry, traditional solvent-based paints and coating are being replaced with water-based system due to concerns regarding the impact of Volatile Organic Compounds (VOC) to human health and the environment. In addition, recently enacted environmental legislation requires the reduction of the amount of Volatile Organic Compound (VOC) in coatings. For example, SCAQMD (South Coast Air Quality Management District) in California and OTC (Ozone Transport Commission) in the East Coast states, have required reduced amounts of VOC emissions of coatings & paints products, especially architectural and industrial paint and coatings (after application of a coating to a substrate, VOCs slowly evaporate into the surroundings). These regulations are forcing polymers and paints manufactures to develop lower VOC products.

[0004] Latex-based paints have captured a significant portion of the indoor and outdoor paint market as a result of the many advantages that such paints have over solvent-based products. The main advantage of latex-based paints include easy clean up, low odor and fast dry.

[0005] There are two types of latex polymer emulsion which are commonly used in formulating paints or coating. One is the acrylic emulsion, e.g. the emulsion employing copolymerized methyl methacrylate, butyl acrylate, or

2-ethylhexylacrylate with small proportion of the above lower alkyl acrylates, e.g. butyl acrylate. All acrylic emulsion has been used in premium quality paints as the emulsions can provide good water resistance, desired leveling, film hardness, durability, scrubability, etc. The other commonly used emulsion system is the vinyl acetate-acrylic copolymer emulsion. It has been widely used in formulation interior flat and semi-gloss paints. The vinyl acetate-butyl acrylate lattices, when used in paint or coating formulations, result in paint films which have excellent toughness and good durability.

[0006] Although there are some advantages to using latex paints, it is known that several drawbacks are associated with the latex paint/coating products versus solvent-based paints. One drawback is that the latex paint/coating tends to have poor scrub resistance, especially vinyl acrylic latex based paint.

[0007] Vinyl acrylic latex vehicles often require coalescing solvents in order for the latex to be suitable for use in paint or coating formulation. Coalescing solvents are incorporated into the paint or coating composition to externally and temporarily plasticize the latex polymer for a time sufficient to develop film formation. Efforts have also been devoted in the past to improve scrub resistance capabilities of latex-based paint or coating. This involved attempts to optimize various paint formulation parameters, such as using silane binders, using specific surfactants in combination with protective colloids.

[0008] U.S. patent no. 3,563,944 discloses a colloid-free vinyl acrylic emulsion suited for producing paint formulations having good scrub resistance, film-forming properties, mechanical stability, etc.

[0009] U.S. patent no. 3,969,296 discloses a process for producing vinyl acetate based emulsion having improved adhesion characteristics against usual wet-cleaning with a cloth, sponge, etc. The emulsion is prepared by copolymerizing a small amount of a glycidyl ester of an alpha-beta ethylenically unsaturated acid with vinyl acetate followed by neutralization with ammonia.

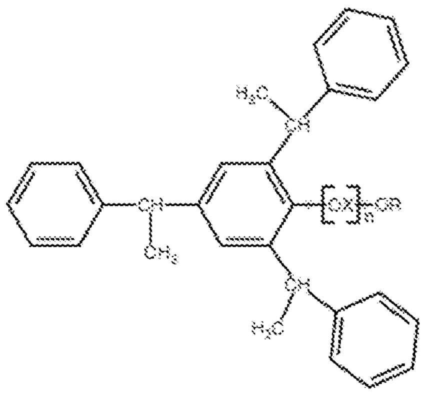
[0010] U.S. patent no. 6,673,854 discloses an aqueous vinyl acetate-ethylene polymer dispersion comprising vinyl acetate, ethylene and an optional third monomer, an alcohol ether phosphate surfactant with 4 to 70 ethylene oxide units, at least one protective colloid, and water.

[0011] PCT patent publication no. WO 2010/082918 discloses an alkoxylated compound which can be used in an aqueous coating composition to have enhanced freeze-thaw stability.

[0012] There is still a need to provide latex-based paints or coating compositions which have good scrub resistance.

Summary of Invention

[0013] In one aspect, the present invention is directed to a method for improving scrub resistance of a coating composition, which comprises a step of adding an alkoxylated tristyrylphenol compound in said coating composition, wherein the alkoxylated tristyrylphenol compound has the general formula (I) :



(I)

wherein n is an integer of from 1 to 100; R is -($H_2PO_3^-$ M^+); M^+ is a cation; and X is C_2H_4, C_3H_6, or C_4H_8. Preferably, X is C_2H_4.

[0014] Preferably, M^+ is selected from the group consisting of H^+, Na^+, NH_4^+, K^+, Li^+ and $-N(R_1)_4^+$, wherein R_1 is a $-H$ or a C_1-C_6 alkyl or hydroxyalkyl group and at least one R_1 is a C_1-C_6 alkyl or hydroxyalkyl group.

[0015] Preferably, the coating composition is an aqueous coating composition. In some embodiments, the coating composition comprises a vinyl acetate-acrylic co-polymer as the binder. In some embodiments, the coating composition comprises a vinyl acetate-ethylene-acrylic co-polymer as the binder.

[0016] The alkoxylated tristyrylphenol compound may be employed as an emulsifier during emulsion polymerization to form a latex polymer which is subsequently processed into a coating composition.

[0017] Alternatively, the alkoxylated tristyrylphenol compound may be employed as an additive to an already formed dispersion of at least one latex polymer or an already formed coating composition.

[0018] In another aspect, the present invention further relates to use of the alkoxylated tristyrylphenol compound described herein in a coating composition for improving scrub resistance.

[0019] Surprisingly and unexpectedly, it has been found that a coating composition comprising the alkoxylated tristyrylphenol compound exhibits excellent water resistance and wet scrub resistance properties when being applied to a substrate.

[0020] Other characteristics, details and advantages of the invention will emerge even more fully upon reading the description which follows.

Detailed Description

[0021] The articles “a”, “an” and “the” are used to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article.

[0022] The term “and/or” includes the meanings “and”, “or” and also all the other possible combinations of the elements connected to this term.

[0023] As used herein, the term “scrub resistance”, which is used in the paint industry to describe the ability of a paint coating to resist erosion when scrubbed. Scrub resistance of a coating is notably tested according to Standard ASTM D-2486.

[0024] As used herein, the term “latex” is in its conventional meaning, i.e. a dispersion of particulate matter in an aqueous phase which contains an emulsifier or surfactant suitable for preparing the latex.

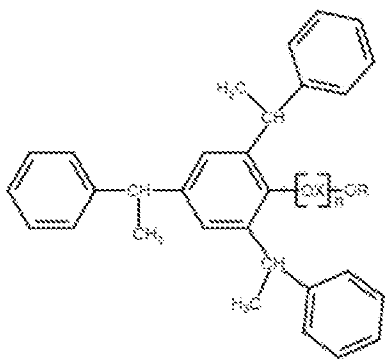
[0025] As used herein, the term “dry” means a substantial absence of liquids.

[0026] As used herein, the term “coating composition” includes and is not limited to latex binders, resins, glues, adhesives which include and are not limited to pressure sensitive adhesives, inks which include and are not limited to UV inks, conventional inks, hybrid inks, and water-based inks, sealants, cement compositions, coatings which include and are not limited to paints.

[0027] As used herein, the term "substrate" means an article or a material which is subject to coatings or paints, such as paper, wood, concrete, metal, glass, ceramics, plastics, plaster, an asphaltic coating, a roofing felt, foamed polyurethane insulation, or a previously painted, primed, undercoated, worn, or weathered article.

[0028] As used herein, the term "pigment" is a coloring agent that is practically insoluble in the application medium under the pertaining ambient conditions.

[0029] According to the present invention, the alkoxylated tristyrylphenol compound has the general formula (I) :



(I)

wherein n is an integer of from 1 to 100; R is -($H_2PO_3^-$ M^+); M^+ is a cation; and X is C_2H_4, C_3H_6, or C_4H_8. Preferably, X is C_2H_4.

[0030] Preferably, n is an integer of from 5 to 30. More preferably, n is an integer of from 10 to 20.

[0031] Preferably, M^+ is selected from the group consisting of H^+, Na^+, NH_4^+, K^+, Li^+ and $-N(R_1)_4^+$ wherein R_1 is a $-H$ or a C_1-C_6 alkyl or hydroxyalkyl group and at least one R_1 is a C_1-C_6 alkyl or hydroxyalkyl group. More preferably, M^+ is Na^+, NH_4^+, K^+, a tetramethylammonium group or a triethanol ammonium group.

[0032] The alkoxylated tristyrylphenol compound may be employed as an emulsifier during the emulsion polymerization reaction used to produce a latex polymer which is subject to be formulated into a coating composition.

Alternatively, the alkoxylated tristyrylphenol compound may be post added, for example, the alkoxylated tristyrylphenol compound can be incorporated into an already formed dispersion of at least one latex polymer. In particular, the alkoxylated tristyrylphenol compound is added to an already formed coating composition.

[0033] In some embodiments, the alkoxylated tristyrylphenol compound can be used as an emulsifier during the emulsion polymerization reaction so as to prepare a latex polymer. The latex polymer is then subject to formulation into a coating composition. Typically, the coating composition is an aqueous coating composition. More typically, the coating composition is an aqueous coating composition comprising a vinyl acetate-acrylic co-polymer or a vinyl acetate-ethylene-acrylic co-polymer.

[0034] In such case, the emulsifier is added in an amount greater than 0.5% by weight of the polymer or monomers used to form the latex polymer, preferably in an amount greater than 1.6% by weight of the polymer or monomers used to form the latex polymer, typically in an amount greater than about 2.0% by weight of the polymer or monomers used to form the latex polymer, more typically in an amount greater than about 4.0% by weight of the polymer or monomers used to form the latex polymer, and most typically in an amount greater than about 7.5% by weight of the polymer or monomers used to form the latex polymer.

[0035] Preferably, the emulsifier is added is between about 0.5% and 7.5% by weight of the polymer or monomers used to form the latex polymer. More preferably, the emulsifier added is between about 0.5% and 4.5% by weight of the polymer or monomers used to form the latex polymer, typically between about 1.6% and 3.5% by weight of the polymer or monomers used to form the latex polymer.

[0036] The latex polymer can be produced by first preparing an initiator solution comprising the initiator and water. A monomer pre-emulsion is also prepared comprising at least a portion of the monomers to be used to form the latex polymer, one or more surfactants (emulsifiers), water, and additional additives such as NaOH. The one or more surfactants in the monomer pre-emulsion include the alkoxylated tristyrylphenol compound of the present invention. Thus, the alkoxylated tristyrylphenol compound is employed as an emulsifier to form a blend with the other monomers which form the latex polymer. The initiator solution and monomer pre-emulsion are then continuously added to the reactor over a predetermined period of time (e.g. 1.5-5 hours) to cause polymerization of the monomers and to thereby produce the latex polymer. Typically, at least a portion of the initiator solution is added to the reactor prior to adding the monomer pre-emulsion. Prior to the addition of the initiator solution and the monomer pre-emulsion, a seed latex such as a polystyrene seed latex can be added to the reactor. In addition, water, one or more surfactants, and any monomers not provided in the monomer pre-emulsion can be added to the reactor prior to adding the initiator and adding the monomer pre-emulsion. The reactor is operated at an elevated temperature at least until all the monomers are fed to produce the polymer latex binder. Once the latex polymer is prepared, it is typically chemically stripped thereby decreasing its residual monomer content. Typically, it is chemically stripped by continuously adding an oxidant such as a peroxide (e.g. t-butylhydroperoxide) and a reducing agent (e.g. sodium acetone bisulfite), or another redox pair such as those described by A. S. Sarac in Progress in Polymer Science 24(1999), 1149-1204, to the latex binder at an elevated temperature and for a predetermined period of time (e.g. 0.5 hours). The pH of the latex binder can then be adjusted and a biocide or other additives added after the chemical stripping step.

[0037] The resulting latex polymer may then be formulated into a coating composition. Typically the coating composition is an aqueous coating composition. More typically, the coating composition is an aqueous coating composition comprising a vinyl acetate-acrylic co-polymer or a vinyl acetate-ethylene-acrylic co-polymer.

[0038] In some embodiments, the present invention relates to a method for improving scrub resistance of a coating composition, comprising a step of adding the alkoxylated tristyrylphenol compound into said coating composition, wherein the alkoxylated tristyrylphenol compound can be employed as an additive to an already formed dispersion of at least one latex polymer. It is understood, that the alkoxylated tristyrylphenol compound can be added any point in the production of the coating composition, including but not limited to during the emulsification step, during formulation, etc. It is also understood that the alkoxylated tristyrylphenol compound can be post-added to the coating composition. Typically, the coating composition is an aqueous coating composition. More typically, the coating composition is an aqueous coating composition comprising a vinyl acetate-acrylic co-polymer or a vinyl acetate-ethylene-acrylic co-polymer.

[0039] In such case, this results in a coating composition, in particular an aqueous coating composition, comprising the alkoxylated tristyrylphenol compound of the present invention. The resulting coating composition contains the alkoxylated tristyrylphenol compound in an amount of about 1 to 10, typically 2 to 8 or 2 to 6, parts per 100 parts by weight of monomers used to form the latex polymer.

[0040] In some embodiments, the present invention relates to a method for improving scrub resistance of a coating composition, comprising a step of adding the alkoxylated tristyrylphenol into said coating composition, wherein alkoxylated tristyrylphenol compound can be employed as an additive to an already formed coating composition. Typically, the coating composition is an aqueous coating composition. More typically, the coating composition is an aqueous coating composition comprising a vinyl acetate-acrylic co-polymer or a vinyl acetate-ethylene-acrylic co-polymer.

[0041] In some embodiments, the alkoxylated tristyrylphenol compound is employed as an additive to an already formed paint or an already formed coating composition, e.g., an aqueous latex coating composition, the resulting composition contains the alkoxylated tristyrylphenol compound typically in an amount greater than about 0.5% by weight of the polymer or monomers used to form the latex polymer, more typically in an amount greater than about 1.6% by weight of the polymer or monomers used to form the latex polymer, yet more typically in an amount greater than about 2% by weight of the polymer or monomers used to form the latex polymer, even more typically in an amount greater than about 4% by weight of the polymer or monomers used to form the latex polymer, and most typically in an amount greater than about 7.5% by weight of the polymer or monomers used to form the latex polymer.

[0042] Preferably, the latex coating composition contains the alkoxylated tristyrylphenol compound in an amount between about 0.5% and 7.5% by weight of the polymer or monomers used to form the latex polymer. More preferably, the latex coating composition contains the alkoxylated tristyrylphenol compound in an amount between about 0.5% and 4.5% by weight of the polymer or monomers used to form the latex polymer, typically between about 1.6% and 3.5%.

[0043] The coating composition may comprise a latex polymer, notably as the binder, which can be selected from pure acrylics (comprising acrylic acid, methacrylic acid, acrylate ester, and/or methacrylate ester as the main monomers); styrene acrylics (comprising styrene and acrylic acid, methacrylic acid, acrylate ester, and/or methacrylate ester as the main monomers); vinyl acetate-acrylic co-polymers (comprising vinyl acetate and one or more selected from acrylic acid, methacrylic acid, acrylate ester and methacrylate ester, as the main monomers); and vinyl acetate-ethylene-acrylic co-polymers (comprising ethylene, vinyl acetate, and one or more selected from acrylic acid, methacrylic acid, acrylate ester and methacrylate ester, as the main monomers).

[0044] Preferably, the latex polymer is a vinyl acetate-acrylic co-polymer or a vinyl acetate-ethylene-acrylic co-polymer.

[0045] According to any one of the invention embodiments, the typical monomers from which the latex polymer is formed may comprise at least one acrylic monomer selected from the group consisting of acrylic acid, acrylic acid esters, methacrylic acid, and methacrylic acid esters. In addition, the other monomers for making the latex polymer can optionally be selected from one or more monomers selected from the group consisting of styrene, a-methyl styrene, vinyl chloride, acrylonitrile, methacrylonitrile, ureido methacrylate, vinyl acetate, vinyl esters of branched tertiary monocarboxylic acids (e.g. vinyl esters commercially available under the mark VEOVA from Shell Chemical Company or sold as EXXAR Neo Vinyl

Esters by ExxonMobil Chemical Company), itaconic acid, crotonic acid, maleic acid, fumaric acid, and ethylene. It is also possible to include C_4-C_8 conjugated dienes such as 1,3-butadiene, isoprene and chloroprene. Typically, the monomers include one or more monomers selected from the group consisting of n-butyl acrylate, methyl methacrylate, styrene and 2-ethylhexyl acrylate.

[0046] In a preferred embodiment, the latex polymer is a vinyl acetate-acrylic co-polymer which is comprised of acrylic monomers and vinyl acetate monomers. The acrylic monomers can be any acrylic compound having acrylic functionality. Suitable acrylic unsaturated functional monomers include, but are not limited to esters of methacrylic acid including methyl methacrylate and butyl methacrylate, and esters of acrylic acid including ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate. Specific examples of acrylate monomers include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, methyl methacrylate, butyl methacrylate, iso-butyl methacrylate, iso-bornyl methacrylate hydroxyl ethyl acrylate and hydroxyl ethyl methacrylate. Suitable vinyl acetate monomers can be vinyl acetate, vinyl isopropyl acetate. The vinyl acetate-acrylic co-polymer suitable for the present invention may comprise a co-polymer containing 10 to 30 percent by weight an acrylic monomer and about 70 to 90 percent a vinyl acetate monomer.

[0047] The vinyl acetate-acrylic co-polymer may comprises one or more additional monomers including ethylenically unsaturated monomers which can be copolymerized with vinyl acetate and/or acrylic compounds, such as vinyl ether, acrylamide, acrylonitrile and unsaturated carboxylic acid.

[0048] In another preferred embodiment, the latex polymer is a vinyl acetate-ethylene-acrylic co-polymer which is comprised of ethylene and vinyl acetate, and unsaturated co-monomer of any acrylic compound having acrylic functionality. The amount of ethylene monomer used to prepare the vinyl acetate-ethylene-acrylic co-polymer may be from about 5 wt% to about 25 wt%, based on the total weight of monomers used to prepare the vinyl acetate-ethylene-acrylic co-polymer. The amount of vinyl acetate used to prepare the vinyl acetate-ethylene-acrylic co-polymer may be from about 75 wt% to about 95 wt%, based on the total weight of monomers used to prepare the vinyl acetate-ethylene-acrylic co-polymer. The vinyl acetate-ethylene-acrylic co-polymer may further comprise one or more optional unsaturated co-monomers. Such optional co-monomers can include, for example, C_1-C_{12} esters of (meth)acrylic acid.

[0049] The latex polymer dispersion typically includes from about 30 to about 75% solids and a mean latex particle size of from about 70 to about 650 nm. In another embodiment, the latex polymer of the present invention has a mean particle size of less than about 400nm, typically a mean particle size of less than about 200 nm, more typically a mean particle size of less than about 190 nm, and most typically a mean particle size of less than about 175 nm. In another embodiment, the polymer has a mean particle size of from about 75 nm to about 400 nm.

[0050] The latex polymer is typically present in the coating composition in an amount from about 5 to about 60 percent by weight, and more typically from about 8 to about 40 percent by weight (i.e. the weight percentage of the dry latex polymer based on the total weight of the coating composition). Typically, the coating composition is an aqueous coating composition. More typically, the coating composition is an aqueous coating composition comprising a vinyl acetate-acrylic co-polymer or a vinyl acetate-ethylene-acrylic co-polymer.

[0051] The aqueous coating composition of the invention includes less than 2 % by weight and typically less than 1.0% by weight of anti-freeze agents based on the total weight of the aqueous coating composition. More typically, the aqueous coating composition is substantially free of anti-freeze agents.

[0052] The aqueous coating composition typically includes at least one pigment. The term "pigment" as used herein includes non-film-forming solids such as pigments, extenders, and fillers. The at least one pigment is typically selected from the group consisting of TiO_2 (in both anastase and rutile forms), clay (aluminum silicate), $CaCO_3$ (in both ground and precipitated forms), aluminum oxide, silicon dioxide, magnesium oxide, talc (magnesium silicate), barytes (barium sulfate), zinc oxide, zinc sulfite, sodium oxide, potassium oxide and mixtures thereof. Suitable mixtures include blends of metal oxides such as those sold under the marks MINEX (oxides of silicon, aluminum, sodium and potassium commercially available from Unimin Specialty Minerals), CELITES (aluminum oxide and silicon dioxide commercially available from Celite Company), ATOMITES (commercially available from English China Clay International), and ATTAGELS (commercially available from Engelhard). More typically, the at least one pigment includes TiO_2, $CaCO_3$ or clay. Generally, the mean particle sizes of the pigments range from about 0.01 to about 50 microns. For example, the TiO_2 particles used in the aqueous coating composition typically have a mean particle size of from about 0.15 to about 0.40 microns. The pigment can be added to the aqueous coating composition as a powder or in slurry form. The pigment is typically present in the aqueous coating composition in an amount from about 5 to about 50 percent by weight, more typically from about 10 to about 40 percent by weight.

[0053] The aqueous coating composition can optionally contain additives such as one or more film-forming aids or coalescing agents. Suitable film-forming aids or coalescing agents include plasticizers and drying retarders such as high boiling point polar solvents. Other conventional coating additives such as, for example, dispersants, additional surfactants (i.e. wetting agents), rheology modifiers, defoamers, thickeners, biocides, mildewcides, colorants such as colored pigments and dyes, waxes, perfumes, co-solvents, and the like, can also be used in accordance with the invention. For example, non-ionic and/or ionic (e.g. anionic or cationic) surfactants can be used to produce the polymer latex. These additives are typically present in the aqueous coating composition in an amount from 0 to about 15% by weight, more typically from about 1 to about 10% by weight based on the total weight of the coating composition.

[0054] In some embodiments, the aqueous coating composition can include less than 2.0% of VOC agents based on the total weight of the aqueous coating composition. Exemplary agents include ethylene glycol, diethylene glycol, propylene glycol, glycerol (1,2,3-trihydroxypropane), ethanol, methanol, 1-methoxy-2-propanol, 2-amino-2-methyl-1-propanol, and FTS-365 (a freeze-thaw stabilizer from Inovachem Specialty Chemicals). More typically, the aqueous coating composition includes less than 1.0% or is substantially free (e.g. includes less than 0.1%) of anti-freeze agents. Accordingly, the aqueous coating composition of the invention typically has a VOC level of less than about 100 g/L and more typically less than or equal to about 50 g/L.

[0055] The balance of the aqueous coating composition of the invention is water. Although much of the water is present in the polymer latex dispersion and in other components of the aqueous coating composition, water is generally also added separately to the aqueous coating composition. Typically, the aqueous coating composition includes from about 10% to about 85% by weight and more typically from about 35% to about 80% by weight water. Stated differently, the total solids content of the aqueous coating composition is typically from about 15% to about 90%, more typically, from about 20% to about 65%.

[0056] The coating composition is typically formulated such that the dried coatings comprise at least 10% by volume of dry polymer solids, and additionally 5 to 90% by volume of non-polymeric solids in the form of pigments. The dried coatings can also include additives such as plasticizers, dispersants, surfactants, rheology modifiers, defoamers, thickeners, biocides, mildewcides, colorants, waxes, and the like, that do not evaporate upon drying of the coating composition.

[0057] The coating composition can be formulated using techniques known to those skilled in the art of manufacturing coating composition.

[0058] The coating composition according to the present invention is a stable fluid that can be applied to a wide variety of materials such as, for example, paper, wood, concrete, metal, glass, ceramics, plastics, plaster, and roofing substrates such as asphaltic coatings, roofing felts, foamed polyurethane insulation; or to previously painted, primed, undercoated, worn, or weathered substrates. The coating composition of the invention can be applied to the materials by a variety of techniques well known in the art such as, for example, brush, rollers, mops, air-assisted or airless spray, electrostatic spray, and the like.

[0059] The disclosure is further described in the following examples. The examples are merely illustrative and do not in any way limit the scope of the disclosure as described and claimed.

[0060] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Examples

[0061] **Materials**

RHODAFAC® PE-3016: tristyrylphenol ethoxylated phosphate ester salt, from Solvay

ABEX® AP-470 : alkyl ethoxylate; from Solvay

RHODASURF® BC8509 : alkyl ethoxylated alcohol; from Solvay

RHODAFAC® RS-610A25 : aliphatic phosphate ester salt; from Solvay

SOPROPHOR® FD : tristyrylphenol ethoxylated sulfate ester salt; from Solvay

Thickener : Cellosize QP-30000; from Dow

Dispersant : Orotan® Kuaiyi; from Dow

pH neutralizer : AMP-95; from Angus

Defoamer : Rhodoline® DF681F; from Solvay

TiO_2 : CR-826; from Tronox

Calcined Clay : CK40; from Kaolin

Coalescing agent : Texonal; from Eastman

Associate thickener : Acrysol TT-935; from Dow

[0062] **Preparation of latex polymers**

[0063] **Example 1**

The monomer solution was prepared by mixing 236.32 g vinyl acetate, 42.00 g butyl acrylate, 1.68 g acrylamide, 50.00 g water, 10.45 g RHODAFAC® PE-3016, 2.00 g ABEX® AP-470 and 0.57 g sodium acetate. The monomer mixture was then emulsified with vigorous stirring to prepare a pre-monomer emulsion. A reactor was charged with 189.84 g water, 4.67 g of RHODAFAC® PE-3016 and 3.29 g RHODSURF® BC8509 and then heated to 74-76°C under nitrogen. A solution of 0.62g ammonium persulfate and 0.11 g sodium acetate in 8.0 water was added into the reactor. Commencing simultaneously, the pre-monomer emulsion and the solution of 0.62 g ammonium persulfate in 12.0 water was added to the reactor by drop-wise feeding. The feed time for monomers and the ammonium persulfate solution was 3h. The temperature of the polymerization reaction was controlled at 74-76 °C, and then cooled down to 65 °C after the completion of the feeding. After adding a solution of 0.39 g of iso-ascorbic acid in 12.0 g water and 0.44 g tri-butyl phosphate in 1.60 g water, the reactor was held at 65 °C for 30 minutes then cooled down to 40°C. The collected latex polymer emulsion is adjusted to pH 4-5 with sodium acetate aqueous solution.

[0064] The particle size of the resulting latex polymer is 232.5 nm.

[0065] **Comparative Example 1**

The polymerization process was similar to that of Example 1, except that the monomer solution was prepared by mixing 236.32 g vinyl acetate, 42.00 g butyl acrylate, 1.68 g acrylamide, 56.00 g of water, 8.96 g of RHODAFAC® RS-610A25, 2.00 g of ABEX® AP-470 and 0.57 g of sodium acetate. The reactor was charged with 190.09 g water, 2.80 g of RHODAFAC® RS-610A25 and 3.29 g RHODASURF® BC8509.

[0066] The particle size of the resulting latex polymer is 261.7 nm.

[0067] **Comparative Example 2**

The polymerization process was similar to that of Example 1, except that the monomer solution was prepared by mixing 236.32 g vinyl acetate, 42.00 g butyl acrylate, 1.68 g acrylamide, 56.00 g of water, 3.23 g of SOPROPHOR® FD, 2.00 g of ABEX® AP-470 and 0.57 g of sodium acetate. The reactor was charged with 189.84 g water, 1.44 g of SOPROPHOR® FD and 3.29 g RHODASURF® BC8509.

[0068] The particle size of the resulting latex polymer is 179.4 nm.

[0069] **Preparation of coating compositions**

The latex polymers of Example 1, Comparative Example 1 and Comparative Example 2 were formulated into coating compositions and tested for scrub resistance.

[0070] The coating compositions were prepared according to the formulations in Table 1 :

Table 1

Components	Weight (g)
Grinding components	
Water	252.0
QP-30000	4.0
Dispersant	7.5
pH neutralizer	2.5
Rhodoline® 2809	2.0
Rhodoline® 681F	1.5
TiO_2	220.0
Calcined Clay	75.0
Honcal 7	80.0
Grind mix subtotal	644.5
Let-down components	
Latex polymer	290.0
Propylene glycol	15.0
Texonal	14.0
Rhodoline® 681F	1.5
Acrysol TT-935	3.0
Water	32.0
Total	1000.0

[0071] The grind components listed in Table 1 were ground for 30 minutes with a high speed mixer. The let-down components were then blended with the grind components using a low speed mixer to form the coating composition.

[0072] **Scrub resistance test**

[0073] The scrub resistance of the coating compositions was tested according to Test method B of ASTM D-2486 using a SHEEN Wet Abrasion Scrub Tester (REF 903) and LENTA SC-2 abrasive type standardized scrub medium. The coating compositions were applied with a film applicator to gloss alkyd scrub panels with a wet thickness of 100 μm. The films were dried in a climate-controlled room (50% Relative Humidity and 25 °C for 7 days before the scrub resistance test).

[0074] In the scrub resistance test, the coating composition which comprises the latex polymers of Example 1 was measured against the reference Comparative Examples. Results are reported as wet scrub resistance cycles (WSR cycles) and are also reported as a percentage of cycles to the cycles of the reference of Comparative Example. The tests were conducted in duplicate to calculate the average value.

[0075] WSR cycles are the numbers of cycles to remove one continuous thin line of coating film across the width of the shim.

[0076] WSR [% comparative example] = $\frac{WSR\ Cycles\ for\ Example\ 1}{WSR\ Cycles\ for\ comparative\ example} \times 100$

[0077] The results of scrub resistance tests for Example 1 and Comparative Example 1 are provided in Table 2.

Table 2

	Example 1	**Comparative Example 1**
WSR cycles (test 1)	3992	2036
WSR [% comparative example]	196.1	100
WSR cycles (test 2)	4605	2467
WSR [% comparative example]	186.7	100
WSR Average [% comparative example]	191.3	100

[0078] The result in Table 2 illustrates that the coating composition comprising the latex polymers of Example 1 with the incorporation of the inventive ethoxylated tristyrylphenol phosphate ester, exhibits enhanced scrub resistance compared to Comparative Example 1 in which the latex polymer was prepared by using an aliphatic phosphate ester.

[0079] The coating composition comprising the latex polymers of Example 1 was measured against Comparative Example 2. Results are reported as wet scrub resistance cycles (WSR cycles) and are also reported as a percentage of cycles to the cycles of the reference of comparative example.

[0080] The results of scrub resistance tests for Example 1 and Comparative example 2 are provided in Table 3.

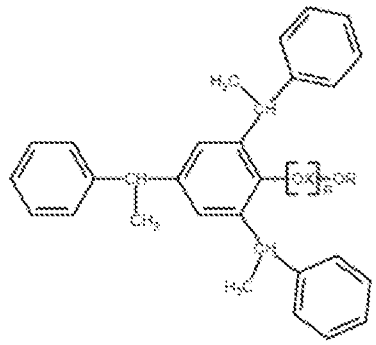
Table 3

	Example 1	**Comparative Example 2**
WSR cycles (test 1)	3709	2956
WSR [% comparative example]	125.5	100
WSR cycles (test 2)	2958	2280
WSR [% comparative example]	129.7	100
WSR Average [% comparative example]	127.6	100

[0081] The result in Table 3 illustrates that the coating composition comprising the latex polymers of Example 1 with the incorporation of the inventive ethoxylated tristyrylphenol phosphate ester exhibits enhanced scrub resistance compared to Comparative Example 2 in which the latex polymer was prepared by using an ethoxylated tristyrylphenol sulfate ester.

Claims

1. A method for improving scrub resistance of a coating composition comprising a step of adding an alkoxylated tristyrylphenol compound in said coating composition, wherein the alkoxylated tristyrylphenol compound has the general formula of (I) :

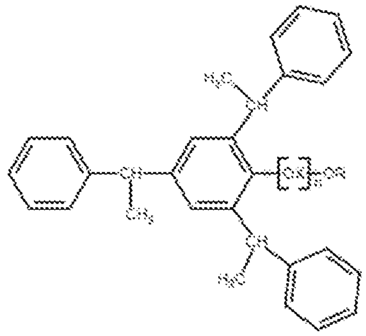


(I)

wherein n is an integer of from 1 to 100; R is -($H_2PO_3^- M^+$); M^+ is a cation; and X is C_2H_4, C_3H_6, or C_4H_8.
2. The method according to claim 1, wherein X is C_2H_4.
3. The method according to claim 1, wherein M^+ is selected from the group consisting of H^+, Na^+, NH_4^+, K^+, Li^+ and $-N(R_1)_4^+$, wherein R_1 is a H or a C_1-C_6 alkyl or hydroxyalkyl group and at least one R_1 is a C_1-C_6 alkyl or hydroxyalkyl group.
4. The method according to any one of claims 1 to 3, wherein M^+ is Na^+, NH_4^+, K^+, a tetramethylammonium group or a triethanol ammonium group.
5. The method according to any one of claims 1 to 4, wherein n is an integer of from 5 to 30.
6. The method according to any one of claims 1 to 5, wherein the coating composition is an aqueous coating composition.
7. The method according to any one of claims 1 to 6, wherein the coating composition comprises a vinyl acetate-acrylic co-polymer or a vinyl acetate-ethylene-acrylic co-polymer.
8. The method according to claim 7, wherein the vinyl acetate-acrylic co-polymer comprises 10 to 30 by weight of an acrylic monomer and 70 to 90 by weight of a vinyl acetate monomer; and wherein the vinyl acetate-ethylene-acrylic

co-polymer comprises 5 to 25 by weight of an ethylene monomer and 75 to 95 by weight of a vinyl acetate monomer.

9. The method according to claim 7 or 8, the vinyl acetate-acrylic co-polymer or the vinyl acetate-ethylene-acrylic co-polymer further comprise one or more co-monomers.
10. The method according to claim 9, wherein the co-monomer is selected from the group consisting of styrene, methyl styrene, vinyl chloride, acrylonitrile, methacrylonitrile, ureido methacrylate, vinyl esters of branched tertiary monocarboxylic acids, itaconic acid, crotonic acid, maleic acid, fumaric acid, vinyl ether, acrylamide, acrylonitrile and unsaturated carboxylic acid and C_1-C_{12} esters of (meth)acrylic acid.
11. The method according to any one of claims 1 to 10, wherein the coating composition contains the alkoxylated tristyrylphenol compound in an amount of from 0.5% to 7.5% by weight of the latex polymers.
12. The method according to any one of claims 1 to 11, wherein the coating composition further comprises at least one auxiliary component selected from the group consisting of wetting agent, dispersants, emulsifiers, fillers, thickeners, antifoams, pigments, preservatives and biocide.
13. The method according to any one of claims 1 to 12, wherein the alkoxylate tristyrylphenol compound is employed as an emulsifier during emulsion polymerization to form a latex polymer.
14. The method according to any one of claims 1 to 13, wherein the alkoxylated tristyrylphenol compound is employed as an additive to an already formed dispersion of at least one latex polymer or an already formed coating composition.
15. Use of an alkoxylated tristyrylphenol compound in a coating composition for improving scrub resistance, wherein the alkoxylated tristyrylphenol compound has the general formula (I) :



(I)

wherein n is an integer of from 1 to 100; R is -($H_2PO_3^-$ M^+), M^+ is a cation and X is C_2H_4, C_3H_6, or C_4H_8.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2018/121666

A. CLASSIFICATION OF SUBJECT MATTER

C07C 43/20(2006.01)i

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)

C07C43/-

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)

CNABS,DWPI,SIPOABS,CNTXT:scrub, tristyrylphenol, resistance, alkoxylat+, compound, VOC, coating

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	CN 106715664 A (UNILEVER PLC) 24 May 2017 (2017-05-24) paragraghs 8-14	1-15
A	CN 107075412 A (UNILEVER PLC) 18 August 2017 (2017-08-18) paragraghs 6-17	1-15
A	WO 2014167375 A1 (SERVICES PETROLIERS SCHLUMBERGER ET AL.) 16 October 2014 (2014-10-16) paragraghs 10-18	1-15

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 March 2019	**15 March 2019**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2018/121666

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International application No.
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