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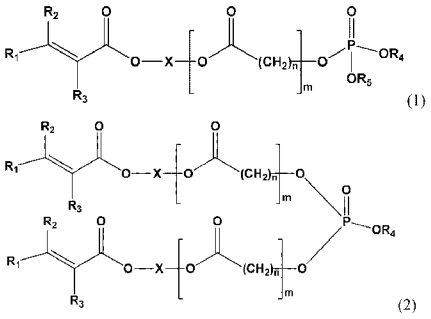
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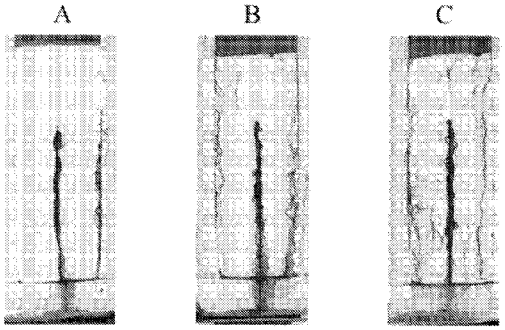
(54) Title: COATING COMPOSITIONS WITH IMPROVED PERFORMANCE



(1)

(2)

FIGURE 1



(57) Abstract: A coating composition comprising a latex polymer is described, where the latex polymer (i.e., an aqueous polymer dispersion) is formed from monomers comprising, consisting essentially of, or consisting of a monomer of Formula (1) and a monomer of Formula (2) as defined, wherein a molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:99 to 99:1. Also described is a substrate coated by the coating composition and a process for preparing the latex polymer.

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COATING COMPOSITIONS WITH IMPROVED PERFORMANCE

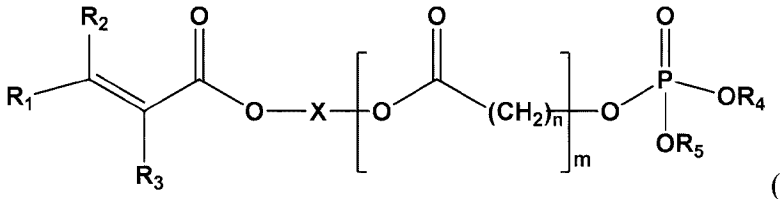
BACKGROUND OF THE INVENTION

Phosphate monomers have been described as functional monomers in the preparation of latex polymers to increase the coating performance (e.g., US 4647638, US6710161, US8318848, US7081488, US9273221, US9303160, and US20210347979). However, the potential impact on such performance due to variations in the spacing between the ethylenically unsaturated group on one end of the phosphate monomer and the phosphate moiety on the other end of the monomer has generally not been reported.

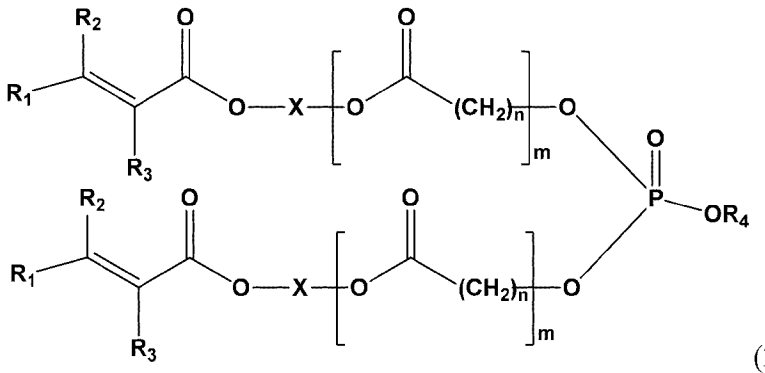
In the present invention, it was unexpectedly discovered that altering the spacing between an ethylenically unsaturated group on one end of the phosphate monomer and the phosphate moiety on the other end of the monomer resulted in enhanced coating performance on substrates, such as metal substrates. Such improved performance increases the durability and service life of substrates containing such coating compositions.

SUMMARY OF THE INVENTION

An aspect of the invention is a coating composition comprising a latex polymer (i.e., an aqueous polymer dispersion) formed from monomers comprising, consisting essentially of, or consisting of a monomer of Formula (1) and a monomer of Formula (2)



(1)



(2)

wherein in Formula (1) and Formula (2):

each R_1 is independently H or C_1-C_6 alkyl;

each R_2 is independently H or C_1-C_6 alkyl;

each R_3 is independently H or C_1-C_6 alkyl;

each X is independently C_1-C_6 alkylene, where a N, O or S atom may be inserted between any two carbon atoms present in the alkylene chain and where carbon atoms in the alkylene chain may be substituted with a C_1-C_3 alkyl group;

each R_4 is independently H or a cation;

each R_5 is independently H or a cation;

each n is independently 4 to 7; and

each m is independently 1 to 10,

wherein a molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:99 to 99:1.

Another aspect of the invention is a substrate comprising a coating composition as described herein, on at least one surface of the substrate.

Another aspect of the invention is a method of increasing adhesion and/or corrosion resistance and/or scrub resistance and/or water resistance of a coating composition applied to at least one surface of a substrate, the method comprising adding to the coating composition a latex polymer formed from monomers comprising, consisting essentially of, or consisting of a monomer of Formula (1) and a monomer of Formula (2) as described herein, where the molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:99 to 99:1.

Another aspect of the invention is a method for increasing corrosion resistance and/or scrub resistance and/or water resistance of at least one surface of a substrate, the method comprising adding to the at least one surface a coating composition as described herein.

Another aspect of the invention is the use of a coating composition as described herein for increasing corrosion resistance and/or scrub resistance and/or water resistance on at least one surface of a substrate.

Another aspect of the invention is the use of a latex polymer as a component in a coating composition for increasing corrosion resistance and/or scrub resistance and/or water resistance on at least one surface of a substrate to which the coating composition is applied, wherein the latex polymer is formed from monomers comprising a monomer of Formula (1) and a monomer of Formula (2) as described herein, where the molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:99 to 99:1.

Another aspect of the invention is a method for preparing the latex polymer as described herein, the method comprising:

reacting by emulsion polymerization at a temperature of 50 to 110 °C a mixture of the monomer of Formula (1) and the monomer of Formula (2) where a molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:99 to 99:1, and optionally at least one ethylenically unsaturated monomer not containing a phosphorus moiety, in a reactor in the presence of water and optionally one or more of a base and an anionic surfactant, where the reaction is maintained at a pH of 3-9 and where the obtained latex polymer has a solids content of at least 10 wt%.

BRIEF DESCRIPTION OF THE DRAWINGS

The following figure represents a particular embodiment of the invention and is not intended to otherwise limit the scope of the invention as described herein.

The **FIGURE** illustrates the salt fog test results for (A) the inventive DTM paint, (B) comparative DTM paint 1, and (C) comparative DTM paint 2.

DETAILED DESCRIPTION OF THE INVENTION

The term “(meth)acrylate group” refers to an acrylate group or a methacrylate group. An acrylate group corresponds to a group of the formula -O-C(=O)-CH=CH_2. A methacrylate group corresponds to a group of the formula -O-C(=O)-C(CH_3)=CH_2.

The term "monofunctional" refers to a compound having a single functional group. For example, a monofunctional (meth)acrylate monomer is a monomer having a single (meth)acrylate group.

The term "monomer" refers to a molecule with one or more polymerizable functional groups. The monomer has a single molecular weight, typically below 1000 g/mol, preferably 100

to 950 g/mol. As is generally recognized in the field, commercial products of a particular monomer may contain impurities or other chemical species.

The term "number-average molecular weight" or "M_n" refers to the statistical average molecular weight of the polymer chains in a sample or grouping. Number-average molecular weights reported herein are determined using a size exclusion chromatography (SEC) unless expressly noted otherwise.

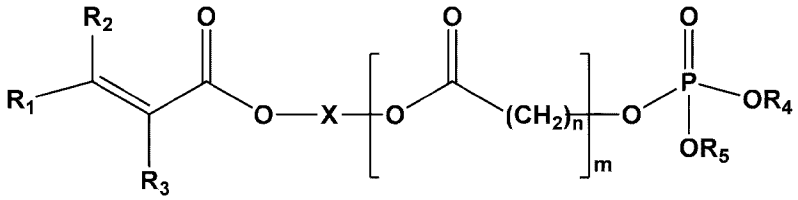
The term "oligomer" refers to molecules with a distribution of molecular weights and may or may not have one or more polymerizable functional groups. An oligomer may be the reaction product of two or more monomers and typically has a number averaged molecular weight greater than or equal to 500 g/mol, preferably 500 g/mol to 30,000 g/mol, more preferably 1,000 g/mol to 8,000 g/mol. An oligomer may not always have a single molecular weight.

The term "optionally substituted group" means that one or more hydrogen atoms of the group may independently be replaced by a substituent selected from alkyl, cycloalkyl, aryl, heteroaryl, alkoxy, alkylaryl, haloalkyl, hydroxy, halogen, isocyanate, nitrile, amine, oxo (=O), carboxylic acid, -C(=O)-R', -C(=O)-OR', -C(=O)NH-R', -NH-C(=O)R', -O-C(=O)-NH-R', -NH-C(=O)-O-R', -C(=O)-O-C(=O)-R' and -SO_2-NH-R', each R' being independently an optionally substituted group selected from alkyl, aryl, and alkylaryl.

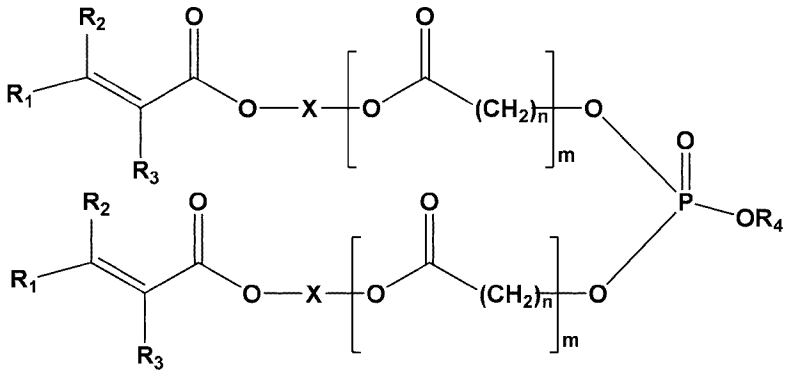
The term "wt%" means weight percentage. Unless otherwise mentioned, the weight percentages of a compound or component of a composition are expressed relative to the weight of the composition.

Monomers

The latex polymer of the invention is formed from (i.e., it comprises polymerized units derived from) monomers that comprise a monomer of Formula (1) and a monomer of Formula (2)



(1)



(2)

wherein:

each R_1 is independently H or C_1-C_6 alkyl;

each R_2 is independently H or C_1-C_6 alkyl;

each R_3 is independently H or C_1-C_6 alkyl;

each X is independently C_1-C_6 alkylene, where a N, O or S atom may be inserted between any two carbon atoms present in the alkylene chain, where carbon atoms in the alkylene chain may be substituted with a C_1-C_3 alkyl group;

each R_4 is independently H or a cation;

each R_5 is independently H or a cation;

each n is independently 4 to 7;

each m is independently 1 to 10.

In an embodiment, the molar ratio of the monomer of Formula (1) to the monomer of Formula (2) ranges from 1:9 to 9:1, such as 1:4 to 4:1, such as 3:7 to 7:3, such as 2:3 to 3:2, such as 1:1. In another embodiment, the monomer of Formula (1) is present in a greater molar amount than the monomer of Formula (2). In another embodiment, the molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is at least 1.0:1, such as at least 1.1:1, such as at least 1.2:1, such as at least 1.3:1, such as at least 1.4:1, such as at least 1.5:1, such as at least 1.6:1,

such as at least 1.7:1, such as at least 1.8:1, such as at least 1.9:1, such as at least 2.0:1, such as at least 2.2:1, such as at least 2.5:1, such as at least 3.0:1, such as at least 3.5:1, such as from 1.1:1 to 3.5:1, such as from 1.1:1 to 2.5:1, such as from 1.1:1 to 2.0:1, such as from 1.1:1 to 1.9:1, such as from 1.2:1 to 3.5:1, such as from 1.2:1 to 2.5:1, such as from 1.2:1 to 2.0:1, such as from 1.2:1 to 1.7:1, such as from 1.3:1 to 3.5:1, such as from 1.3:1 to 2.5:1, such as from 1.3:1 to 2.0:1, such as from 1.3:1 to 1.7:1, such as from 1.4:1 to 3.5:1, such as from 1.4:1 to 2.5:1, such as from 1.4:1 to 2.0:1, such as from 1.4:1 to 1.7:1, such as from 1.5:1 to 3.5:1, such as from 1.5:1 to 3.0:1.

In Formula (1) and (2), each R_1 is independently H or C_1-C_6 alkyl. In a preferred embodiment, each R_1 is H.

In Formula (1) and (2), each R_2 is independently H or C_1-C_6 alkyl. In a preferred embodiment, each R_2 is H.

In Formula (1) and Formula (2), each R_3 is independently H or C_1-C_6 alkyl. In a preferred embodiment, each R_3 is H or methyl.

In Formula (1) and Formula (2), each X is independently C_1-C_6 alkylene, where a N, O or S atom may be inserted between any two carbon atoms present in the alkylene chain. In a preferred embodiment each X is selected from the following Formula (5) or Formula (6):

$$-(CR_6R'_6)_e- \quad (5)$$

$$-[(CR_7R'_7)_f-O]_g-(CR_7R'_7)_h- \quad (6)$$

wherein:

R_6 and R'_6 are independently H or C_1-C_3 alkyl;

each R_7 and R'_7 is independently H or methyl;

e is an integer from 1 to 6;

f is an integer from 1 to 4;

g is an integer from 1 to 3;

h is an integer from 1 to 4; and

$f + g + h \leq 6$.

In Formula (1) and Formula (2), R_4 and R_5 are independently H or a cation. Examples of suitable cations include a metal (e.g., Na^+, Li^+, K^+, Ca^{2+}, Ba^{2+}, etc.), an ammonium group (NH_4^+), a primary ammonium group (RNH_3^+), a secondary ammonium group ($(R)_2NH_2^+$), or a tertiary ammonium group ($(R)_3NH^+$) where each R is independently a non-hydrogen moiety (e.g., alkyl, heterocyclyl, aryl, heteroaryl, and the like).

In an embodiment, each R_4 and R_5 for the monomer of Formula (1) and R_4 for the monomer of Formula (2) is independently selected from an ammonium group (NH_4^+), a primary ammonium group (RNH_3^+), a secondary ammonium group ($(R)_2NH_2^+$), a tertiary ammonium group ($(R)_3NH^+$) where each R is independently a non-hydrogen moiety (e.g., alkyl, heterocyclyl, aryl, heteroaryl, and the like), and a metal (e.g., Na^+, Li^+, K^+, Ca^{2+}, Ba^{2+}, etc.). In an embodiment, at least one of R_4 and R_5 is an ammonium group. In another embodiment, at least one of R_4 and R_5 is a metal. In another embodiment, both R_4 and R_5 are ammonium groups. In another embodiment, both R_4 and R_5 are metals.

In formula (1) and (2), each n is independently 4 to 7. In a preferred embodiment, each n is 5.

In formula (1) and (2), each m is independently 1 to 10. In a preferred embodiment, each m is 1 or 2.

In an embodiment of the monomer of Formula (1), n is 5 and m is 1 to 4.

In an embodiment of the monomer of Formula (1), n is 5 and m is 1 or 2.

In an embodiment of the monomer of Formula (2), each n is 5 and each m is the same and is 1 to 4.

In an embodiment of the monomer of Formula (2), each n is 5 and each m is the same and is 1 or 2.

In an embodiment of the monomer of Formula (1), n is 5, m is 1 to 4 and X is $-CH_2-CH_2-$.

In an embodiment of the monomer of Formula (1), n is 5, m is 1 or 2 and X is $-CH_2-CH_2-$.

In an embodiment of the monomer of Formula (2), each n is 5, each m is the same and is 1 to 4 and X is $-CH_2-CH_2-$.

In an embodiment of the monomer of Formula (2), each n is 5, each m is the same and is 1 or 2 and each X is $-CH_2-CH_2-$.

In an embodiment of the monomer of Formula (1), n is 5, m is 2 and X is $-CH_2-CH_2-$.

In an embodiment of the monomer of Formula (2), each n is 5, each m is 2 and each X is $-CH_2-CH_2-$.

In an embodiment of the invention, the two (meth)acrylate substituents of Formula (2) are identical to each other.

In an embodiment of the invention, the (meth)acrylate substituent of Formula (1) and the two (meth)acrylate substituents of Formula (2) are identical.

Other than the required presence of a monomer of Formula (1) and Formula (2), other monomers may be used to form the latex polymer. The latex polymer of the invention may be formed from (i.e., it may comprise polymerized units derived from) monomers that comprise one or more ethylenically unsaturated monomers not containing a phosphorus moiety.

The other monomers are not particularly limited and may include one, two, three, or four or more ethylenically unsaturated compounds containing at least one polymerizable carbon-carbon double bond, i.e., a carbon-carbon double bond capable of participating in a free radical polymerization reaction or anionic polymerization reaction, such as a polymerization reaction initiated by persulfates, peroxides, azo-containing compounds or other conventional radical initiators.

As used herein, the term "(meth)acrylate" refers to both acrylate and methacrylate functionalized compounds. In various embodiments, a (meth)acrylate-functionalized compound may contain one, two, three, four, five or more (meth)acrylate functional groups per molecule. Any of the (meth)acrylate-functionalized compounds listed below may, for example, be employed in the latex polymer of the invention.

Suitable ethylenically unsaturated monomers include vinyl acetate, (meth)acrylamide and/or derivatives thereof (e.g., hydroxymethyl)acrylamide, N-(hydroxyethyl) acrylamide, 2-hydroxypropyl methacrylamide, methacrylamide poly(ethylene glycol) amine hydrochloride, N-tris(hydroxymethyl)methylacrylamide, (4-hydroxyphenyl)methacrylamide, 2-aminoethylmethacrylamide hydrochloride, and N-phenylacrylamide), various C_1-C_{30} alkyl esters

of (meth)acrylic acid (e.g., methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-octyl (meth)acrylate, n-decyl (meth)acrylate, n-dodecyl (meth)acrylate, tetradecyl (meth)acrylate, lauryl (meth)acrylate, oleyl (meth)acrylate, palmityl (meth)acrylate, and stearyl (meth)acrylate), isobornyl (meth)acrylate, benzyl (meth)acrylate, phenyl (meth)acrylate, 2-phenylethyl (meth)acrylate, 1-naphthyl (meth)acrylate, ethoxyethyl (meth)acrylate, ethyl maleate, dimethyl fumarate, ethyl methyl itaconate, (meth)acrylic acid, itaconic acid, fumaric acid, maleic acid, styrene, α-methyl styrene, vinyl toluene, divinyl toluene, vinyl naphthalene, caprolactone (meth)acrylate, diethylene glycol methyl ether (meth)acrylate, diethylene glycol ethyl ether (meth)acrylate, diethylene glycol butyl ether (meth)acrylate, triethylene glycol methyl ether (meth)acrylate, polyethylene glycol (meth)acrylate, poly(propylene glycol) (meth)acrylate, crosslinker monomers include but not limited to divinyl naphthalene, allyl (meth)acrylate, tripropylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, ethylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,2-butylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,4-butylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, dodecyl di(meth)acrylate, cyclohexane dimethanol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tricyclodecane dimethanol diacrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, diallyl phthalate, trimethylolpropane tri(meth)acrylate, triethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, and combinations thereof.

Other suitable optional monomers include acrylonitrile, vinyl cyanide, vinylpyrrolidone, polypropylene glycol mono(meth)acrylate, polyethylene glycol mono(meth)acrylate, sulfur-based monomers (e.g., vinyl- and allyl- sulfonic and sulfuric acids, sulfoethyl (meth)acrylate, aryl- sulfonic and sulfuric acids, (meth)acrylamidoethane- sulfonic and sulfuric acids, methacrylamido-2-methyl propane- sulfonic and sulfuric acids, and salts (e.g., alkali metal or ammonium salts) of these sulfonic and sulfuric acids), hydroxyl functionalized co-monomers (e.g., 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate), silane co-monomers (e.g., methacryloxypropyl trimethoxysilane, methacryloxypropyl triethoxysilane, methacryloxypropyl tripropoxysilane, vinyltriacetoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane), crosslinkable co-monomers capable of reacting with a separate crosslinking agent (e.g., acetoacetate co-monomers containing (meth)acrylate,

allyl or vinyl functional groups including, but not limited to, acetoacetate moieties such as: 2-acetoacetoxyethyl (meth)acrylate, 3-acetoacetoxypropyl (meth)acrylate, 4-acetoacetoxybutyl (meth)acrylate, 2-cyanoacetoxyethyl (meth)acrylate, 3-cyanoacetoxypropyl (meth)acrylate, 4-cyanoacetoxybutyl (meth)acrylate, N-(2-acetoacetoxyethyl) (meth)acrylamide, allyl acetoacetate, 2,3-di(acetoacetoxy)propyl (meth)acrylate, vinyl acetoacetate and combinations thereof.

Preferred crosslinkable monomers include acetoacetoxyethyl methacrylate and diacetone acrylamide. Water soluble crosslinking agents capable of reacting with moieties of these crosslinkable co-monomers may also be included in composition. For example, crosslinking agents containing at least two hydrazine and/or hydrazide groups may be included in certain embodiments of the one-part aqueous composition. Such crosslinking agents are preferably water soluble. Non-limiting examples of suitable crosslinking agents include one or more of oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide (ADH), sebacic acid dihydrazide, maleic acid dihydrazide, fumaric acid dihydrazide and itaconic acid dihydrazide. Adipic acid dihydrazide is a preferred water-soluble cross-linking agent for use in the compositions as described herein, especially those produced from monomer compositions containing diacetone acrylamide (DAAM). Other suitable water-soluble cross-linking agents are compounds which contain at least two amine functional moieties such as ethylene diamine and hexamethylene diamine. Such cross-linking agents are preferred in combination with polymers comprising 1,3- dicarbonyl groups as the crosslinkable moiety, such as acetoacetoxyethyl methacrylate (AAEM).

The relative proportions of ethylenically unsaturated compounds utilized to form the latex polymer of the invention may be varied as appropriate depending upon the particular components selected and the properties of the coating composition obtained therefrom which are desired.

Suitable (meth)acrylate-functionalized oligomers include, for example, polyester (meth)acrylates, polyether (meth)acrylates, epoxy (meth)acrylates, urethane (meth)acrylates (also referred to as polyurethane (meth)acrylates or urethane (meth)acrylate oligomers) and combinations thereof, as well as amine-modified and sulfide-modified variations thereof.

Examples of suitable epoxy (meth)acrylate oligomers include the reaction products of acrylic or methacrylic acid or mixtures thereof with glycidyl ethers or esters. For example, the

glycidyl ether may be a polyglycidyl ether of a bisphenol such as bisphenol A or oligomer thereof.

Suitable polyether (meth)acrylate oligomers include, but are not limited to, the condensation reaction products of acrylic or methacrylic acid or mixtures thereof with polyetherols which are polyether polyols (such as polyethylene glycol, polypropylene glycol or polytetramethylene glycol). Suitable polyetherols can be linear or branched compounds containing ether bonds and terminal hydroxyl groups. Polyetherols can be prepared by ring opening polymerization of cyclic ethers such as tetrahydrofuran or alkylene oxides with a starter molecule. Suitable starter molecules include, but are not limited to, water, polyhydroxyl functional compounds, polyester polyols and amines.

Suitable polyurethane (meth)acrylate oligomers may be prepared by reacting aliphatic and/or aromatic diisocyanates with OH-group terminated polyester polyols (including aromatic, aliphatic and mixed aliphatic/aromatic polyester polyols), polyether polyols, polycarbonate polyols, polycaprolactone polyols, polyorganosiloxane polyols (*e.g.,* polydimethylsiloxane polyols), or polydiene polyols (*e.g.,* polybutadiene polyols), or combinations thereof to form isocyanate-functionalized oligomers which are then reacted with hydroxyl-functionalized (meth)acrylates such as hydroxyethyl acrylate or hydroxyethyl methacrylate to provide terminal (meth)acrylate groups. For example, the polyurethane (meth)acrylate oligomers may contain two, three, four or more (meth)acrylate functional groups per molecule.

Latex Polymer

The present invention relates to coating compositions containing latex polymers (i.e., aqueous polymer dispersions). The latex polymer comprises polymer particles dispersed in an aqueous phase, where the aqueous phase is a liquid comprising, consisting essentially of, or consisting of water. In an embodiment, the liquid may further comprise organic solvents, such as, for example, ethanol. However, the aqueous phase is preferably substantially free of organic solvents, i.e., contains less than 5 wt%, such as less than 3 wt%, such as less than 1 wt%, such as 0 wt% of organic solvents relative to the total weight of the aqueous phase of the coating composition.

The latex polymer is prepared by any process which provides copolymerization of ethylenically unsaturated monomers. Suitable processes include, but are not limited to,

suspension or emulsion polymerization. The polymer in particle form may also be prepared by solution polymerization techniques followed by the conversion of the solution polymer to polymer particles by conventional methods known in the art. In an embodiment, polymerization is carried out in the presence of water or an organic solvent. Various synthesis adjuvants such as initiators, chain transfer agents, and surfactants are optionally utilized in the polymerization. In a preferred embodiment, the polymer particles of the latex are prepared by aqueous emulsion polymerization techniques well known in the art (Emulsion Polymerization: Theory and Practice" by D. C. Blackley published by Wiley in 1975; Emulsion Polymerization by F. A. Bovey et al. published by Interscience Publishers in 1965; Emulsion Polymerization and Emulsion Polymers by P.A. Lovell et al. published by Wiley Science in 1997; and Biomacromolecules (2020) 21(11), 4396–4441).

The latex polymer is formed from (i.e., it comprises polymerized units derived from) monomers that comprise the monomer of Formula (1), the monomer of Formula (2) and optionally one or more other monomers as defined above.

In an embodiment, the latex polymer is formed from the monomer of Formula (1), the monomer of Formula (2) and one or more ethylenically unsaturated monomers selected from methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, n-octyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, itaconic acid, methacrylic acid and acrylic acid, preferably from methyl methacrylate, ethyl acrylate, butyl acrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, methacrylic acid and acrylic acid.

In an embodiment, the amount of the combination of the monomers of Formula (1) and Formula (2) ranges from 0.01 to 20 wt%, such as from 0.01 to 15 wt%, such as from 0.01 to 10 wt%, preferably from 0.1 to 15 wt%, most preferably from 0.1 to 10 wt%, such as from 1 to 15 wt%, such as from 1 to 10 wt%, such as 5 to 15 wt% relative to the total weight of the monomers used to form the latex polymer.

In an embodiment, the amount of any ethylenically unsaturated monomers that are also present during formation of the latex polymer (other than the monomer of Formula (1) and the

monomer of Formula (2)) ranges from 80 to 99.99 wt%, such as from 80 to 99.9 wt%, such as from 85 to 99.8 wt%, such as from 90 to 99.8 wt%, such as from 95 to 99.5 wt% relative to the total weight of the monomers used to form the latex polymer.

In an embodiment, the solids content of the latex polymer ranges from 10 to 80 wt%, such as from 20 to 70 wt%, such as from 30 to 65 wt%, such as from 35 to 65 wt%, such as at least 10 wt%, preferably such as at least 20 wt%. In an embodiment, the latex polymer contains at least 20 wt% water, such as at least 40 wt% water, such as at least 50 wt% water, such as at least 60 wt% water, such as at least 70 wt% water, such as at least 80 wt% water.

The mixture of components used to form the latex polymer may further comprise one or more, such as two or more, such as three or more of a surfactant, an initiator, a chain transfer agent and a buffer.

The mixture of components used to form the latex polymer may comprise at least one, such as least two or more surfactants. The surfactant may be a compound having both a hydrophilic and a hydrophobic portion that is able to form micelles of the monomer components. The surfactant may act as a stabilizer during and/or after the emulsion polymerization.

The surfactant may be selected from an anionic surfactant, a non-ionic surfactant and mixtures thereof, preferably a mixture of an anionic surfactant and a non-ionic surfactant. Examples of preferred surfactants include, but are not limited to an alkyl sulfate, an alkyl ether sulfate, an alkyl sulfonate, an alkyl benzenesulfonate, an optionally substituted diphenyl oxide disulfonate, an optionally ethoxylated sulfosuccinate mono- or diester, a phosphonate mono- or diester, a phosphate mono- or diester, an ethoxylated fatty alcohol, an optionally ethoxylated fatty acid, an ethoxy-propoxy copolymer (EO-PO copolymer), salts thereof, and mixtures thereof. A list of suitable surfactants is available in the book "Surfactants and Polymers in Aqueous solutions" (Holmberg et al., 2002, John Wiley & Sons). The surfactant may be a polymerizable surfactant, preferably a mixture of a polymerizable anionic surfactant and a polymerizable non-ionic surfactant.

Examples of suitable alkyl sulfates and alkyl ether sulfates are optionally ethoxylated C6-C22 fatty alcohol sulfates, such as decyl sulfate, lauryl sulfate (like Disponil® SLS), stearyl sulfate, C12-C14 fatty alcohol ether sulfate with 2 to 50 EO units (like Disponil® FES 77, Disponil® FES 27, Disponil® FES 993, Disponil® FES 32, Rhodapex LA 120s).

Examples of suitable alkyl sulfonates are C6-C22 fatty alcohol sulfonates such as decyl sulfonate, lauryl sulfonate and stearyl sulfonate.

Examples of suitable alkyl benzenesulfonates are benzene sulfonates substituted with a linear or branched C6-C22 alkyl group such as sodium dodecylbenzene sulfonate (like POLYSTEP® A-16-22 or Rhodacal® DS-4).

An example of a suitable diphenyl oxide disulfonate is sodium dodecyl diphenyl oxide disulfonate (like Dowfax® 2A1, Calfax® DB45).

Examples of suitable ethoxylated fatty alcohols are ethoxylated C6-C22 fatty alcohols with EO degree of 2 to 50, such as C12-C14 alcohol ethoxylates with EO degree of 2 to 50 (like Disponil® A 3065, Polirol® AL 1065, Rhodasurf® 3065), C12-C14 secondary alcohol ethoxylates, with EO degree of 2 to 50 (like Tergitol® 15-S-20), C13 alcohol ethoxylates with EO degree of 2 to 50 (like Emulan® TO 4070, Emulan® TO 2080 and Polirol® AL 1328), C16-C18 alcohol ethoxylates with EO degree of 2 to 100 (like Empilan® KM 80).

Examples of suitable sulfosuccinate mono- or diesters are optionally ethoxylated C6-C20 alkyl monoesters or diesters of sulfosuccinic acid (like Aerosol® A-102, Aerosol® MA-80, Aerosol® GPG).

Examples of suitable phosphate mono- or diesters are optionally alkoxylated alkyl phosphate monoester-diacids or salts, optionally alkoxylated alkyl diphosphate diester-monoacids or salts or mixtures thereof (like Rhodafac® Rs 410, Rhodafac® Rs 610 Rhodafac® Rs 710, Rhodafac® Rs 960).

Examples of suitable polymerizable surfactants are Polyoxyethylene 9-octadecenyl ether phosphate (XIV, Maxemul® 6106), an ethylenically unsaturated phosphate ester (like Maxemul® 6112) an allyl nonyl phenol ethoxylated sulphate (like respectively Hitenol® AR or BC series) or a polyoxyalkylene alkenyl ether sulfate (like Hitenol® KH series, Reasoap® SR or SE series, Latemul® PD series).

In one embodiment, the surfactant is a mixture of an optionally ethoxylated sulfosuccinate mono- or diester and an ethoxylated fatty alcohol. In another embodiment, the surfactant is a mixture of an alkyl ether sulfate, a diphenyl oxide disulfonate and an optionally ethoxylated sulfosuccinate mono- or diester. In another embodiment, the surfactant is a mixture

of a phosphate mono- or diester and at least one of the following surfactants: an alkyl ether sulfate, an optionally ethoxylated sulfosuccinate mono- or diester and mixtures thereof as described in WO 2018/184852. In another embodiment, the surfactant is a mixture of a diphenyl oxide disulfonate and an ethoxylated fatty alcohol (such as C13 alcohol ethoxylates with EO degree of 2 to 50 and/or C16-C18 alcohol ethoxylates, with EO degree of 2 to 100).

The total amount of surfactant may be from 0.01 to 15 wt%, such as from 0.05 to 10 wt%, such as from 0.1 to 5 wt%, relative to the total weight of the monomers used to form the latex polymer.

The mixture of components used to form the latex polymer may comprise at least one initiator, such as at least two or more initiators.

The initiator may comprise a water-soluble free radical initiator. Such initiators are well known in the art and include, for example, peroxides as described above for the post-polymerization treatment, especially inorganic persulfate compounds such as ammonium persulfate, potassium persulfate and sodium persulfate; hydrogen peroxide; organic hydroperoxides such as cumene hydroperoxide, t-butyl hydroperoxide, acetyl peroxide, benzoyl peroxide, lauroyl peroxide; peracetic acid and perbenzoic acid; redox systems comprising a peroxide and a reducing agent (such as ferrous compounds, carboxylic acids and/or sodium metabisulfite), which promote the decomposition of the peroxide; as well as other free radical producing materials such as an azo-initiator, for example 2,2'-azobisisobutyronitrile, 4,4'-azobis(4-cyanovaleric acid) or 2,2'-azobis(2-methylbutyronitrile); and combinations thereof.

In one embodiment, the initiator comprises a peroxide, in particular an inorganic persulfate compound such as ammonium persulfate, potassium persulfate, sodium persulfate and mixtures thereof. More particularly, the initiator may be sodium persulfate.

In another embodiment, the initiator comprises a redox system comprising a peroxide and a reducing agent selected from polyunsaturated carboxylic acids, hydroxylated carboxylic acids and mixtures thereof.

The total amount of initiator may be from 0.01 to 5 wt%, such as from 0.1 to 3 wt%, such as from 0.2 to 2 wt%, relative to the total weight of the monomers used to form latex polymer.

The mixture of components used to form the latex polymer may further comprise at least one, such as at least two or more chain transfer agents.

The chain transfer agent may be a compound able to react with a growing polymer chain to form a "dead" polymer with the concurrent formation of a new center for polymer growth. Chain transfer agents are also referred to as molecular weight modifiers as they are used to control the molecular weight of the polymer chain. Suitable chain transfer agents are well known in the art and include, for example, thiols such as n-dodecyl mercaptan, tert-dodecyl mercaptan, iso-octyl 3-mercaptopropionate, iso-octyl mercaptoacetate and 2-ethylhexyl thioglycolate; halocarbons such as carbon tetrachloride and carbon tetrabromide. In one embodiment, the mixture of monomers comprises a chain transfer agent comprising a thiol group, more particularly a chain transfer agent selected from n-dodecyl mercaptan, tert-dodecyl mercaptan, iso-octyl 3-mercaptopropionate, iso-octyl mercaptoacetate or 2-ethylhexyl thioglycolate. Even more particularly, the chain transfer agent may be n-dodecyl mercaptan or tert-dodecyl mercaptan,

In an embodiment, the mixture of components used to form the latex polymer may comprise from 0 to 0.2 wt%, such as from 0 to 0.15 wt%, such as from 0 to 0.1 wt%, such as from 0 to 0.05 wt%, such as from 0 to 0.02 wt%, such as from 0 to 0.01 wt%, such as from 0 to 0.005 wt%, such as from 0 to 0.002 wt%, such as from 0 to 0.001 wt%, or even 0 wt%, of at least one chain transfer agent based on the total weight of the monomers used to form the latex polymer.

The mixture of components used to form the latex polymer may comprise at least one, such as at least two or more buffers. The buffer may be a compound that controls and maintains the pH during the polymerization step in a controlled range, for example from 2 to 10, in particular 3 to 9. In particular, the buffer may be selected from ammonia, sodium bicarbonate, sodium carbonate, sodium acetate, 2-amino-2-methyl-1-propanol and sodium hydroxide.

The mixture of components used to form the latex polymer may comprise 0 to 1.0 wt%, such as from 0.01 to 0.5 wt%, of at least one buffer based on the total weight of the monomers used to form the latex polymer.

Coating Composition

The coating composition of the invention comprises, consists essentially of, or consists of the latex polymer/aqueous polymer dispersion as described herein.

The coating composition of the invention may further comprise one or more additives that include, but are not limited to, antioxidants, ultraviolet absorbers, photostabilizers, defoamers, solvents, coalescing agents, rheology modifiers, flow or leveling agents, colorants, adhesion promoters, pigments, dispersants, wetting agents, slip additives, fillers, thixotropic agents, matting agents, waxes, neutralizers, biocides, preservatives, or other various additives, including any of the additives conventionally utilized in the paint, coating, sealant or adhesive arts.

Suitable pigments include zinc oxide, antimony oxide, zirconium oxide, chromium oxide, iron oxide, lead oxide, zinc sulfide, lithopone, and forms of titanium dioxide such as anatase and rutile.

Suitable fillers include alkaline earth metal carbonates such as calcium carbonate, clay minerals, aluminosilicates such as kaolin, andalusite, kyanite, and sillimanite, alkaline earth metal sulfate such as calcium sulfate and barium sulfate, talc, aluminum stearate, diatomaceous earth, wollastonite, nepheline syenite, alumina, silica, and silicon oxide, or combinations thereof.

Suitable wetting agents include alkoxylated surfactants, silicone surfactants, sulfosuccinates and fluorinated polymers.

Suitable ultraviolet absorbers include benzophenones (such as benzophenone and hydroxybenzophenone), benzotriazoles (such as hydroxyphenyl benzotriazole), hydroxyphenyl triazines (such as oxanilide) and thioxanthone.

In an embodiment, the coating composition is present on at least one surface of a substrate, where the substrate comprises one or more of a metal, asphalt, concrete, stone, ceramic, wood, paper, paperboard, and plastic. Specific substrates include, but are not limited to, rail cars, agricultural machinery, automobile parts and surfaces, log cabins, decks, residential housing, industrial surfaces, interior surfaces, exterior surfaces, and the like. The coating compositions of the invention are especially suitable for direct to metal applications and/or architectural applications.

Prior to curing, the coating composition may be applied to a substrate surface in any known conventional manner, for example, by spraying, jetting, knife coating, roller coating, casting, drum coating, dipping, and the like and combinations thereof. Indirect application using a transfer process may also be used.

The substrate on which the coating composition is applied before curing may be any kind of substrate. Suitable substrates are detailed below.

The substrate may be a ceramic, metallic, mineral, cellulosic, animal-based or polymeric substrate. The substrate may also be a part of a human body, such as a tooth or a nail.

The substrate may be porous or substantially non-porous. The substrates may be transparent, translucent or opaque.

Examples of ceramic substrates include alumina-based ceramics and zirconia-based ceramics.

Examples of metallic substrates include titanium, gold, silver, copper, brass, steel and bronze.

Examples of mineral substates include glass, asbestos and basalt.

Examples of cellulosic substrates include plain paper or resin coated paper (e.g., polyethylene or polypropylene coated paper). There is no real limitation on the type of paper, which includes newsprint paper, magazine paper, office paper, wallpaper but also paper of higher grammage, usually referred to as boards, such as white lined chipboard, corrugated board and packaging board. Further examples of cellulosic substrates include bamboo, cotton, flax, hemp, jute, lyocell, modal, rayon, raffia, ramie and sisal.

Examples of cellulosic substrates include wool, fur, silk and leather.

Examples of polymeric substrates include polyethylene, polypropylene, polycarbonate, polyvinyl chloride, polyethylene terephthalate, polyethylene naphthalate, polylactide, polyamide, polyimide, polyacrylonitrile, polyurethane, acrylonitrile butadiene styrene.

There is no restriction on the shape of the substrate, which can be a sheet, a film, a non-woven or woven fiber mat or a three dimensional object.

The substrate may be selected from a food and beverage packaging, a pharmaceutical packaging, a textile, a medical device, a food and beverage processing equipment, a water pipe or a toy.

The cured product obtained with the process of the invention may be a coating (in particular a scratch-resistant wood coating, a concrete coating or a plastic coating), an ink, a varnish, an encapsulation or potting material, a 3D-printed article, a molded article, a sealant, an adhesive, a nail polish or a dental material.

Aspects of the Invention

Aspect 1. A coating composition comprising a latex polymer (i.e., an aqueous polymer dispersion) formed from monomers comprising, consisting essentially of, or consisting of a monomer of Formula (1) and a monomer of Formula (2) as defined herein, wherein a molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:99 to 99:1.

Aspect 2. The coating composition of Aspect 1, wherein the molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:9 to 9:1, such as 1:4 to 4:1, such as 3:7 to 7:3, such as 2:3 to 3:2, such as 1:1.

Aspect 3. The coating composition of Aspect 1 or Aspect 2, wherein the molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1.0:1, such as at least 1.1:1, such as at least 1.2:1, such as at least 1.3:1, such as at least 1.4:1, such as at least 1.5:1, such as at least 1.6:1, such as at least 1.7:1, such as at least 1.8:1, such as at least 1.9:1, such as at least 2.0:1, such as at least 2.2:1, such as at least 2.5:1, such as at least 3.0:1, such as at least 3.5:1, such as from 1.1:1 to 3.5:1, such as from 1.1:1 to 2.5:1, such as from 1.1:1 to 2.0:1, such as from 1.1:1 to 1.9:1, such as from 1.2:1 to 3.5:1, such as from 1.2:1 to 2.5:1, such as from 1.2:1 to 2.0:1, such as from 1.2:1 to 1.7:1, such as from 1.3:1 to 3.5:1, such as from 1.3:1 to 2.5:1, such as from 1.3:1 to 2.0:1, such as from 1.3:1 to 1.7:1, such as from 1.4:1 to 3.5:1, such as from 1.4:1 to 2.5:1, such as from 1.4:1 to 2.0:1, such as from 1.4:1 to 1.7:1, such as from 1.5:1 to 3.5:1, such as from 1.5:1 to 3.0:1.

Aspect 4. The coating composition of any of Aspects 1 to 3, wherein m is 1 to 4.

Aspect 5. The coating composition of any of Aspects 1 to 4, wherein for the monomer of Formula (1) and the monomer of Formula (2), n is 5.

Aspect 6. The coating composition of any of Aspects 1 to 5, wherein for the monomer of Formula (1) and the monomer of Formula (2), m is 1 to 4 and n is 5.

Aspect 7. The coating composition of any of Aspects 1 to 6, wherein for the monomer of Formula (1) and the monomer of Formula (2), m is 1 to 4, n is 5 and X is $-CH_2-CH_2-$.

Aspect 8. The coating composition of any of Aspects 1 to 7, wherein for the monomer of Formula (1) and the monomer of Formula (2), m is 1.

Aspect 9. The coating composition of any of Aspects 1 to 7, wherein for the monomer of Formula (1) and the monomer of Formula (2), m is 2.

Aspect 10. The coating composition of any of Aspects 1 to 7, wherein for the monomer of Formula (1) and the monomer of Formula (2), m is 1 and n is 5.

Aspect 11. The coating composition of any of Aspects 1 to 7, wherein for the monomer of Formula (1) and the monomer of Formula (2), m is 2 and n is 5.

Aspect 12. The coating composition of any of Aspects 1 to 7, wherein for the monomer of Formula (1) and the monomer of Formula (2), m is 1, n is 5 and X is $-CH_2-CH_2-$.

Aspect 13. The coating composition of any of Aspects 1 to 7, wherein for the monomer of Formula (1) and the monomer of Formula (2), m is 2, n is 5 and X is $-CH_2-CH_2-$.

Aspect 14. The coating composition of any of Aspects 1 to 13, wherein for the monomer of Formula (1) and the monomer of Formula (2), R_4 is an ammonium ion.

Aspect 15. The coating composition of any of Aspects 1 to 13, wherein for the monomer of Formula (1) and the monomer of Formula (2), R_4 is H.

Aspect 16. The coating composition of any of Aspects 1 to 13, wherein for the monomer of Formula (1) and the monomer of Formula (2), R_4 is Na^+, Li^+, K^+, Ca^{2+} or Ba^{2+}.

Aspect 17. The coating composition of any of Aspects 1 to 16, wherein for the monomer of Formula (1), R_5 is an ammonium ion.

Aspect 18. The coating composition of any of Aspects 1 to 16, wherein for the monomer of Formula (1), R_5 is H.

Aspect 19. The coating composition of any of Aspects 1 to 16, wherein for the monomer of Formula (1), R_5 is Na^+, Li^+, K^+, Ca^{2+} or Ba^{2+}.

Aspect 20. The coating composition of any of Aspects 1 to 19, wherein the latex polymer is also formed from one or more ethylenically unsaturated monomers selected from methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, n-octyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, itaconic acid, methacrylic acid and acrylic acid, preferably from methyl methacrylate, ethyl acrylate, butyl acrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, methacrylic acid and acrylic acid .

Aspect 21. The coating composition of any of Aspects 1 to 19, wherein latex polymer is also formed from two or more ethylenically unsaturated monomers selected methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, n-octyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, itaconic acid, methacrylic acid and acrylic acid, preferably from methyl methacrylate, ethyl acrylate, butyl acrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, methacrylic acid and acrylic acid .

Aspect 22. The coating composition of any of Aspects 1 to 19, wherein the latex polymer is also formed from three or more ethylenically unsaturated monomers selected from methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, n-octyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, itaconic acid, methacrylic acid and acrylic acid, preferably from methyl methacrylate, ethyl acrylate, butyl acrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, methacrylic acid and acrylic acid.

Aspect 23. The coating composition of any of Aspects 1 to 22, wherein the latex polymer is formed by emulsion polymerization.

Aspect 24. The coating composition of any of Aspects 1 to 23, wherein the coating composition contains one or more additives selected from antioxidants, ultraviolet absorbers, photostabilizers, foam inhibitors, solvents, flow or leveling agents, colorants, adhesion promoters, pigments, dispersants (wetting agents), slip additives, organic solvents, fillers, thixotropic agents, matting agents and waxes.

Aspect 25. The coating composition of any of Aspects 1 to 23, wherein the coating composition contains one or more pigments selected from zinc oxide, antimony oxide, zirconium oxide, chromium oxide, iron oxide, lead oxide, zinc sulfide, lithopone, and titanium dioxide.

Aspect 26. The coating composition of any of Aspects 1 to 6, 8-11 and 14-25, wherein X has the Formula (5) as defined.

Aspect 27. The coating composition of any of Aspects 1 to 6, 8-11 and 14-25, wherein X has the Formula (6) as defined.

Aspect 28. The coating composition of any of Aspects 1 to 27, wherein the aqueous phase of the latex polymer contains less than 5 wt%, such as less than 3 wt%, such as less than 1 wt%, such as 0 wt% of organic solvents relative to the total weight of the aqueous phase of the coating composition.

Aspect 29. The coating composition of any of Aspects 1 to 28, wherein the latex polymer has a solids content ranging from 10 to 80 wt%, such as from 20 to 70 wt%, such as from 30 to 65 wt%, such as from 35 to 65 wt%.

Aspect 30. The coating composition of any of Aspects 1 to 29, wherein the latex polymer contains at least 20 wt% water, such as at least 40 wt% water, such as at least 50 wt% water, such as at least 60 wt% water, such as at least 70 wt% water, such as at least 80 w% water.

Aspect 31. The coating composition of any of Aspects 1 to 30, wherein the amount of the combination of the monomers of Formula (1) and Formula (2) in the coating composition ranges from 0.01 to 20 wt%, such as from 0.01 to 15 wt%, such as from 0.01 to 10 wt%, such as from 0.1 to 15 wt%, such as from 0.1 to 10 wt%, such as from 1 to 15 wt%, such as from 1 to 10 wt%, such as 5 to 15 wt% relative to the total weight of the monomers used to form the latex polymer.

Aspect 32. A latex polymer formed from monomers comprising, consisting essentially of, or consisting of a monomer of Formula (1) and a monomer of Formula (2), wherein a molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:99 to 99:1.

Aspect 33. The latex polymer of Aspect 32, wherein the latex polymer is also formed from one or more ethylenically unsaturated monomers selected from methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, n-octyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, itaconic acid, methacrylic acid and acrylic acid.

Aspect 34. The latex polymer of Aspect 32, wherein the latex polymer is also formed from two or more ethylenically unsaturated monomers selected from methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, n-octyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, itaconic acid, methacrylic acid and acrylic acid, preferably from methyl methacrylate, ethyl acrylate, butyl acrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, methacrylic acid and acrylic acid.

Aspect 35. The latex polymer of Aspect 32, wherein the latex polymer is also formed from three or more ethylenically unsaturated monomers selected from methyl methacrylate, ethyl methacrylate, methyl acrylate, ethyl acrylate, butyl acrylate, butyl methacrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, n-octyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, itaconic acid, methacrylic acid and acrylic acid, preferably from methyl methacrylate, ethyl acrylate, butyl acrylate, lauryl acrylate, lauryl methacrylate, styrene, 2-ethylhexyl acrylate, 2-octyl acrylate, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid, methacrylic acid and acrylic acid .

Aspect 36. A substrate comprising a coating composition of any of Aspects 1 to 31.

Aspect 37. A method of increasing adhesion and/or corrosion resistance and/or scrub resistance and/or water resistance of a coating composition applied to at least one surface of a substrate, the method comprising adding to the coating composition a latex polymer of any of Aspects 32 to 35.

Aspect 38. A method of increasing corrosion resistance and/or scrub resistance and/or water resistance of at least one surface of a substrate, the method comprising adding to the at least one surface a coating composition of any of Aspects 1 to 31.

Aspect 39. The use of a coating composition of any of Aspects 1 to 31 for increasing corrosion resistance and/or scrub resistance and/or water resistance on at least one surface of a substrate.

Aspect 40. The use of a latex polymer of any of Aspects 32 to 35 as a component in a coating composition for increasing corrosion resistance and/or scrub resistance and/or water resistance on at least one surface of a substrate to which the coating composition is applied.

Aspect 41. A method for preparing the latex polymer of any of Aspects 32 to 35 the method comprising: reacting by emulsion polymerization at a temperature of 50 to 110 °C a mixture of a monomer of Formula (1) and a monomer of Formula (2) as defined in any of Aspects 1 to 31 and at least one different ethylenically unsaturated monomer in a reactor in the presence of water and optionally one or more of a base and an anionic surfactant, where the reaction is maintained at a pH of 3-9, preferably at a pH of 3-7; where the obtained latex polymer has a solids content of at least 10 wt%, preferably at least 20 wt%.

EXAMPLES

Preparation of Latex Polymer for Direct-to-Metal (DTM) Coating (DTM Latex)

A monomer mixture was prepared from 455 parts of styrene (STY), 397 parts of 2-ethylhexyl acrylate (2-EHA), 36 parts of methyl methacrylate (MMA), 16 parts of an active ammonium neutralized mixture of a monomer of Formula (3) and a monomer of Formula (4), 2 parts of an active anionic surfactant, and 380 parts of water. The latex polymer was prepared by introducing 365 parts of deionized water, 0.6 parts of an active anionic surfactant, and 0.4 parts of ammonium hydroxide into a reactor equipped with a stirrer, reflux condensers, thermocouples, and stainless-steel feed lines. After the reactor was heated to 80-85°C, 5 wt% of the monomer mixture was added into reactor, followed by the addition of 2 parts of ammonium persulfate in 15 parts of water. After 5 mins, the remainder of the monomer mixture was fed into the reactor over 225 mins. During the monomer feed, a solution of 1 parts of ammonium persulfate in 32 parts of water was fed into the reactor over 260 mins separately. In addition, 4 parts of

ammonium hydroxide in 29 parts of water were fed into the reactor over 260 min separately. The in-process pH was controlled between 3-9. After the end of ammonium persulfate feed, the reaction was held for an additional 30 mins. To reduce the residual monomer concentrations, 3 parts of tertiary butyl hydroperoxide (tBHP, 70% active) and 2 parts of Bruggolite FF6M were fed into the reactor over 75 minutes at 80°C. The final pH of the formed latex was adjusted to –8-9 using ammonium hydroxide. The final latex polymer had a solids content of approximately 50%.

Preparation of Latex Polymer for Architectural Coating (Architectural latex)

A monomer mixture was prepared from 511 parts of ethyl acrylate (EA), 312 parts of methyl methacrylate (MMA), 95 parts of lauryl methacrylate (LMA), 7 parts of methacrylic acid (MAA), 18 parts of diacetone acrylamide (DAAM), 17 parts of an active ammonium neutralized mixture of a monomer of Formula (3) and a monomer of Formula (4), 17 parts of an active anionic surfactant mixture, and 252 parts of water. The latex polymer was prepared by introducing 525 parts of deionized water, 2 parts of an active anionic surfactant, 8 parts of acrylamide (30% active), and 20 parts of Encor ®9710 seed into a reactor equipped with a stirrer, reflux condensers, thermocouples, and stainless-steel feed lines. After the reactor was heated to 88-92°C, 0.5 parts of sodium persulfate in 8 parts of water was added into the reactor. Afterwards, the monomer mixture was fed into the reactor over 210 mins. During the monomer feed, a solution of 1 parts of sodium persulfate in 41 parts of water was fed into the reactor over 210 mins separately. The in-process pH was controlled between 3-9. At the end of monomer feed, the reaction was held for additional 15 mins, followed by adjustment of the reaction pH to 7 using ammonium hydroxide solution. To reduce the residual monomer concentrations, 2 parts of tertiary butyl hydroperoxide (tBHP, 70% active) and 2 parts of sodium metabisulfite were fed into the reactor over 60 minutes at 65°C. Afterwards, a mixture of 9 parts of adipic dihydrazide (ADH) and 9 parts of active phosphate surfactant in 40 parts of water was added into the reaction mixture. The final pH of the formed latex polymer was adjusted to –8-9 using ammonium hydroxide. The final latex polymer had a solids content of approximately 50%.

Volume Average Particle Size

The volume average particle size of the latex polymers was measured using dynamic light scattering using a Microtrac UPA 150 or Nanotrac UPA 150 manufactured by Microtrac.

pH Measurement

The pH measurements were carried out using an Oakton pH 150 Waterproof Portable Meter under room temperature (i.e., 25 ºC).

Viscosity

The viscosity of the latex polymers was measured with a DVII+ Brookfield viscometer with #3 spindle at 60 rpm.

Adhesion

The adhesion test was conducted according to ASTM D-3359B (2017). Briefly, the coatings were applied at a wet film thickness of 7 mils over testing panels and allowed to dry for 1 day at 77°F and 50% relative humidity. For the dry adhesion test, the dried coating films were crosshatched using a sharp blade to produce a 10 x 10 grid, followed by applying adhesion tape to each of the films. To ensure good contact with films, the tape was rubbed firmly with a tongue depressor. The tape was then immediately pulled off with a constant force at a 180° angle. For the wet adhesion test, the dried coating films were prepared and cross-hatched following the same procedure described above for the dry adhesion test, except that a piece of paper towel was wetted by water droplets and then applied onto the crosshatched area. Afterwards, the wet paper towel was removed, and the surface of the dried coating film was blotted dry. The wet adhesion test was performed using the same procedure described above for the dry adhesion test. The adhesion performance was visually rated on a scale of 0-5, with 0 being complete film removal (undesired) and 5 being no film removal (highly desired).

Corrosion Resistance (Salt fog test)

The salt fog test was conducted according to ASTM B 117. Briefly, the coatings were applied at a wet film thickness of 7 mils over cold-rolled steel panel and allowed to dry for 7 days at 77°F and 50% relative humidity. The cured films were scribed using a sharp blade, followed by placement into a Q-Fog corrosion tester. The panels were evaluated by visual examination after 500 hours of incubation. This test corresponds to the resistance of the coated substrate against corrosion.

Sn*w2025Scrub Resistance

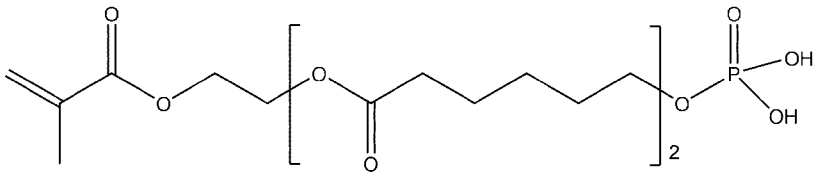
Scrub resistance was evaluated on the Garner Straight Line Washability and Wear Abrasion machine. The coatings were applied at a wet film thickness of 7 mils over Leneta black plastic charts and allowed to dry for 7 days at 77°F and 50% relative humidity. A standardized abrasive scrub media (#SC-2 from the Leneta Company) was used in the test. The testing paint was drawn down and scrubbed side by side with the same control paint. The number of cycles to failure was recorded, and the results of the testing paints were normalized to the control paint.

Water Absorption Quantification of Paint Films

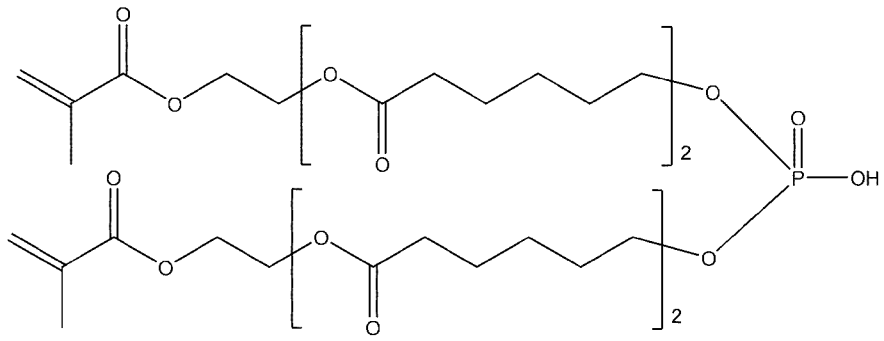
A paint film was drawn down using a 20 mil draw down bar on a Leneta black scrub test panel, followed by drying for 3 days at 77°F and 50% relative humidity to determine the dry paint mass (mo). The dried film was then soaked in water for 1 hour, followed by removing surface water using paper towels. The mass of the water-soaked paint film was determined to be $m_{water\ soaked}$. The water absorption was calculated using the following equation:

$$\%\ \text{water absorption} = (m_{water\ soaked} - m_0)/\ m_0 \times 100\%$$

The exemplary phosphate monomer used in the preparation of the tested latex polymers of the below tables was a mixture of a caprolactone-based monoester of Formula (1) and a caprolactone-based diester of Formula (2) having the following structures of Formula (3) and Formula (4), respectively:



(3)



(4)

The molar ratio of Formula (3) to Formula (4) was 1.5, as determined by ^{31}P NMR.

[0001] Listing of Components

SIPOMER® PAM 4000: 2-hydroxyethyl methacrylate phosphate monomer (Solvay)

SIPOMER® PAM 600: polypropylene glycol methacrylate phosphate monomer (Solvay)

Disperbyk 190: wetting agent (BYK USA)

Surfynol 104DPM: surfactant (Evonik)

BYK 028: silicone defoamer (BYK USA)

Ti-Pure™ R-706: rutile titanium dioxide (Chemours)

ACRYSOL™ RM2020: non-ionic urethane rheology modifier (Dow)

Disponil® FES 32: fatty alcohol polyglycol ether sulfate, Na-salt emulsifier (BTC Europe)

Acticide® MBS: biocide (Thor)

DOWANOL™ DPnB: hydrophobic glycol ether solvent (Dow)

HALOX® 570 [30% solution]: organic corrosion inhibitor (ICL)

ACRYSOL™ RM-8W: non-ionic urethane rheology modifier (Dow)

Coadis 123K: dispersant (Arkema)

HYDROPALAT® WE 3320: non-ionic surfactant (BASF)

TEGO® Foamex 810: defoamer (Palmer Holland)

Ti-Pure™ R-746: rutile titanium dioxide (Chemours)

MINEX® 10: micronized functional filler (Sibelco)

COAPUR™ 2025: alkyl phenol ethoxylate solvent (Arkema)

Vikoflex® 2200: bio-based coalescent (Cargill)

Latex polymers formed from the phosphate monomers SIPOMER® PAM 4000 and SIPOMER® PAM 600 were selected as comparative examples to the latex polymers of the

invention formed from the mixture of the monomers of Formula (3) and Formula (4) as shown in Table 1. All of the tested latex polymers had a similar solids content and particle size.

Table 1. Physical properties of the latex polymers according to the invention and the comparative latex polymers

Examples	**Phosphate monomer**	**Volume Average Particle Size (nm)**	**Viscosity (cps)**
Inventive DTM Latex	Mixture of monomers of Formula (3) and Formula (4) (in a molar ratio of 1.5:1)	114	380
Comparative DTM Latex 1	SIPOMER® PAM 4000	115	300
Comparative DTM Latex 2	SIPOMER® PAM 600	114	300
Inventive Architectural Latex	Mixture of monomers of Formula (3) and Formula (4) (in a molar ratio of 1.5:1)	109	260
Comparative Architectural Latex 1	SIPOMER® PAM 4000	108	4500
Comparative Architectural Latex 2	SIPOMER® PAM 600	111	300

Table 2 lists the grind and letdown components of the inventive and comparative paint formulations tested for direct-to-metal (DTM) application.

Table 2. Direct-to-metal (DTM) paint formulations

	Inventive DTM Paint	**Comparative DTM Paint 1**	**Comparative DTM Paint 2**
Grind	**Parts**	**Parts**	**Parts**
Water	83.2	83.2	83.2
Disperbyk 190	9.4	9.4	94.4
Surfynol 104DPM	4.2	4.2	4.2
BYK 028	4.2	4.2	4.2
R-706	161.2	161.2	161.2
Ammonium hydroxide [28% aq]	2.1	2.1	2.1
RM2020	3.1	3.1	3.1
Individual Letdown			
Inventive DTM Latex	604.5	0	0
Comparative DTM Latex 1	0	597.8	0
Comparative DTM Latex 2	0	0	596.3
Disponil FES 32	4.8	4.8	4.8
Acticide MBS	4.2	4.2	4.2
Ammonium hydroxide [28% aq]	4.6	4.6	4.6
Dowanol DPnB	15.7	15.7	15.7

Halox 570 [30% solution	12.7	12.7	12.7
RM2020	7.8	7.8	7.8
RM8W	1.0	1.0	1.0
Water	48.4	55.0	56.6

Table 3 shows that the inventive DTM paint exhibited a similar Krebs Unit (KU) viscosity response and 60 gloss (i.e., gloss measured at a 60° angle) to comparative DTM paint 1 and comparative DTM paint 2. All the paints also showed good adhesion on cold-rolled steel and galvanized steel. Corrosion resistance is considered the most critical performance for DTM paints. As shown in the **FIGURE**, the inventive DTM paint exhibited superior corrosion resistance compared to the comparative DTM paints, thereby demonstrating the technical advantages conferred by using a caprolactone based phosphate monomer (e.g., as the mixture of monomers of Formula (3) and Formula (4)) for DTM latex synthesis.

Table 3. Paint properties for inventive and comparative DTM paints

Examples	**KU**	**60 gloss**	**Adhesion on cold-rolled steel (dry/wet)**	**Adhesion on galvanized steel (dry/wet)**
Inventive DTM Paint	92	85.0	5/5	5/5
Comparative DTM Paint 1	92	89.3	5/5	5/5
Comparative DTM Paint 2	89	85.5	5/5	5/5

Table 4 describes the paint formulations tested for interior architectural applications.

Table 4. Interior architectural paint formulation

	Inventive Architectural Paint	**Comparative Architectural Paint 1**	**Comparative Architectural Paint 2**
Grind	**Parts**	**Parts**	**Parts**
Water	40.0	40.0	40.0
Coadis 123K	7.0	7.0	7.0
Hydropalat 3320	2.0	2.0	2.0
Foamex 810	2.0	2.0	2.0
LiOH solution [10%]	2.0	2.0	2.0
R-746	360.0	360.0	360.0
Minex 10	20.0	20.0	20.0
Coapur 2025	24.0	24.0	24.0
Individual Letdown			
Inventive Architectural Latex	583.6	0	0
Comparative Architectural Latex 1	0	567.2	0
Comparative Architectural Latex 2	0	0	572.0
Vikoflex 2200	18.0	18.0	18.0

Table 5 shows that the inventive architectural paint showed a similar KU response and 60 gloss compared to comparative architectural paint 1 and comparative architectural paint 2. However, as further shown in Table 5, the inventive architectural paint exhibited a superior scrub resistance of 3809 as compared to the scrub resistant values of 2489 and 2147 of the comparative architectural paints 1 and 2, respectively. This superior performance demonstrated by the inventive architectural paint is particularly important in view of scrub resistance being one of the most critical requirements for interior architectural coatings.

The results of the water absorption test shown in Table 5 also demonstrated that the inventive architectural paint was significantly more water resistant than the comparative architectural paints as evidenced by its lower water uptake. These data demonstrated additional technical advantages associated with using a caprolactone-based phosphate monomer mixture for architectural latex synthesis.

Table 5. Paint properties for inventive and comparative architectural paints

Examples	**KU**	**60 gloss**	**Scrub Resistance (cycles)**	**1 hour water absorption (%)**
Inventive Architectural Paint	87	53.6	3809	6.7
Comparative Architectural Paint 1	89	53.9	2489	11.7
Comparative Architectural Paint 2	73	47.6	2147	9.5

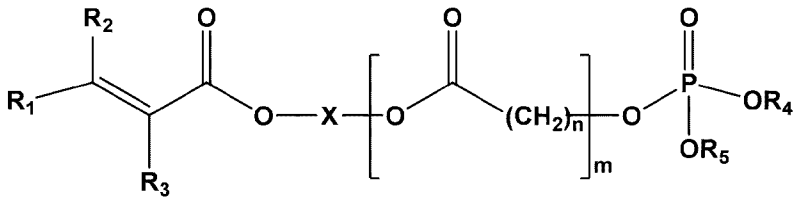
Discussion

The improved corrosion resistance, scrub resistance, and water resistance associated with the inventive coating compositions as described herein enhance their value over conventional coatings due their increased durability which extends the service life of the underlying substrates. These benefits demonstrate the unexpected advantages associated with using latex polymers formed from a mixture of monomers of Formula (1) and Formula (2) as described herein in coating applications.

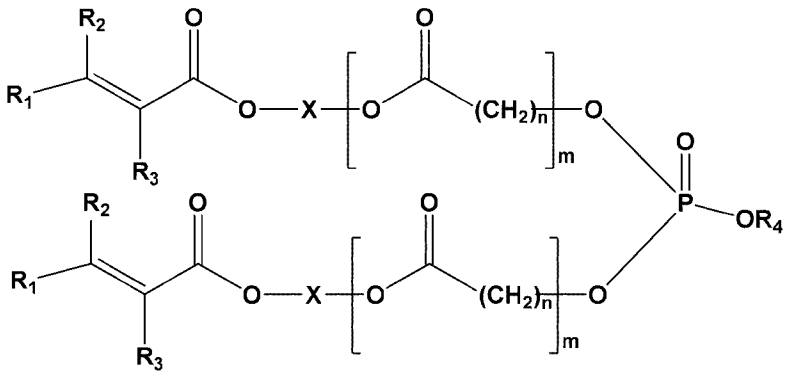
The invention as described is intended to cover not only individual aspects or exemplary embodiments of the invention but also combinations of all aspects and embodiments.

CLAIMS

1. A coating composition comprising an latex polymer, where the latex polymer is formed from monomers comprising a monomer of Formula (1) and a monomer of Formula (2)



(1)



(2)

wherein in Formula (1) and Formula (2):

each R_1 is independently H or C_1-C_6 alkyl;

each R_2 is independently H or C_1-C_6 alkyl;

each R_3 is independently H or C_1-C_6 alkyl;

each X is independently C_1-C_6 alkylene, where a N, O or S atom may be inserted between any two carbon atoms present in the alkylene chain and where carbon atoms in the alkylene chain may be substituted with a C_1-C_3 alkyl group;

each R_4 is independently H or a cation;

each R_5 is independently H or a cation;

each n is independently 4 to 7; and

each m is independently 1 to 10,

wherein a molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:99 to 99:1.

2. The coating composition according to claim 1, wherein the latex polymer is formed from monomers that further comprise at least one ethylenically unsaturated monomer not containing a phosphorus moiety.

3. The coating composition according to claim 1 or claim 2, wherein the latex polymer is formed from monomers that further comprise at least two ethylenically unsaturated monomers not containing a phosphorus moiety.

4. The coating composition according to any one of claims to 1-3 , wherein the monomer of Formula (1) is present in a greater molar amount than the monomer of Formula (2).

5. The coating composition according to any one of claims 1-4, wherein the combination of the monomer of Formula (1) and the monomer of Formula (2) is present in an amount of 0.01 to 20 wt%, preferably 0.1 to 15 wt%, most preferably 0.1 to 10 wt% relative to the weight of the monomers used to form the latex polymer.

6. The coating composition according to any one of claims 1-5, wherein m is 1 to 4.

7. The coating composition according to any one of claims 1-6, wherein the cation of R_4 and R_5 is independently an ammonium group, a primary ammonium group, a secondary ammonium group, a tertiary ammonium group or a metal.

8. The coating composition according to any one of claims 1-7, wherein at least one of R_4 and R_5 is a cation that is an ammonium group.

9. The coating composition according to any one of claims 1-8, wherein n is 5 and m is 2.

10. The coating composition according to any one of claims 1-9, wherein X is selected from $-CH_2-CH_2-$, Formula (5) or Formula (6)

$$-(CR_6R'_6)_e- \quad (5)$$

$$-[(CR_7R'_7)_f-O]_g-(CR_7R'_7)_h- \quad (6)$$

wherein:

R_6 and R'_6 are independently H or C_1-C_3 alkyl;

each R_7 and R'_7 is independently H or methyl;

e is an integer from 1 to 6;

f is an integer from 1 to 4;

g is an integer from 1 to 3;

h is an integer from 1 to 4; and

$f + g + h \leq 6$.

11. The coating composition according to any one of claims 1-10, wherein n is 5, m is 2 and X is $-CH_2-CH_2-$.

12. The coating composition according to any one of claims 1-10, wherein n is 5, m is 1 and X is $-CH_2-CH_2-$.

13. The coating composition according to any one of claims 1-12, wherein the composition further comprises one or more additives selected from pigments, fillers, dispersants, rheology modifiers, wetting agents, defoamers, coalescing agents, neutralizers, and biocides.

14. The coating composition according to any one of claims 1-13, wherein the latex polymer contains at least 20 wt% water.

15. A substrate comprising the coating composition according to any one of claims 1-14 on at least one surface of the substrate.

16. The substrate according to claim 15, wherein the substrate comprises one or more of a metal, asphalt, concrete, stone, ceramic, wood, paper, paperboard and plastic.

17. The substrate according to claim 15, wherein the substrate comprises a metal.

18. A method of increasing corrosion resistance and/or scrub resistance and/or water resistance of at least one surface of a substrate, the method comprising adding to the least one surface a coating composition as defined in any one of claims 1-14.

19. The method according to claim 18, wherein the substrate comprises a metal.

20. A method for preparing the latex polymer as defined in claim 1, the method comprising:

reacting by emulsion polymerization at a temperature of about 50 to 110 °C, a mixture of the monomer of Formula (1) and the monomer of Formula (2), where a molar ratio of the monomer of Formula (1) to the monomer of Formula (2) is 1:99 to 99:1, and optionally at least one ethylenically unsaturated monomer not containing a phosphorus moiety,

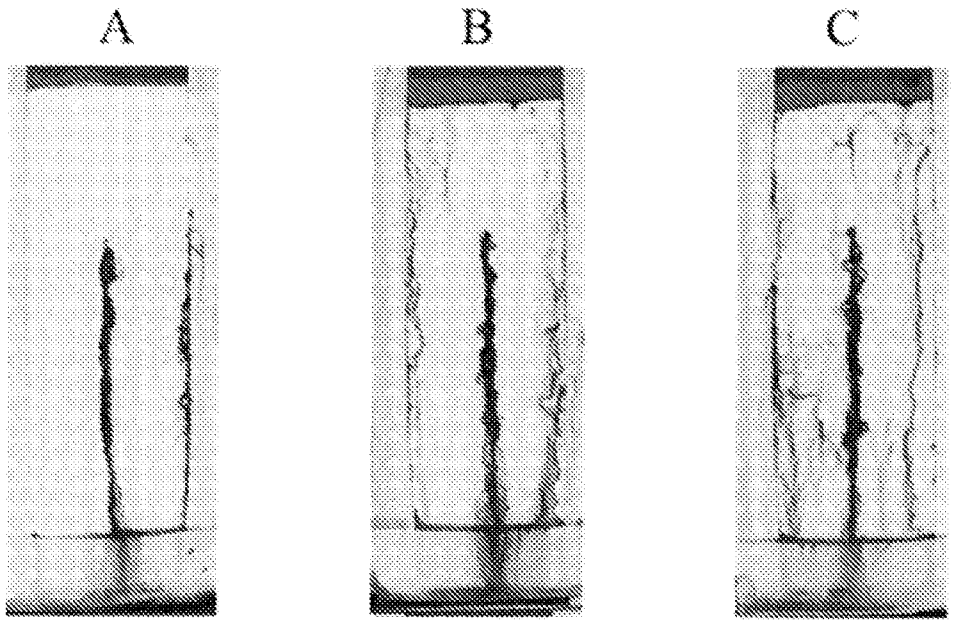
in a reactor in the presence of water and optionally one or more of a base and an anionic surfactant, where the reaction is maintained at a pH of 3-9, preferably at a pH of 3-7,

where the obtained latex polymer has a solids content of at least 10 wt%, preferably at least 20%.

21. Use of the coating composition according to any one of claims 1-14 for increasing adhesion and/or corrosion resistance and/or scrub resistance and/or water resistance on at least one surface of a substrate.

22. Use of the latex polymer as defined in claim 1 as a component in a coating composition for increasing adhesion and/or corrosion resistance and/or scrub resistance and/or water resistance on at least one surface of a substrate to which the coating composition is applied.

FIGURE 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/059484

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C08F 220/14*** (2025.01); ***C08F 230/02*** (2025.01); ***C09D 133/04*** (2025.01); *C08F 2/22* (2025.01)

CPC: ***C08F 220/14; C08F 230/02; C09D 133/04;*** *C08F 2/22*

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)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2018/0327562 A1 (Rohm and Haas Company) 15 November 2018 (15.11.2018) para [0006], [0013], [0031], [0036]-[0039]	1-3, 20, 22
A	US 2011/0009540 A1 (Terrenoire et al.) 13 January 2011 (13.01.2011) entire document	1-3, 20, 22
A	WO 2019/158609 A1 (ARKEMA FRANCE) 22 August 2019 (22.08.2019) entire document	1-3, 20, 22
A	US 2022/0235231 A1 (The University of the Basque Country/Institute et al.) 28 July 2022 (28.07.2022) entire document	1-3, 20, 22
A	US 2023/0250205 A1 (Rohm and Haas Company) 10 August 2023 (10.08.2023) entire document	1-3, 20, 22

☐ 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

"D" document cited by the applicant in the international application

"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
07 February 2025 (07.02.2025)	**18 February 2025 (18.02.2025)**

Name and mailing address of the ISA/US	Authorized officer
COMMISSIONER FOR PATENTS **MAIL STOP PCT, ATTN: ISA/US** **P.O. Box 1450** **Alexandria, VA 22313-1450** **UNITED STATES OF AMERICA**	**KARI RODRIQUEZ**
Facsimile No. **571-273-8300**	Telephone No. **PCT Help Desk: 571-272-4300**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/059484

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☑ Claims Nos.: **4-19, 21**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).