

Aqueous Coating Composition

Field of the Invention

[0001] This invention pertains to waterborne coating composition containing i) acrylic modified polymer containing diacetone acrylamide “DAAM” functionality and ii) dihydrazine, which crosslink upon drying. These coating can be used as exterior coatings.

[0002] BACKGROUND

[0003] Fluorine-containing paints are used as weather-resistant paints for exteriors and interiors of buildings and structures. Fluorine-containing paints are often dispersed in organic solvents, but the use of organic solvents is problematic in terms of safety and environmental protection. Water borne coatings are more environmentally friendly than solvent borne coatings, but they are not preferred for protective coating applications because they tend to have less water resistance, because the surfactants that are needed to stabilize the water dispersion. Crosslinked protective coatings are preferred for protective coating because they boost hardness, chemical resistance but the crosslinking reaction can also traps surfactant and other hydrophilic species in the coating film, reducing the water resistance. Non-isocyanate crosslinking approaches are especially preferred for worker health and safety reasons, all the more so if they offer the convenience of being “one pack” or at least very long potlife (days to weeks). The ketone – hydrazide reaction is an ambient crosslinking reaction of this type, and the crosslinking reaction is driven by the loss of water such as in physical drying of the coating.

[0004] We have discovered that PVDF-acrylic hybrids where the acrylic portion contains ketone functionality specifically DAAM, for crosslinking with a dihydrazide provides a stable 1 pack composition for coating applications.

[0005] Japanese patent JPH09165490A discloses acrylic modified fluoropolymers and in the examples AAEM is a monomer used in the acrylic portion of the acrylic modified fluoropolymer. There is no teaching of diacetone acrylamide in the acrylic modified fluoropolymer.

[0006] WO2017/091408 discloses an aqueous, fluoropolymer hybrid composition used in coatings having superior weathering resistance while maintaining excellent mechanical properties in coatings, paints, caulks and adhesives. There is no teaching of diacetone or dihydrazine.

[0007] SUMMARY OF THE INVENTION

[0008] An aqueous coating composition comprising:

- i) acrylic modified fluoropolymer composition comprising a fluoropolymer portion and an acrylic portion, and
- ii) dihydrazide, and

iii) optionally additional polymer that is not part of the acrylic modified fluoropolymer wherein the acrylic modified fluoropolymer composition ("AMF") comprises at least 1 wt% DAAM monomer units and less than 15 wt% based on total acrylic monomer units in the acrylic modified fluoropolymer. The molar ratio of dihydrazide to DAAM functionality is from 0.02 to 0.5.

[0009] Preferably, the aqueous coating composition comprises a pigment.

[0010] Preferably, the aqueous coating composition comprises greater than 50wt% polymer based on total solids content of the aqueous coating composition.

[0011] The acrylic portion of the AMF is substantially comprised of acrylic and/or methacrylic monomer units. The amount of diacetone acrylamide "DAAM" in the acrylic portion of the AMF is greater than 1% and less than 20 wt%, preferably less than 15wt%. The total amount of DAAM is based on the cumulative sum of all the acrylic polymers in the AMF.

[0012] Preferably the acrylic portion of the AMF comprises at least one monomer with an acid functionality, for example an acrylic acid or a methacrylic acid or other monomer having acid functionality.

[0013] The aqueous coating composition once applied to the substrate is dried. Crosslinking of the DAAM and the hydrazide occurs upon drying. The aqueous coating composition is stable and does not crosslink until drying.

[0014] The invention provide for a coating on a substrate, the coating being provided by drying the aqueous coating composition on the substrate. The dried coating containing AMF polymer having DAAM- dihydrazide crosslinks.

[0015] The coatings of the present invention are intended to be used as architectural or protective coatings such as against weathering.

[0016] Aspects of the Invention

[0017] Aspect 1. An aqueous coating composition comprising

- i.) an acrylic modified fluoropolymer comprising a fluoropolymer portion and an acrylic portion
- ii) a dihydrazide, and
- iii) optionally additional polymer that is not part of the acrylic modified fluoropolymer, wherein the acrylic modified fluoropolymer composition comprises at least 1 wt% DAAM and up to 20 weight percent based on total acrylic monomer units in the acrylic modified fluoropolymer composition.

[0018] Aspect 2. The aqueous coating composition of aspect 1, wherein the aqueous coating composition comprises greater than 50wt% polymer based on total solids content of the aqueous coating composition.

[0019] Aspect 3 The aqueous coating composition of aspect 1 or 2, wherein the acrylic portion further comprises an acrylic or methacrylic monomer with acid functionality.

- [0020] Aspect 4. The aqueous coating composition of any one or more of the preceding aspects, wherein the acrylic portion of the acrylic modified fluoropolymer further comprises a (meth)acrylic acid from 0.01 to 10% based on total acrylic monomer units in the acrylic modified fluoropolymer composition.
- [0021] Aspect 5. The aqueous coating composition of any one or more of the preceding aspects, wherein the molar ratio of dihydrazide to DAAM is between 0.02 and 0.5.
- [0022] Aspect 6. The aqueous coating composition of any one or more of the preceding aspects, wherein the aqueous coating composition further comprises a pigment.
- [0023] Aspect 7. The aqueous coating composition of any one or more of the preceding aspects, wherein the aqueous coating composition further comprises an acrylic polymer that is separate from the acrylic modified fluoropolymer.
- [0024] Aspect 8. The aqueous coating composition of any one or more of the preceding aspects, wherein the additional polymer that is not part of the acrylic modified fluoropolymer is selected from polymers and copolymers based on at least one of acrylics and/or vinyls, polyurethanes, polyesters, melamine resins, or epoxies.
- [0025] Aspect 9. The aqueous coating composition of any one or more of the preceding aspects, wherein the additional polymer that is not part of the acrylic modified fluoropolymer comprises at least one of acrylic latex, polyvinyl acetate (PVA) latex, styrene/butadiene latex, vinyl latex or vinyl acrylic latex.
- [0026] Aspect 10. The aqueous coating composition of any one or more of the preceding aspects, wherein said fluoropolymer portion comprises 50 to 100 weight percent of vinylidene fluoride units, and 0 to 50 weight percent of monomer units copolymerizable with vinylidene fluoride based on wt of fluoropolymer portion, preferably said fluoropolymer portion comprises 50 to 100 weight percent of vinylidene fluoride units.
- [0027] Aspect 11. The aqueous coating composition of any one or more of the preceding aspects, wherein the fluoropolymer portion comprises from 3 to 30 wt% hexafluoropropylene units based on the total weight of the fluoropolymer portion.
- [0028] Aspect 12. The aqueous coating composition of any one or more of the preceding aspects 6, wherein the fluoropolymer portion comprises a polyvinylidene fluoride-hexafluoropropylene copolymer, wherein the total weight percent of hexafluoropropylene monomeric units in the acrylic modified fluoropolymer is from 5 to 20%, preferably from 10 to 20 wt% based on the weight of acrylic modified fluoropolymer.
- [0029] Aspect 13. The aqueous coating composition of any one or more of the preceding aspects, wherein the total weight percent of acrylic monomeric units in the acrylic modified fluoropolymer is from 10 to 50 wt%, preferably, from 15 to 40 wt% in the acrylic modified fluoropolymer.

[0030] Aspect 14. The aqueous coating composition of any one or more of the preceding aspects, wherein said acrylic modified fluoropolymer comprises from 3 to 100 weight percent of the total polymer in the aqueous coating composition.

[0031] Aspect 15. The aqueous coating composition of any one or more of the preceding aspects, further comprising UV stabilizers, pH adjustment agents, colorants, dyes, water soluble resins, rheology control additives and thickeners, and pigments and pigment extenders, and filler.

[0032] Aspect 16. A method of coating a substrate comprising providing a substrate, providing the coating composition of any one or more of the preceding aspects, applying the coating composition to the substrate, drying the coating composition on the substrate to form a coated substrate.

[0033] Aspect 17. A coated substrate comprising a substrate having coated on at least one surface with the aqueous coating composition of any one or more of aspects 1-15 and wherein said coating composition is dried to form a coated substrate.

[0034] Aspect 18. The coated substrate of aspect 17, wherein said substrate is selected from the group consisting of primed or unprimed metals, wood, glass, plastic, and composites.

[0035] Aspect 19. The coated substrate of aspect 18, wherein the coating is an exterior coating selected from architectural coating, marine coating, and protective coating.

[0036] Aspect 20. Use of the aqueous coating composition of any one or more of aspects 1 to 15 in exterior construction.

DETAILED DESCRIPTION

[0037] Within this specification, embodiments have been described in a way which enables a clear and concise specification to be written, but it is intended and will be appreciated that embodiments may be variously combined or separated without parting from the invention. For example, it will be appreciated that all preferred features described herein are applicable to all aspects of the invention described herein.

[0038] All references listed in this application are incorporated herein by reference. All percentages in a composition are weight percent, unless otherwise indicated.

[0039] Crystallinity and melting temperature are measured by DSC as described in ASTM D3418 at heating rate of 10 C/min. Melt viscosity is measured in accordance with ASTM D3835 at 230°C expressed in k Poise @100 Sec⁻¹.

[0040] The term “polymer” is used to mean both homopolymers, copolymers unless otherwise stated. “Copolymer” is used to mean a polymer having two or more different monomer units. For example, as used herein, “PVDF” and “polyvinylidene fluoride” is used to connote both the homopolymer and copolymers, unless specifically noted otherwise. The polymers may be homogeneous, heterogeneous,

and may have a gradient distribution of co-monomer units.

[0041] Crosslinkable means that the acrylic portion of the acrylic modified fluoropolymer polymer has functionality in the monomers that can crosslink or contains a crosslinking agent.

[0042] By acrylic modified fluoropolymer composition means a composition in which an acrylic has been polymerized in the presence of a fluoropolymer seed. Such hybrid compositions are described in US patents and applications such as US5349003, US 6680357 and US 2011/0118403.

[0043] Acrylic encompasses both acrylic and meth acrylic monomers unless otherwise specified. Acrylic polymer encompasses having acrylic and/or meth acrylic monomer units unless otherwise specified.

[0044] "DAAM" means diacetone acrylamide.

[0045] Stable means after one month in a 50 °C oven, the composition performs with no more than a 10% difference in the double rub test as compared to the fresh made composition.

[0046] The present invention provides for an aqueous coating composition which is stable and comprising a crosslinkable acrylic modified fluoropolymer and dihydrazide.

[0047] According to this invention, there is provided an aqueous coating composition comprising an acrylic modified fluoropolymer having DAAM monomer units, dihydrazide and optionally pigment. The molar ratio of dihydrazide to DAAM functionality is from 0.02 to 0.5.

[0048] The aqueous coating composition comprises greater than 50wt% polymer based on total solids content. Polymer in this context meaning the total of the AMF plus any optionally additional polymer that is not part of the acrylic modified fluoropolymer.

[0049] Acrylic modified fluoropolymer "AMF" is comprised of seed fluoropolymer and acrylic polymer(s), where the acrylic monomer composition(s) having been polymerized, "acrylic polymerization", in the presence of the seed fluoropolymer, thereby producing an acrylic modified fluoropolymer.

[0050] The weight percent of fluoropolymer seed, preferably vinylidene fluoride polymer in the AMF is at least 50% and preferably greater than 60 wt% of the AMF.

[0051] Seed Fluoropolymers

[0052] The fluoropolymers used in the invention as seed for the acrylic polymerization are formed primarily of fluoromonomers. The term "fluoromonomer" or the expression "fluorinated monomer" means a polymerizable alkene which contains at least one fluorine atom, fluoroalkyl group, or fluoroalkoxy group attached to the double bond of the alkene that undergoes polymerization. The term "fluoropolymer" means a polymer formed by the polymerization of at least one fluoromonomer, and it is inclusive of homopolymers, copolymers, which are thermoplastic in their nature, meaning they are capable of being formed into useful pieces by flowing upon the application of heat, such as is done in

molding and extrusion processes. The fluoropolymer preferably contains at least 50 weight percent, preferably at least 70 weight percent of one or more fluoromonomers.

[0053] The vinylidene fluoride copolymer is comprised of a polymer made from vinylidene fluoride monomer and at least one other monomer to form a copolymer, with a monomer composition selected to contain at least 50 wt%, preferably at least 70 wt% vinylidene fluoride monomer units. The fluoropolymers used in the invention can be made by means known in the art, such as by an emulsion, suspension, solution, or supercritical CO₂ polymerization process. Preferably, the fluoropolymer is formed by an emulsion process. The process is free of fluorinated surfactant. The fluoropolymer seed is free of fluorinated surfactant meaning no fluorinated surfactant is used in any part of the emulsion polymerization process.

[0054] The vinylidene fluoride polymer is in an aqueous dispersion that can be produced by any conventional fluoropolymer emulsion polymerization method as long as the fluoropolymer particle size remains under 900 nm, more preferably under 700 nm.

[0055] Fluoropolymer emulsion polymerization processes are well known in the literature, with US Pat. No. 3,051,677, US Pat. No. 3,178,399, US Pat. No. 3,475,396, US Pat. No. 3,857,827, US Pat. No. 6,187,885, US Pat. No. 6,586,547, US Pat. No. 6,841,616, US Pat. No. 7,122,610, and US Pat. No. 8,338,518 as some specific examples. The fluoropolymer dispersion is preferably synthesized using free-radical initiation. Chain transfer agents, buffering agents, antifoulants, and other additives typically used in a fluoropolymer emulsion process may be present.

[0056] Fluoromonomers useful in the practice of the invention include, for example, vinylidene fluoride (VDF), tetrafluoroethylene (TFE), trifluoroethylene (VF₃), chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP), vinyl fluoride (VF), hexafluoroisobutylene, perfluorobutylethylene (PFBE), pentafluoropropene, 2,3,3,3-tetrafluoropropene (HFO-1234yf), 2-chloro-1,1-difluoroethylene (R-1122), 3,3,3-trifluoro-1-propene, 2-fluoromethyl-3,3,3-trifluoropropene, a fluorinated vinyl ether, a fluorinated allyl ether, a non-fluorinated allyl ether, a fluorinated dioxole, and combinations thereof.

[0057] The fluoropolymer seed is preferably a vinylidene fluoride polymer obtained by emulsion-polymerization. Such an aqueous vinylidene fluoride polymer dispersion can be produced by a conventional emulsion polymerization method, for example, by emulsion-polymerizing the starting monomers in an aqueous medium in the presence of a polymerization initiator, this process is known in the art. Specific examples of the vinylidene fluoride polymer obtained by emulsion-polymerization include vinylidene fluoride homopolymer and copolymers of (1) vinylidene fluoride and (2) a fluorine-containing ethylenically unsaturated compound (e.g. tetrafluoroethylene (TFE), trifluoroethylene (VF₃), chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP), vinyl fluoride (VF), hexafluoroisobutylene, perfluorobutylethylene (PFBE), pentafluoropropene, 2,3,3,3-tetrafluoropropene (HFO-1234yf), 2-chloro-1,1-difluoroethylene (R-1122), 3,3,3-trifluoro-1-propene, 2-fluoromethyl-3,3,3-trifluoropropene, a

fluorinated vinyl ether, a fluorinated allyl ether, a non-fluorinated allyl ether, a fluorinated dioxole, perfluoroacrylic acid), a fluorine-free ethylenically unsaturated compounds (e.g. cyclohexyl vinyl ether, hydroxyethyl vinyl ether or the like), a fluorine-free diene compound (e.g. butadiene, isoprene, chloroprene), all of them being copolymerizable with vinylidene fluoride.

[0058] Especially preferred fluoropolymers are homopolymers of VDF, and copolymers of VDF with HFP, TFE or CTFE, comprising from about 50 to about 99 weight percent VDF, more preferably from about 70 to about 99 weight percent VDF. Especially preferred copolymers are copolymers of VDF and HFP where the weight percent of VDF in the copolymer is from 50 to 99 weight percent, preferably from 65 to 95 weight percent based on total monomers in the copolymer. In one preferred embodiment of a VDF /HFP copolymer the weight percent of HFP is from 5 to 30%, preferably from 8 to 25% based on the total monomer in the polymer.

[0059] The fluoropolymer preferably has a high molecular weight. By high molecular weight, as used herein, is meant PVDF having a melt viscosity of greater than 1.0 kilopoise, preferably greater than 5 kilopoise, more preferably greater than 10 kilopoise, according to ASTM method D-3835 measured at 230 °C and 100 sec-1.

[0060] The fluoropolymer seed may be functionalized by copolymerization using 0.1 to 25 weight percent, and preferably 0.1 to 10 weight percent of at least one functional comonomer based on the total weight of the fluoropolymer seed. The copolymerization could add one or more functional comonomers to the fluoropolymer backbone, or be added by a grafting process. The fluoropolymer seed could also be functionalized by polymerized using from 0.1 to 25 weight percent of one or more low molecular weight polymeric functional chain transfer agents. By low molecular weight is meant a polymer with a degree of polymerization of less than or equal to 1,000, and preferably less than 800. The low molecular weight functional chain transfer agent is a polymer or an oligomer having two or more monomer units, and preferably at three or more monomer units, as for example polyacrylic acid. The residual polymeric chain transfer agents may provide functionality to the fluoropolymer. The fluoropolymer seed could have both functional comonomer and residual functional polymeric chain transfer agents. By functional polymeric chain transfer agents, as used in the invention, is meant that the low molecular weight polymeric chain transfer agent contains one or more different functional groups, such as an acid functionality. Examples of some useful functional comonomers include, phosphate (meth)acrylates, (meth) acrylic acid, and hydroxyl-functional (meth)acrylic comonomers.

Acrylic portion

[0061] The AMF polymer contains an acrylic portion. The acrylic portion comprises one or more acrylic polymer(s). The acrylic portion of the AMF polymer contains diacetone acrylamide ("DAAM") units in at least one of the acrylic polymers making up the acrylic portion. The acrylic portion is obtained by emulsion

polymerizing a monomer mixture containing at least one monomer selected from the group consisting of: alkyl acrylates whose alkyl groups have 1-18 carbon atoms, alkyl methacrylates whose alkyl groups have 1-18 carbon atoms and ethylenically unsaturated compound copolymerizable with the alkyl acrylates and the alkyl methacrylates, in an aqueous medium in the presence of a fluoropolymer seed, preferably vinylidene fluoride polymer is the fluoropolymer. The acrylic portion contains at least 1 wt% DAAM monomer units and up to 20 weight percent based on total acrylic monomer units in the acrylic modified fluoropolymer composition.

[0062] The alkyl acrylate with an alkyl group having 1-18 carbon atoms, , includes, for example, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, amyl acrylate, isoamyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, lauryl acrylate. Of these, alkyl acrylates with an alkyl group having 1-8 carbon atoms are preferred, and alkyl acrylates with an alkyl group having 1-5 carbon atoms are more preferable. The alkyl methacrylate with an alkyl group having 1-18 carbon atoms, , includes, for example, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, amyl methacrylate, isoamyl methacrylate, hexyl methacrylate, lauryl methacrylate. Of these, alkyl methacrylates with an alkyl group having 1-8 carbon atoms are preferred, and alkyl methacrylates with an alkyl group having 1-5 carbon atoms are more preferable. These compounds (alkyl acrylate and alkyl methacrylate) may be used alone or in admixture of two or more. The acrylate and/or methacrylate monomer units after polymerization should, preferably be 50 or greater weight percent of the total monomer units, and more preferably, should be 70 or greater weight percent in the acrylic modified fluoropolymer.

[0063] The ethylenically unsaturated compound copolymerizable with the alkyl acrylate and the alkyl methacrylate may optionally be a functional group-containing monomer copolymerizable with the alkyl acrylate and the alkyl methacrylate. The ethylenically unsaturated compound copolymerizable are generally used in amount of less than 29 weight percent based on the acrylic portion of the modified fluoropolymer. The functional group-containing monomers include, for example, α,β -unsaturated carboxylic acids such as acrylic acid, methacrylic acid, fumaric acid, crotonic acid, itaconic acid vinyl phosphonic and sulfonic acids; vinyl ester compounds such as vinyl acetate and the like; amide compounds such as acrylamide, methacrylamide, N-methylacrylamide, N-methylmethacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N-alkylacrylamide, N-alkylmethacrylamide, N,N-dialkylacrylamide, N,N-dialkylmethacrylamide; acrylic acid esters such as 2-hydroxyethyl acrylate, N-dialkylaminoethyl acrylate, glycidyl acrylate, fluoroalkyl acrylate; methacrylic acid esters such as dialkylaminoethyl methacrylate, fluoroalkyl methacrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate, ethylene glycol dimethacrylate ; and alkenyl glycidyl ether compounds such as allyl glycidyl ether; hydroxyl-containing monomers such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate, hydroxybutyl methacrylate, diethylene glycol ethyl

ether acrylate, polyethylene glycol acrylates and methacrylates, and polypropylene glycol acrylates and methacrylates; allyl ether methacrylate; acetoacetoxyethyl methacrylate; vinyl acetate; epoxy containing monomers such as glycidyl acrylate and glycidyl methacrylate; monomers containing cyclic substituents, such as cyclohexyl acrylate, tetrahydrofurfuryl acrylate and methacrylate, and isobornyl acrylate; monomers containing silanols; fluoroalkyl acrylates and methacrylates; acrylonitrile and methacrylonitrile. The functional group-containing monomer units may have more than one functional unit as part of their compositions, examples of which are polyol acrylates and methacrylates, including diol-diacrylates, diol-dimethacrylates, triol-triacrylates and triol-trimethacrylates, and tetraol-tetraacrylates, representative of which are 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, tetraethylene glycol diacrylate, tripropylene glycol diacrylate, ethylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,3-butanediol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, trimethylol propane triacrylate, trimethylolpropane trimethacrylate, and pentaerythritol tetraacrylate. Of these, preferred are acrylic acid, methacrylic acid, itaconic acid, fumaric acid, N-methylolacrylamide, N-methylolmethacrylamide, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate and allyl glycidyl ether. These ethylenically unsaturated compounds may be used alone or in admixture of two or more.

[0064] When both the alkyl acrylate and the alkyl methacrylate are used, the proportions of these two esters are not critical and can be appropriately varied depending upon the desired properties of the resulting fluorine-containing polymer. With the proviso that the major portion of the monomers (meaning greater than 50 wt percent of the acrylic portion) must be selected from acrylic esters and methacrylic esters and DAAM must be incorporated into the acrylic portion.

Emulsion Polymerization

[0065] The acrylic modified fluoropolymer composition can be obtained by emulsion-polymerizing 5-100 parts by weight, particularly preferably 5 to 95, preferably 20-90 parts by weight, of the acrylic monomer(s) mentioned above, in an aqueous medium in the presence of 100 parts by weight of the vinylidene fluoride polymer particles ("fluoropolymer seed") mentioned above. The emulsion polymerization can be run using ordinary emulsion polymerization conditions. The emulsion polymerization process is known in the art. In general, elements of conventional seeded emulsion polymerizations may include monomers, initiators, surfactants, chain-transfer agents, pH regulators, and chelating agents, some or all of which may be added to a seed latex to effect further polymerization. Temperatures used are normally in the range of 20 to 150 °C. The reactions are normally targeted to run at atmospheric pressure, but pressure might build and require venting, normally at less than 3 or 4 atmospheres. The reactions are normally run in inert atmospheres, such as under nitrogen. The emulsion-polymerization using the fluoropolymer seed, preferably vinylidene fluoride polymer as the seed, can be effected according to a known method, for example, a method wherein

the whole amount of the monomers is fed into the reaction system at one time in the presence of the fluoropolymer seed, preferably vinylidene fluoride polymer, a method wherein part of the monomers are fed and reacted and then the rest of the monomers is fed continuously or in portions, a method wherein the whole amount of the monomers is fed continuously, or a method wherein the fluoropolymer seed is added in portions or continuously while allowing the monomers to react. Different acrylic monomer mixtures can be sequentially polymerized around the fluoropolymer seed.

[0066] The fluoropolymer seed, preferably vinylidene fluoride polymer, may be added in any state to the polymerization system as long as they are dispersed in an aqueous medium in the form of particles. Since the vinylidene fluoride polymer is usually produced as an aqueous dispersion, it is convenient that the aqueous dispersion as produced be used as fluoropolymer seed. The particle diameters of the fluoropolymer seed, preferably vinylidene fluoride polymer, may vary depending upon the diameters of polymer particles present in an objective aqueous dispersion of said polymer but ordinarily is in the range of 50-900 nm. In a preferred embodiment, the diameter of the polymer particles is preferably 50 nm to 700 nm.

[0067] The acrylic portion of the AMF is made of acrylic polymer(s) which are made by successive polymerization of monomers on the fluoropolymer seed. The acrylic portion of the AMF can be just one acrylic polymer or can be two or more acrylic polymers. The acrylic polymers are generally acrylic copolymers. Some of the monomer units of the acrylic polymer(s) may optionally contain functional groups. As used herein, the weight percent of functional monomer means the weight percent of monomers having a functional group. Generally, successive polymerization of monomers on the fluoropolymer seed use different monomer compositions resulting in different acrylic polymers making up the acrylic portion of the AMF. As an example, a first monomer composition can contain methyl methacrylate, butyl acrylate and DAAM, and the second monomer composition, different from the first monomer composition, can contain methyl methacrylate, butyl acrylate, DAAM and methacrylic acid. The first monomer composition can be polymerized onto the fluoropolymer seed followed by a second polymerization of the second monomer composition resulting in two acrylic polymer making up the acrylic portion of the AMF.

Cross linker

[0068] The acrylic modified fluoropolymer resin is crosslinkable. The acrylic portion crosslinks using dihydrazide.

[0069] The hydrazine derivatives have at least two hydrazine residues. Aliphatic carboxylic acid dihydrazides having 2 to 10 carbon atoms can be used. Most common dihydrazides include adipic acid dihydrazide (ADH), sebacic acid dihydrazide (SDH), malonic acid dihydrazide, succinic acid dihydrazide,

glutaric acid dihydrazide, valine dihydrazide (VDH), isophthalic dihydrazide (IDH). Carbonic polyhydrazides such as carbonic dihydrazide, may also be used. Other hydrazine derivatives that can be used include di- hydrazine-triazine, thiocarbohydrazide, N, N'-diaminogliadin, hydrazine-pyridine derivative, bis-thiosemicarbazide, bishydrazine of alkylenebisacrylamide, di Examples thereof include hydrazine alkanes, dihydrazides of aromatic hydrocarbons or dihydrazides of monoolefinically unsaturated dicarboxylic acids. Aliphatic carboxylic acid dihydrazides having 2 to 10 carbon atoms are preferred and most preferred is Adipic acid dihydrazide.

[0070] The present invention is stable without the use of heavy metal ion. Heavy metals included copper, zinc, iron, chromium, manganese, lead, vanadium, cobalt and / or nickel.

[0071] The aqueous coating composition may contain additional polymer that is not part of the acrylic modified fluoropolymer. Additional polymer include latex-based binders such as polymers and copolymers based on acrylics and/or vinyls, acrylic latex, polyvinyl acetate (PVA) latex, styrene/butadiene latex, vinyl latex, vinyl acrylic latex, polyurethanes, polyesters, melamine resins, epoxies, and/or oils and other suitable monomeric species.

[0072] Coalescing solvents may also optionally be added to the formulations. The latex formulations will generally have low VOCs, below 100g/liter, preferably below 50 g/liter as defined in EPA Method 24.

[0073] The coating compositions may contain additives typical for use in a coating, including but not limited to, pH adjustment agents, UV stabilizers, foam control agents, wetting agents, pigments, pigment extenders, fillers, dyes, matting and texturing agents, pigment enhancers, emulsifiers, surfactants, dispersants, curing agents, coalescents, wetting agents, biocides, thickeners, rheology modifiers, plasticizers, waxes, anti-oxidants, antifoaming agents, antissettling agents, antiskinning agents, corrosion inhibitors, dehydrators, antigassing agents, dispersion aids, driers, antistatic additives, flash corrosion inhibitors, floating and flooding additives, in-can and in-film preservatives, insecticidal additives, optical whiteners, reodorants, water-soluble resins and other agents used in the art.

[0074] Pigments include colored and opacifying pigments. Pigment volume concentration is used in an amount of less than 40 volume percent, or less than 20 volume percent, based on dry components of the coating composition. Pigment volume concentration = volume of pigment/volume of total solids.

[0075] Colored pigments are finely ground natural or synthetic, insoluble particles used to impart color when added to paints and coatings compositions. Pigment refers to a class of organic or inorganic matter that is insoluble in water, not soluble in the use of media, but has been highly dispersed so that the colored matter is colored. Pigments used for coating are well known in the art. Non limiting examples of

pigments include anatine, brookite, cadmium yellow, cadmium red, cadmium green, orange cobalt, cobalt blue, cerulean blue, aureolin, cobalt yellow, copper pigments, azurite, Han purple, Han blue, Egyptian blue, malachite, Paris green, phthalocyanine blue BN, phthalocyanine green G, verdigris, viridian, iron oxide pigments, sanguine, caput mortuum, oxide red, red ochre, Venetian red, Prussian blue, clay earth pigments, yellow ochre, raw sienna, burnt sienna, raw umber, burnt umber, marine pigments (e.g., ultramarine, and ultramarine green shade), and zinc pigments (e.g., zinc white, and zinc ferrite).

[0076] Opacifying pigment reflect light and are used to make a coating opaque or less transparent. They prevent light transmission and provide ideal brightness and whiteness to the end product. The most commonly used is Titanium dioxide (TiO_2), Barium Sulphate, zinc oxide, calcium carbonate, talc, nepheline syenite and combinations thereof. The most common and preferred is TiO_2 . Extenders can also be added to the formulation. Suitable examples of extenders include precipitated grades of calcium carbonate, directly mined calcium carbonates, clean grades of magnesium calcium carbonate (Dolomite), clean grades of calcined, pulverized clays (aluminosilicates), and clean purified grades of magnesium silicate.

[0077] Coalescing agent- The coalescing agent may be a component of water-based latex or emulsion coating compositions. As the coating dries after being applied to a substrate, the purpose of the coalescent agent in these compositions is to aid the discrete particles of polymer that are present in the latex to form into a continuous film. Coalescent works by softening the polymer particles, allowing them to fuse into a tough, continuous film. Common coalescents include ester alcohols, esters, and glycol ethers, esters, alcohols, amides, and polymers.

[0078] The MFFT is the lowest temperature at which a binder agent or composition form a continuous film. A MFFT can be measured on a gradient temperature instrument in accordance to ASTM D 2354-10 (2012). An example of a suitable gradient temperature instrument is the Rhopoint Minimum Film Forming Temperature Bar (MFFT) is a self-contained bench top instrument available from Paul Gardner, Inc. Generally, coating composition of the invention can be applied to a substrate at temperatures above the MFFT of the composition. For example, an improved coating composition having an MFFT of 5 °C can be applied to a substrate and dried at ambient temperatures at or above about 5 °C. As can be appreciated, both the binder agent and the composition can have respective MFFT values. In certain embodiments, the AMF in the invention can exhibit an MFFT of about 25 °C or less in certain embodiments, an MFFT of about 15 °C or less in certain embodiments, an MFFT of about 5 °C or less in certain embodiments, or an MFFT of about 2 °C or less in certain embodiments.

[0079] For increased usability, the MFFT of a coating composition can be lowered in certain embodiments through inclusion of a suitable coalescing agent into the coating composition. Such

coalescing agents can generally be selected from slow evaporating solvents having elevated boiling points meaning between about 160 °C to about 240 °C. Non-limiting examples of suitable coalescing agents can include dipropylene glycol methyl ether, dipropylene glycol methyl ether acetate, dipropylene glycol n-butyl ether, ethylene glycol n-butyl ether, Texanol® ester-alcohol (Eastman Chemical Co.), and dipropylene glycol dimethyl ether. In certain embodiments, the coalescing agent can be about 2% or less of the total weight of the coating composition (including water), about 1.7% or less or about 1.5% or less of the total weight of the coating composition. As can be appreciated however, the lowest necessary quantity of a coalescing agent necessary to reach a suitable MFFT may be desired to allow for faster drying times and to ensure that the VOC of the coating composition remains below any applicable limits.

[0080] Plasticizers can also be added to lower the MFFT. Plasticizers can generally be distinguished from coalescing agents, however, by exhibiting a higher boiling point such as a boiling point of about 250 °C or more.

[0081] It is preferably the coating composition has a MFFT of less than 25C.

[0082] The aqueous coating composition of the invention is used as a coating on an architectural substrate, including but are not limited to wood, metal, plastic, and composites. The aqueous coating composition of the invention can be used for architectural coatings.

[0083] The aqueous coating composition may be used for field-applied protective coatings for structures or objects made out of typical building materials, for example wood, plastic, composites, cementitious substrates, stone, or metals- for instance, as the polymer binder for a highly weatherable topcoat on steel structures, such as bridges, tanks, or water towers, or in factory applied coatings on steel pipes. In some cases, as is well known in the protective coatings industry, they may be applied not directly over the substrate, but over a primer layer, or multiple layers of primer and midcoat, for improved adhesion and system corrosion performance. For instance, they may be used in pigmented topcoat formulations applied over an epoxy, polyamide, acrylic or alkyd primer on steel in a field applied protective coating, with the pigment(s) chosen to bring decorative as well as protective attributes to the coating.

[0084] The coatings may be applied in the field, without the application of additional heat, or they may be applied in a factory, optionally with the application of heat to accelerate the rate of removal of water and the development of full properties.

[0085] Within this specification embodiments have been described in a way which enables a clear and concise specification to be written, but it is intended and will be appreciated that embodiments may be variously combined or separated without parting from the invention. For example, it will be appreciated that all preferred features described herein are applicable to all aspects of the invention described herein.

[0086] EXAMPLES**[0087] Test Methods and Definitions**

[0088] Calculated glass transition temperatures were by use of the Fox equation as described in T.G. Fox Bull. Am. Phys. Soc. 1, 123 (1956) from accepted differential scanning calorimetry measured values.

[0089] MMA means methyl methacrylate. BA means butyl acrylate. DAAM means diacetone acrylamide. MAA means methacrylic acid. The ratio of the monomers in the examples is by weight.

[0090] Solids contents of latexes were measured gravimetrically on samples of weights of at least 1 gram. Weight percent solids were measured using a drying temperature of 125 °C, with an endpoint indication of 1 mg mean weight loss over a period of 50 seconds.

[0091] Example 1 (Resin 1): Preparation of acrylic modified fluoropolymer composition with diacetone acrylamide (DAAM)

[0092] A polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) copolymer latex was used as seed to synthesize a latex containing acrylic modified fluoropolymer composition using emulsion polymerization process. To a 2 liter reactor were added 1400g of PVDF-HFP copolymer latex seed and 100g of deionized water. The reactor was purged with Argon/Nitrogen, followed with low flow rate Argon/Nitrogen purge through the reaction. The reactor was agitated at 160rpm while 120.0g of monomer mixture (36.5MMA/9.5BA/4.0DAAM by weight) was fed into the reactor in 30 minutes. An initiator solution (1.7g of VAZO-67 in 17.0g of TPM (Tripropylene glycol methyl ether)) was also added during this period. Then the reactor was agitated at room temperature for 30 minutes followed by heating to 75°C. The reactor was hold at 75 °C for 30 minutes. 120.0g of monomer mixture (34.3MMA/9.8BA/4.0DAAM/1.9MAA) was then fed into the reactor in 60 minutes. The reactor was hold at 75 °C for additional 10 minutes. Chase catalyst and activator (t-butyl hydroperoxide/sodium metabisulfite) solutions were fed into the reactor in 30 minutes while the reactor was cooling to room temperature. Neutralizer (NH₄OH) and biocide (Proxel BZ Plus) were charged when reactor temperature was below 50 °C. At 30 °C, agitation was stopped, and the reactor was drained. Solids content (47.8%), pH (8.3), particle size (178nm) were measured on the obtained latex.

[0093] Example 2 (Resin 2): Preparation of acrylic modified fluoropolymer composition with diacetone acrylamide (DAAM)

[0094] A polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) copolymer latex was used as seed to synthesize a latex containing acrylic modified fluoropolymer composition using emulsion polymerization process. To a 2 liter reactor were added 1400g of PVDF-HFP copolymer latex seed and 100g of deionized water. The reactor was purged with Argon/Nitrogen, followed with low flow rate Argon/Nitrogen purge

through the reaction. The reactor was agitated at 160rpm while 120.0g of monomer mixture (26.1MMA/19.9BA/4.0DAAM by weight) was fed into the reactor in 30 minutes. An initiator solution (1.7g of VAZO-67 in 17.0g of TPM (Tripropylene glycol methyl ether)) was also added during this period. Then the reactor was agitated at room temperature for 30 minutes followed by heating to 75 °C. The reactor was hold at 75 °C for 30 minutes. 120.0g of monomer mixture (23.6MMA/20.6BA/4.0DAAM/1.8MAA) was then fed into the reactor in 60 minutes. The reactor was hold at 75 °C for additional 10 minutes. Chase catalyst and activator (t-butyl hydroperoxide/sodium metabisulfite) solutions were fed into the reactor in 30 minutes while the reactor was cooling to room temperature. Neutralizer (NH₄OH) and biocide (Proxel BZ Plus) were charged when reactor temperature was below 50 °C. At 30 °C, agitation was stopped, and the reactor was drained. Solids content (47.8%), pH (8.3), particle size (178nm) were measured on the obtained latex.

[0095] Comparative Example 1 (Resin 3): Preparation of acrylic modified fluoropolymer composition with acetoacetoxy ethyl methacrylate (AAEM)

[0096] A polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) copolymer latex was used as seed to synthesize a latex containing acrylic modified fluoropolymer composition using emulsion polymerization process. To a 2 liter reactor were added 1400g of PVDF-HFP copolymer latex seed and 100g of deionized water. The reactor was purged with Argon/Nitrogen, followed with low flow rate Argon/Nitrogen purge through the reaction. The reactor was agitated at 160rpm while 120.0g of monomer mixture (36.5MMA/9.5BA/4.0AAEM by weight) was fed into the reactor in 30 minutes. An initiator solution (1.7g of VAZO-67 in 17.0g of TPM (Tripropylene glycol methyl ether)) was also added during this period. Then the reactor was agitated at room temperature for 30 minutes followed by heating to 75 °C. The reactor was hold at 75 °C for 30 minutes. 120.0g of monomer mixture (34.3MMA/9.9BA/4.0AAEM/1.8MAA) was then fed into the reactor in 60 minutes. The reactor was hold at 75 °C for additional 10 minutes. Chase catalyst and activator (t-butyl hydroperoxide/sodium metabisulfite) solutions were fed into the reactor in 30 minutes while the reactor was cooling to room temperature. Neutralizer (NH₄OH) and biocide (Proxel BZ Plus) were charged when reactor temperature was below 50 °C. At 30 °C, agitation was stopped and the reactor was drained. Solids content (47.7%), pH 8.1, particle size (175nm) were measured on the obtained latex.

[0097] Comparative Example 2 (Resin 4): Preparation of acrylic modified fluoropolymer composition

[0098] A polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) copolymer latex was used as seed to synthesize a latex containing acrylic modified fluoropolymer composition using emulsion polymerization process. To a 2 liter reactor were added 1400g of PVDF-HFP copolymer latex seed and 100g of deionized water. The reactor was purged with Argon/Nitrogen, followed with low flow rate Argon/Nitrogen purge through the reaction. The reactor was agitated at 160rpm while 120.0g of monomer mixture (40 MMA/10

BA by weight) was fed into the reactor in 30 minutes. An initiator solution (1.7g of VAZO-67 in 17.0g of TPM (Tripropylene glycol methyl ether)) was also added during this period. Then the reactor was agitated at room temperature for 30 minutes followed by heating to 75 °C. The reactor was hold at 75 °C for 30 minutes. 120.0g of monomer mixture (37.4 MMA/10.2 BA/2.4 MAA) was then fed into the reactor in 60 minutes. The reactor was hold at 75 °C for additional 10 minutes. Chase catalyst and activator (t-butyl hydroperoxide/sodium metabisulfite) solutions were fed into the reactor in 30 minutes while the reactor was cooling to room temperature. Neutralizer (NH₄OH) and biocide (Proxel BZ Plus) were charged when reactor temperature was below 50 °C. At 30 °C, agitation was stopped, and the reactor was drained. Solids content (44%), pH (8.0), particle size (185nm) were measured on the obtained latex.

[0099] Resins from Example 1, Example 3 were following same synthesis route, and used same PVDF-HFP copolymer latex seed. The difference between Example 1 and Example 3 is the type of functional monomer with keto-functionality, resin 1 with diacetone acrylamide (DAAM) and resin 3 with acetoacetoxy ethyl methacrylate (AAEM).

[0100] Preparation of grey colored paints

[0101] Each grey colored paint (A, B, C and D) was prepared from the following mixture of ingredients in Table 2. In comparison, A and C both used resin 1, but A used freshly made resin 1 and C used heat-aged resin 1 with adipic acid dihydrazide. B and D both used resin 3, but B used freshly made resin 3 and D used heat-aged resin 3 with adipic acid dihydrazide. Heat aged resins with adipic acid dihydrazide were made in the following process: first mixing resins with adipic acid dihydrazide, then putting the mixtures in sealed glass jars, then putting the sealed glass jars in the 50 °C oven for 4 weeks. After 4 weeks in 50 °C oven, the heat aged resin mixtures were formulated into C and D with the other ingredients in the formula.

Table 1. Grey colored paints.

Ingredients	Paints (grams)				
	A	B	C	D	E
Resin 1 from Example 1	100	-	100	-	-
Resin 3 from Comparative Example 1	-	100	-	100	-
Resin 4 from Comparative Example 2	-	-	-	-	108
ADH ¹	0.47	0.37	0.47	0.37	-
Byk 346 ²	0.3	0.3	0.3	0.3	0.3
Dowanol DPM ³	7.2	7.2	7.2	7.2	7.2
Pigment dispersion ⁴	32.0	32.0	32.0	32.0	32.0

¹ Adipic acid dihydrazide, available from Millipore Sigma.

² Dewetting agent available from BYK Chemie (Wesel, Germany).

³ Dowanol DPM, Dipropylene glycol methyl ether, available from The Dow Chemical.

⁴ A mixture of deionized water (56.0 grams), Tamol 165A (5.1 grams, available from The Dow Chemical.), aqueous ammonia with a concentration of 28% (0.3 grams), Surfynol AD-01 (1.1 grams,

available from Evonik), Shepherd black 30C965 (52.0 grams), and R-960 TiO₂ (191.0 grams, available from The Chemours Company), grinded into a dispersion with a Hegman rating of 7 or above.

[0102] The paints were drawdown on chromated aluminum substrates (AL-412, available from Q-lab) using BYK square frame applicator with 8 mils gap. The drawdown film was dried and cured at ambient temperature for 10 days before solvent resistance test.

[0103] The solvent resistance test was performed on each cured coating composition using the following procedure:

1. Place the test panel on a flat table or other suitable flat firm surface.
2. Affix a piece of Felt over the ball end of a one-pound Ball-Peen hammer. The Felt should be snugly held in place with a rubber band.
3. Saturate the Felt with the appropriate solvent (methyl ethyl ketone (MEK) was used for these tests) for the material being tested, gauze should be re-saturated every 50 double rubs.
4. Immediately rub the saturated gauze over the test area using a back and forth stroke of ~4-6 inches.
5. Do not exert any downward or upward pressure on the hammer handle. The weight of the hammer controls the downward pressure.
6. Continue this back and forth action counting one "double rub" for each forward and backward motion completed until bare substrate is exposed in the center of the strip where the rubs are performed.
7. Record the test result as the number of double rubs required to expose bare substrate in the center of the rub strip.
8. After the testing of each individual sample, the Felt was removed and replaced with a piece of Felt.

[0104] Paint A through paint E were drawdown on PVC (polyvinyl chloride) substrate using BYK square frame applicator with 8 mils gap. The drawdown film was ambient flash at room temperature for 10 minutes and then cured at 50 °C for 30 minutes before detergent resistance test. Detergent resistance test is based on AAMA 2605-13.

[0105] The solvent resistance test results (MEK double rubs) and detergent resistance results are shown in Table 2.

Table 2. Solvent resistance (MEK double rubs) of the cured panels out of paint A, B, C, and D.

Panels out of Paint	MEK double rubs	Detergent resistance test
A - Invention	50	Passed
B (AAEM) comparison	100	Failed
Aged C -Invention	50	Passed

Aged D (AAEM) comparison	15	Failed
E (no x-linking)	8	Blistered/failed

[0106] It was noted that the AAEM containing AMF composition (aged D) exhibited a pink color after being aged. The DAAM containing AMF composition (Aged C) did not show any color change during aging.

[0107] Panels made out of Paint A and Paint C had similar solvent resistance, but panels made out of Paint B and Paint D had significant difference in solvent resistance. The results indicated resin 1 with DAAM functionality had good heat aging stability, while resin 2 with AAEM functionality had poor heat aging stability. The poor stability was also consistent with the color change before and after hot room stability test.

[0108] Comparing A and C this showed that aging of the composition did not affect the solvent resistance with the use of DAAM in the acrylic modified fluoropolymer. Comparing B and D this showed that aging of the composition did affect the solvent resistance with the use of AAEM in the acrylic modified fluoropolymer. The solvent resistance of the composition using AAEM was severely reduced with aging shown by the MEK double rubs degrading from 100 with fresh polymer to 15 using the aged polymer.

[0109] In detergent resistance test, PVC panel coated with paint E (no cross linking) blistered badly and failed the test, while PVC panel coated with paint A and C (containing DAAM) passed the detergent resistance test. PVC panel coated with paint B and D (containing AAEM) failed the detergent resistance test.

[0110] DAAM was stable and provided solvent resistance and passed the detergent resistance test. Stable means after one month in a 50 °C oven, the composition performed with no more than a 10% difference in the double rub test as compared to the fresh made composition.

[0111] Clearcoat Formulation:

[0112] Approximately 65-75 g of neutralized latex both 100% acrylic and acrylic modified fluoropolymer dispersion latex (having a PVDF seed), (35 g of resin solids), were admixed with Texanol® ester-alcohol (coalescent, 0.7 g), BYK-346 (wetting agent, 0.5 g) and water (to obtain 40% volume solids) to obtain a clearcoat. These clearcoats were drawn down over Leneta Opacity charts with a 6 mil doctor blade to determine their dry film properties. (ASTM D4062-11 Standard Test Method for Leveling of Paints by Draw-Down Method). Clearcoats were cured at either 25 °C/ 50 % relative

humidity or 5 °C for at least 12 hours. Gloss was then measured. After 1 week of curing at ambient conditions (25 °C/50% RH), dirt pick up resistance was measured.

[0113] Dirt Pick Up Resistance is measured testing using an aqueous slurry comprised of hydrophobic carbon black (Birla Raven 22) and BYK 346 as a wetting agent. The slurry is applied onto the dried coating at room temperature for 4 hours, and then gently rinsed away with cold water and a paper towel. ΔE^* measurements on made after the film has dried, comparing the soiled versus unsoiled parts of the coating. Lower ΔE^* indicate better Dirt Pick Up Resistance.

[0114] Acrylic 1 is a commercial acrylic latex with a minimum film formation temperature (MFFT) of 15 °C and a weight % solids of 58%.

Table 3

(amount of each component is in grams)	Run 1	Run 2
Acrylic 1	43.4	43.4
Resin 3 from Comparative Example 2- no ketone functionality	22.9	
Resin 2 from Example 2 (DAAM functional)		21.1
adipic acid dihydrazide	0	0.12
Texanol® ester-alcohol	0.7	0.7
BYK-346	0.2	0.2
Water	11.6	11.6
Coapur™ XS-71 (50% in water)	0.4	0.4
Total (grams)	78.8	78.8
Total polymer solids (grams)	35.2	35.2
Weight % Solids	44.9%	44.9%
volume solids %	40.0%	40.0%
DPUR (ΔE^*)	8.4	13.9
Gloss @ 25 °C	34.5	79.7
Gloss @ 5 °C	Cracked	74.5

These examples showed that the acrylic modified fluoropolymer containing DAAM allowed for higher gloss at room temperature and prevented cracking at low temperature curing while maintaining similar performance of dirt pick up performance.

What is Claimed is:

1. An aqueous coating composition comprising
 - i.) an acrylic modified fluoropolymer comprising a fluoropolymer portion and an acrylic portion
 - ii) a dihydrazide, and
 - iii) optionally additional polymer that is not part of the acrylic modified fluoropolymer,wherein the acrylic modified fluoropolymer composition comprises at least 1 wt% DAAM and up to 20 weight percent based on total acrylic monomer units in the acrylic modified fluoropolymer composition.
2. The aqueous coating composition of claim 1, wherein the aqueous coating composition comprises greater than 50wt% polymer based on total solids content of the aqueous coating composition.
3. The aqueous coating composition of claim 1, wherein the acrylic portion further comprises an acrylic or methacrylic monomer with acid functionality.
4. The aqueous coating composition of claim 1, wherein the acrylic portion of the acrylic modified fluoropolymer further comprises a (meth)acrylic acid from 0.01 to 10% based on total acrylic monomer units in the acrylic modified fluoropolymer composition.
5. The aqueous coating composition of claim 1, wherein the molar ratio of dihydrazide to DAAM is between 0.02 and 0.5.
6. The aqueous coating composition of claim 1, wherein the aqueous coating composition further comprises a pigment.
7. The aqueous coating composition of any one or more of claim 1 to 6, wherein the aqueous coating composition further comprises an acrylic polymer that is separate from the acrylic modified fluoropolymer.
8. The aqueous coating composition of claim 1, wherein the additional polymer that is not part of the acrylic modified fluoropolymer is selected from polymers and copolymers based on at least one of acrylics, vinyls, polyurethanes, polyesters, melamine resins, or epoxies.
9. The aqueous coating composition of any one or more of claim 1 to 6, wherein the additional polymer that is not part of the acrylic modified fluoropolymer comprises at least one of acrylic latex, polyvinyl acetate (PVA) latex, styrene/butadiene latex, vinyl latex or vinyl acrylic latex.
10. The aqueous coating composition of any one or more of claim 1 to 6, wherein said fluoropolymer portion comprises 50 to 100 weight percent of vinylidene fluoride units, and 0 to 50 weight percent of monomer units copolymerizable with vinylidene fluoride based on weight of fluoropolymer portion, preferably said fluoropolymer portion comprises 50 to 100 weight percent of vinylidene fluoride units.
11. The aqueous coating composition of any one or more of claim 1 to 6, wherein the fluoropolymer portion comprises from 3 to 30 wt% hexafluoropropylene units based on the total weight of the

fluoropolymer portion.

12. The aqueous coating composition of any one or more of claim 1 to 6, wherein the fluoropolymer portion comprises a polyvinylidene fluoride-hexafluoropropylene copolymer, wherein the total weight percent of hexafluoropropylene monomeric units in the acrylic modified fluoropolymer is from 5 to 20%, preferably from 10 to 20 wt% based on the weight of acrylic modified fluoropolymer.
13. The aqueous coating composition of any one or more of claim 1 to 6, wherein the total weight percent of acrylic monomeric units in the acrylic modified fluoropolymer is from 10 to 50 wt%, preferably, from 15 to 40 wt% in the acrylic modified fluoropolymer.
14. The aqueous coating composition of any one or more of claim 1 to 6, wherein said acrylic modified fluoropolymer comprises from 3 to 100 weight percent of the total polymer in the aqueous coating composition.
15. The aqueous coating composition of any one or more of claim 1 to 6, further comprising UV stabilizers, pH adjustment agents, colorants, dyes, water soluble resins, rheology control additives and thickeners, and pigments and pigment extenders, and filler.
16. A method of coating a substrate comprising providing a substrate, providing the coating composition of any one or more of the preceding claims, applying the coating composition to the substrate, drying the coating composition on the substrate to form a coated substrate.
17. A coated substrate comprising a substrate having coated on at least one surface with the aqueous coating composition of any one or more of claims 1-15 and wherein said coating composition is dried to form a coated substrate.
18. The coated substrate of claim 17, wherein said substrate is selected from the group consisting of primed or unprimed metals, wood, glass, plastic and composites.
19. The coated substrate of claim 18, wherein the coating is an exterior coating selected from architectural coating, marine coating, and protective coating.
20. Use of the aqueous coating composition of any one or more of claims 1 to 15 in exterior construction.
21. An aqueous coating composition comprising
 - i.) an acrylic modified fluoropolymer comprising a fluoropolymer portion and an acrylic portion
 - ii) a dihydrazide, and
 - iii) additional polymer that is not part of the acrylic modified fluoropolymer, and
 - iv) pigment,

wherein the acrylic modified fluoropolymer composition comprises DAAM monomer units, wherein the aqueous coating composition comprises greater than 50wt% polymer based on total solids content of the aqueous coating composition,

wherein the acrylic portion further comprises an acrylic or methacrylic monomer with acid

functionality, and wherein the molar ratio of dihydrazide to DAAM is between 0.02 and 0.5.

22. The aqueous coating composition of claim 21, wherein the acrylic portion of the acrylic modified fluoropolymer further comprises a (meth)acrylic acid from 0.01 to 10% based on total acrylic monomer units in the acrylic modified fluoropolymer composition.