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(54) Title: FAST DRYING WATERBORNE COATINGS

(57) Abstract: Coating and ink formulations are disclosed that are comprised of an anionically colloidally stabilized copolymer dispersion, a polyamine additive that can react with anionic groups, and a volatile base that can help shift the pH of the copolymer dispersion early in the drying process of films or coatings from the copolymer dispersion. The formulations are used in construction and roof coatings.

FAST DRYING WATERBORNE COATINGS

FIELD OF INVENTION

[0001] The present invention relates to anionically colloidally stabilized polymer dispersions with a polyamine additive that as a coating or film show early development of resistance to washing off and damage by rain or other water sources. The polyamine additive of this disclosure can be added to the formulated paint during manufacture or just before using the paint and results in a long shelf life for the formulated paint. In the construction and roofing industries, early development of water resistance in coatings is desirable as it minimizes damage to freshly applied paint surfaces that may be exposed to an unexpected rain shower or other water exposure.

BACKGROUND OF THE INVENTION

[0002] Polyamine curatives are known in the road marking industry for their ability to help speed the conversion of a dispersion of binder, pigments, etc. in a continuous media to an aggregated material, continuous film or dry film.

[0003] US 5,527,853 (equivalent to EP0409459) discloses a shelf stable fast-cure Aqueous coating composition using a polyfunctional amine and a volatile base.

[0004] US 5,705,560 discloses an aqueous coating composition using a latex having anionic property, a water-soluble polymer formed from a monomer mixture containing at least 20 wt.% of amine functional groups containing monomer and a volatile base to raise the pH.

[0005] US 7,892,131 discloses a fast drying aqueous composition suitable for use in making roadway markings from a composition comprising an anionically stabilized binder having phosphorus acid functional polymer component, a polyfunctional amine component and a volatile base.

[0006] US2015/0259559 to BASF discloses compositions containing anionically stabilized copolymer dispersions, a volatile base, and a derivatized polyamine that functions to decrease the setting time of the anionically stabilized copolymer dispersions.

SUMMARY OF THE INVENTION

[0007] Polyfunctional amines of various types have been used with anionically stabilized polymer dispersions and emulsions as curatives for fast dry roadway marking. Improvements in the polyfunctional amine additive are possible for other coatings by incorporating repeating

units into the polyamine of side-chain poly(alkylene oxide) of specific molecular weight. The repeating units with side-chain poly(alkylene oxide) provide better in-can stability of the coating (minimizing undesirable reactions between the polyamine additive and the polymer binder particles during storage), and provide better moisture permeability and evaporation rates after the initial aggregation of the dispersed polymer in the drying step than does prior art polyamine additives.

[0008] Polyamine additives function with anionically stabilized polymer dispersions and emulsions by being available to interact anionic groups, such as carboxylic acid, and aggregate multiple polymer particles into aggregates that speed the colloidal destabilization of the polymer particle dispersion forming a water resistant film surface (with dispersion including emulsions). The reaction of the amine groups of the polyamine is hastened by a pH change (often associated with evaporation of base by volatilization of a volatile amine during drying). Different amine groups (e.g., primary, secondary, tertiary, and quaternized amine groups) react with anionic groups at different reaction rates and form bonds (amide, salt, etc.) of different durability.

[0009] The poly(alkylene oxide) side-chains of the currently disclose polyamine additive slow down the interaction of the nitrogen of the polyamine with the surface anionic groups of the polymer particles until the appropriate time in the film formation process. This may be due to steric factors where the polyalkylene oxide physically separates the amine from the anionic groups on the particles. As any volatile base present in the coating composition becomes more deficient at the film interface during drying of the film, the polyamine additive becomes more active at the surface of a film than the layers below the surface because of the faster pH change from pH basic towards pH neutral or slightly acidic occurs fastest at the film surface with surrounding air.

[0010] After the polyamine additive forms aggregates, because the bonds between the polyamine additive and anionic groups on the polymer particles are ionic interactions or covalent bonds, the addition of water in the form of rain does not cause the particles to de-aggregate and the aggregated polymer particles repel the water from the surface and protect the coating composition (or film) below them from becoming diluted or washed off with the rain or water. At the same time, the side-chain poly(alkylene oxide) within the polyamine additive is porous to moisture vapor from the coating composition in a film and allows evaporation to

proceed from a film at effective rates to allow the film to dry quickly. Absent the polyamine additive of this disclosure, the skin on a drying coating film has very little porosity and can slow the evaporation of water from deeper within the film to the surface.

DETAILED DESCRIPTION OF THE INVENTION

[0011] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0012] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. The use of (meth) in a monomer or repeat unit indicates an optional methyl group, such as methyl (meth)acrylate.

[0013] The use of (meth) in a chemical name in this document is meant to indicate that a methyl substituent is optionally present. Thus, the term "(meth)acrylate monomer" includes acrylate, methacrylate, diacrylate, and dimethacrylate monomers.

[0014] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, the polyamine species can react to form coupled material with the polymer dispersions. The polymer dispersions can aggregate, close pack with the volatilization of the continuous phase, and fuse into polymer masses such as films. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

[0015] In this disclosure, we will use the term polymer dispersion to describe dispersions of polymer having a number average particle size from about 50 nanometers to about 10 micrometers; more desirably 80 nanometers to 5 microns by light scattering, irrespective of whether the polymer dispersions were made by dispersing a pre-synthesized polymer in an

aqueous media or forming a polymer dispersion by an emulsion polymerization process. These particle sizes are common for many different types of polymers and can be colloidally stable for long periods of time provided a good steric or electrostatic barrier is provided to each particle as Brownian motion is generally sufficient to keep polymer particles of these sizes randomly distributed in an aqueous media even though the polymer has lower density than the aqueous phase and might otherwise (if the particles were larger in diameter) cream to the top of the vessel or container. Some authors for their own reasons distinguish between polymer dispersions and polymer emulsions, but in this disclosure the word polymer dispersion will mean polymer dispersions made by dispersing polymer in aqueous media and polymer dispersions made by emulsion polymerization.

[0016] It is the intent of coating formulators that additives/curatives added to polymer dispersions and emulsions should remain inactive in the formulation (composition) until the time when the formulator desires the composition to form a film. It is the desire of the formulator that the additives/curative(s) not interact via chemical reactions with the dispersed polymer during storage of the composition prior to film formation. Desirably, colloidal stability of polymer dispersions and dispersions of fillers, pigments, and other dispersed components to the coating remain colloidally stable for months and potentially year (minimizing waste of coating formulations due to shelf life constraints or slow inventory turnover). However, curatives tend to interact with polymer dispersions during storage and during times of colloidal stability reduction and can cause aggregates of polymer particles during storage.

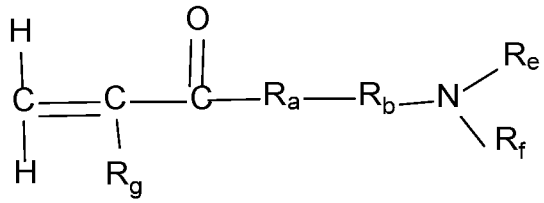
[0017] While, not wishing to be bound by theory, it is believed that the repeating units having side chain poly(alkylene oxide) of molecular weight from about 132 to about 1100 g/mole when incorporated into the polyamine additive in the amounts specified herein provide an environment for the amine groups of the polyamine additive of this disclosure within the continuous aqueous phase where the amine groups are partially sterically hindered from interacting with anionic colloidal stabilizing groups on the dispersed polymer phase while the composition is at high pH above 7, more desirably from 7.5 or 8.5 to 12.5 and preferably from 8.5 or 9 to 10.5 or 11. Longer storage times benefit from higher pH values. The pH value can be very near the lower limit if the polyamine additive is only added a few hours or days before use of the coating composition. Formulated paints tolerate the polyamine additive at lower pH

values than non-formulated polymer dispersions. Poly(alkylene oxide) chains incorporated in the backbone of the polyamine generally don't provide the same environment as side chain or pendant poly(alkylene oxide) chains. Poly(alkylene oxide) chains lower in molecular weight than 132 or above 1100 g/mole do not provide the optimal environment for this steric effect on the interaction of the amine groups of the polyamine with anionic stabilizing groups on the polymer dispersion. It is also theorized that the poly(alkylene oxide) of molecular weight from 132 to 1100 inclusive of the end points can allow, when the pH is dropped, the interaction of the amine groups of the additive with the anionic groups on the particles surfaces and help form a water resistant coating surface when coating compositions formulated with the polyamine additive of this disclosure are applied as a film to a surface. This additive effect protects the film from the coating compositions from smudging and protects the coatings from water if the coatings would happen to get rained upon or see water spray from some other source.

[0018] So, the benefit of the polyamine additive of this disclosure is that it can have very long shelf stability at room temperature (arbitrarily 22-25°C) or even at elevated temperatures of a warehouse such as 48.9°C (120°F) when formulated into an anionically or partially anionically and partially non-ionically stabilized colloidally stabilized polymer dispersion or coating composition including such a polymer dispersion. The polyamine additive of this disclosure can also cause a polymer dispersions and/or coating composition with such polymer dispersion to form a water resistant film surface within a shorter period of time than the identical polymer dispersion or coating composition without the amine additive (enhancing quick film formation and resistance to water and/or smudging of the film or coating). The polyamine additive in some formulations seems to act as a flash rust inhibitor (minimizing rust colored stains and/or formation of corrosion on metal surfaces) as the coating composition dries on a metal surface.

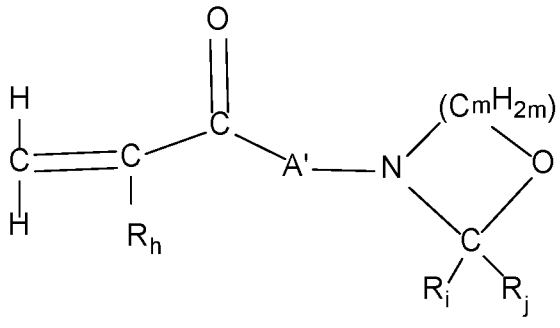
[0019] The amine additive of this disclosure is a polyamine additive derived from polymerizing at least two different monomers and optionally including repeating units from other co-polymerizable monomers. The first monomer can be a free radically polymerizable tertiary amine monomer of the formula A_1 or A_2 or a blend thereof. The tertiary amine monomer is desirably present as repeating units in the amount from about 30 to about 90 wt.%, more desirably from about 55 to about 85 wt.% of the amine additive, preferably from about 60 to about 80 wt.% and more preferably from about 65 to 75 wt.% of the amine additive.

[0020] The A_1 monomer is according to the formula:



A_1

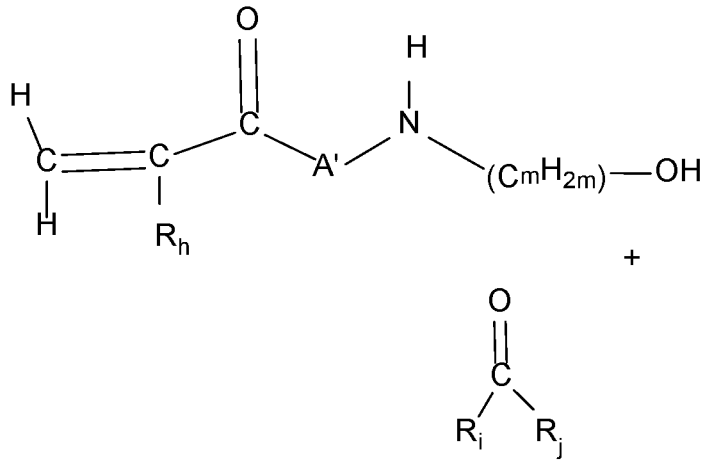
and the A_2 monomer is according to the formula:



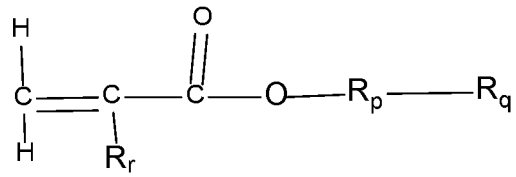
A_2

wherein R_a is O or NR_k, R_b is a C_1 to C_6 alkylene, R_e is a C_1-C_4 alkyl, R_f is a C_1-C_4 alkyl, R_g is H or methyl or ethyl, R_h is H or a CH_3, and R_k is H, a C_1-C_4 alkyl, or a C_1-C_4 acyl group, A' is poly(oxy-C_2H_4 and/or oxyC_3H_6) homopolymer or copolymer of number average molecular weight of 88-348g/mole, m is 2 or 3, Ri is selected from a group comprising hydrogen, phenyl group, benzyl group, and a C_1-C_{12} alkyl group if it is not liked directly to Rj to form a cyclic ring with the C atom connected to R_i and R_j, Rj is selected from a group comprising hydrogen, a C_1-C_4 alkyl group, if it is not linked directly to Ri, and optionally Ri and Rj can be link together with a chemical covalent bond to form a C_4 or C_5 alkylene group forming a five or 6 membered ring with the C atom to which they are bonded in the structure A_2 above.

[0021] An interesting feature of the A_2 monomer and the repeating unit from the A_2 monomer is that it can react with water and the tertiary amine group can become a secondary amine and the monomer or repeating unit is hydroxyl terminated and a ketone group (leaving group) is formed. While it is the intent of the authors of this disclosure to use A_2 in the form as specified it is noted that some portion (such as 5, 10, 20, 30 or 50 wt.% of the A_2 monomer may be in the form shown below or the obvious repeating unit derived from polymerizing this monomer.



[0022] The other required monomer (B) is a poly(alkylene oxide) monomer or repeating unit from this monomer. These are commercially available under the Bisomer trademark from GEO Specialty Chemicals, Inc. or can be made by esterifying an acrylic or (alk)acrylic acid with a poly(alkylene oxide)



B

wherein R_p is a polyalkylene oxide of number average molecular weight from about 88 to about 1200 g/mole, more desirable from about 132-1100; with 2 or 3 or 4 carbons per alkylene group (more desirably at least 90 wt.% of the alkylene oxide groups are ethylene oxide), R_q is H or C_1-C_8 alkylene group and more desirably H, methyl or ethyl, and R_r is H or methyl or ethyl.

[0023] The repeating units from polymerizing the B monomer (side chain poly(alkylene oxide) monomer) is desirably present from about 10 to about 60 wt.% of the amine additive of this disclosure, more desirably from about 15 to about 45 wt.%; preferably from about 20 to about 40 wt.% and more preferably from about 25 to about 35 wt.% of the amine additive.

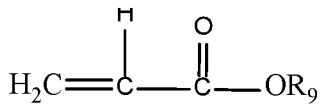
[0024] An optional third, fourth, etc. repeating unit or monomer(s) defined as (C) could be present in the amine additive, provided the specified amount of tertiary amine repeating units and poly(alkylene oxide) monomer are present as recited above. The optional third or more monomer is desirably present from about 0 to about 60 wt.% of the repeating units of said amine additive, more desirably from about 0 to about 30 wt.% of other repeating units from

free radically polymerizable monomers, preferably from about 0 to about 10 or 20 wt.% of said repeating units and more preferably from about 0 to about 5 wt.% of the repeating units in the amine additive other than monomer A_1 and/or A_2 and monomer B, free radical initiator fragments, and chain transfer molecule fragments.

[0025] In one embodiment of the general disclosure, it is desirable that a C repeating unit or monomer forming the C repeating unit, if it is n-vinyl pyrrolidone or the repeating unit from n-vinyl pyrrolidone is not present at 10 wt.% or above in the amine additive of this disclosure.

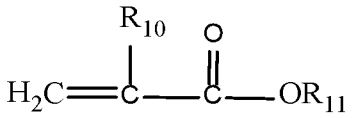
[0026] Suitable polyamine curing additives can possess a variety of molecular weights and degrees of nitrogen-derivatization. For example, the polyamine curing additive can have an average molecular weight of between 500 and 5,000,000 and preferably between 1,000 and 500,000 Daltons. In some embodiments, the polyamine curing additive is present in the coating composition at between 0.1% by weight and 5% by weight, based on the dry weight of the anionically colloidally stabilized copolymer.

[0027] Various additional monomers can optionally be copolymerized with the prepolymer. For instance, the acrylic polymer or copolymer can be derived from a variety of unsaturated monomers such as from acrylate, alkyl (alk)acrylate, vinyl chloride, vinylidene chloride, vinyl acetate, styrene, and dienes such as butadiene. The various alkyl acrylates (or esters of acrylic acid) are of the formula:



wherein R_9 is an alkyl group containing one to about 15 carbon atoms, an alkoxyalkyl group containing a total of one to about 8, 9 or 10 carbon atoms, a cyanoalkyl group containing one to about 10 carbon atoms, or a hydroxy alkyl group containing from one to about 18 carbon atoms. The alkyl structure can contain primary, secondary, or tertiary carbon configurations and normally contains one to about 10 carbon atoms with 2 to 8 carbon atoms being preferred. Examples of such acrylic esters include methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-pentyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-methylpentyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, n-decyl acrylate, n-dodecyl acrylate, n-octadecyl acrylate, and the like. Preferred examples include ethylacrylate, butyl acrylate, 2-ethyl hexyl acrylate, and the like.

[0028] The various alkyl alkacrylates (or esters of alkacrylic acid) are of the formula:



wherein R_{10} is H or a C_{1-2} alkyl, and R_{11} is an alkyl group containing one to about 15 carbon atoms, an alkoxyalkyl group containing a total of one to about 10 carbon atoms, a cyanoalkyl group containing one to about 10 carbon atoms, or a hydroxy alkyl group containing from one to about 18 carbon atoms (as described above). Examples of various alkyl (alk)acrylates include methyl methacrylate, ethyl methacrylate, methoxymethyl acrylate, methoxyethyl acrylate, ethoxyethyl acrylate, butoxy ethyl acrylate, ethoxypropyl acrylate, and the like. Derivatives include hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, and the like. Mixtures of two or more of the above monomers can also be utilized.

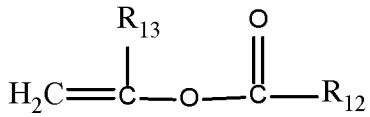
[0029] Unsaturated carboxylic acid containing monomers are not intentionally used in the polyamine additive. These monomers not intentionally included are acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, 2-carboxyethyl acrylate and the like. Half esters of the above di-carboxylic acids are not intentionally added to the polyamine additive to be used as monomers wherein the ester portion is desirably an alkyl having from one to about 10 carbon atoms and specific examples include mono methyl maleate, mono methyl fumerate, mono methyl itaconate, and the like.

[0030] Other co-polymerizable (ethylenically unsaturated) monomers may be utilized to make copolymers including styrenic monomers (as a co-monomer in amine additive), vinyl chloride type monomers, acrylonitrile type monomers, various vinyl ester monomers, various acrylamides monomers, various alkynol acrylamides and the like. Considering the styrenic monomers (as both a primary monomer in styrene-butadiene polymers or a co-monomer in acrylate polymers), they are often referred to as vinyl substituted aromatic compounds (styrenic monomers) and include styrene, alkyl substituted styrene 1-vinylnaphthalene, 2-vinylnaphthalene, and the alkyl, cycloalkyl, aryl, alkaryl and aralkyl derivatives thereof, in which the total number of carbon atoms, in the combined, substituents is generally from 8 to about 12. Examples of such compounds include 3-methylstyrene vinyltoluene; alpha-methylstyrene; 4-n-propylstyrene, 4-t-butylstyrene, 4-methoxy- styrene; 4-dimethylaminostyrene; 3,5-diphenoxystyrene; 4-p-tolylstyrene; 4-phenylstyrene; 4,5-dimethyl-

1-vinylnaphthalene; 3-n-propyl-2-vinyl- naphthalene, and the like. Styrene is typically preferred.

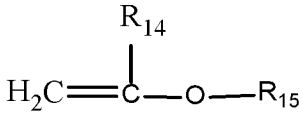
[0031] The vinyl chloride type monomers include vinyl chloride, vinylidene chloride, and the like.

[0032] The vinyl esters can generally be represented by the formula:



wherein R_{13} is H or a C_{1-2} alkyl, and R_{12} is an alkyl group generally having from one to about 10 or 12 carbon atoms with from about one to about 6 carbon atoms being preferred. Accordingly, suitable vinyl esters include vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, and the like. Vinyl esters with larger R_{12} groups include the vinyl versatate monomers, such as Veo VA-P, Veo Va-10, and Veo Va-11.

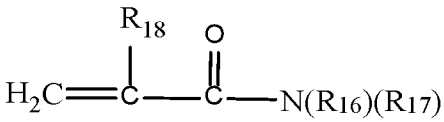
[0033] The various vinyl ethers can be represented by the formula:



wherein R_{14} is H or a C_{1-2} alkyl, R_{15} is desirably an alkyl having from one to about 10 carbon atoms. Specific examples include methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, and the like with methyl vinyl ether being preferred.

[0034] The acrylonitrile type monomers that can be utilized include acrylonitrile, or methacrylonitrile, or ethacrylonitrile, and the like.

[0035] The acrylamide monomers which can be polymerized to form a copolymer generally have the following formula:



wherein R_{18} is H or a C_{1-2} alkyl, and each R_{16} and R_{17} individually represents a hydrogen atom or an alkyl group (straight chained or branched) containing from one to about

18 carbon atoms. Specific examples include acrylamide, ethyl acrylamide, butyl acrylamide, tert-octyl acrylamide, tert-butyl methacrylamide, and the like.

[0036] Functionalized acrylamides can also be utilized. Examples of such acrylamides include AMPS, i.e., 2-acrylamido-2-methylpropanesulfonic acid, DMAPMA, i.e., dimethylaminopropyl methacryamide, and the like.

[0037] Carbonyl containing unsaturated comonomers may be copolymerized with the above monomers to make acrylic or vinyl polymers. Examples of carbonyl-containing monomers, which may be mentioned, include acrolein, methacrolein, diacetone-acrylamide, crotonaldehyde, 4-vinylbenzaldehyde, vinyl alkyl ketones of 4 to 7 carbon atoms such as vinyl methyl ketone, and acryloxy- and methacryloxy-alkyl propanols. Further examples include acrylamidopivalaldehyde, methacrylamidopivalaldehyde, 3-acrylamidomethyl-anisaldehyde, diacetone acrylate, acetonyl acrylate, diacetone methacrylate, acetoacetoxyethylmethacrylate, 2-hydroxypropylacrylate acetylacetate, and butanediolacrylate acetylacetate.

[0038] We should mention vinyl pyrrolidone here and any related cyclic nitrogen containing monomers.

[0039] For enablement of the invention, the normal drying mechanism for aqueous based coating compositions is that the continuous phase is evaporated from the surface(s) of the film or coating until the disperse phase of the film and/or coating (the polymer binder and the particulate phase if any) comes in close proximity to each other and begins to form a continuous aggregate across the surface of the film or coating. This large continuous aggregate only forms when enough continuous phase has evaporated to cause the dispersed phase to come into very close contact with each other and compress the steric and/or ionic barrier between the various particles of the dispersed phase. Then, the colloidal stabilization layer on the particles of the dispersed phase begins to interpenetrate the colloidal stabilization later of the adjacent phase and the barrier effect of the barrier layer on each dispersed phase loses its barrier effect and promotes aggregation of the particles. The particles, to the extent they are capable at the film formation temperature deform to close pack as efficiently as possible. The steric and/or ionic barrier remains intact to some extent due to incompatibility between the barrier layer and the contents of each particle. In some areas of the film, the barrier layer gets pushed out of the interfaces and the particles of the dispersed phase come in direct contact with other particles in the dispersed phase. This is the agglomeration phase of film formation where addition

contraction is achieved by merging particles together and pushing surface active molecules to the interfaces with other surfaces (such as the top of the film, the interface between the films and the substrate, etc.). To some extent, the molecular weight and viscosity of the barrier layers prevent complete migration of the barrier layers to interfaces and some portion of the barrier layers from the particles are trapped in the film in various forms.

[0040] Having explained film formation in the above paragraph in the absence of an amine additive, we will now explain film formation of an anionically (partially or fully) stabilized polymer dispersion in the presence of an active amine additive of this disclosure. Typically, the composition will have been pH adjusted to above 7 with a volatile base. As evaporation takes place, the volatile base will be evaporated from the surface of the film and the reactivity of the amine groups of the amine additive with the anionic groups (such as carboxyl) of the anionic stabilization for the particles will be more favored as the pH drops to nearer 7. The amine additive is highly water swollen or dissolved in the water and bridges between particles in the dispersed phase. The pH drops faster at the interface between the film or coating and the air (interface of the film) because the volatile base is more volatile than the water of the aqueous phase. The particles of the surface of the film become aggregated at a lower solids content than an equivalent composition without the amine additive because the aqueous phase contained in the swollen or dissolved or dissolved amine additive is not available to separate the particles from each other and maintain the barrier between the particles. The interaction of the amine additive with the anionic groups on the surface of the dispersed phase promotes aggregation more than the collision of equivalent dispersed phase particles in the absence of the amine additive. Basically, a continuous aggregate of particles at the surface of the film (skin) forms as soon as the amine additive can start to connect particles at the pH at the surface. The high poly(alkylene oxide) content of the amine additive continuous to absorb water from below the surface of the skin and transport it to the surface (skin) of the film where the aqueous molecules can evaporate.

[0041] So, the amine additive promotes a skinning process of the film or coating composition earlier in the evaporation of the continuous phase when the amine additive is present. This skinning creates a barrier to water (from things like rain) from entering the film and redispersing the particles and binder. This means that the coating is resistant to redispersion of the particles of the dispersed phase earlier in the drying process (before evaporation has

proceeded sufficiently to cause normal aggregation of the particles by conventional compression of the particles with each other during the drying process.

[0042] Drying of films can be a problem when the film is being generated at a temperature where evaporation of the aqueous phase is slow (low temperatures such as 15, 20 or 25°C), when the moisture content of the air at the drying temperature is high and aqueous evaporation is slowed because the air is partially or fully saturated with water (such as in humid areas of the world or on humid days), and when the coating composition is applied very thick (such as $\geq$ 40 mils or $\geq$ 50 mils and a relatively large volume of water needs to evaporate (due to the depth of the film) through a limited amount of exposed surface area for the film or coating (relative to thinner films used on metals or wood coatings). This occurs a lot with roof coatings where it is desirable to put down a thick coat in a single application and avoid multiple applications and get a thicker barrier to water penetration, UV deterioration, and abrasive wear. Mils is an abbreviation in the English measurement scale of 0.001 inch. Each mil is equivalent to 0.0254 millimeters.

[0043] The amine additive is particularly effective in combination with volatile bases such as ammonia hydroxide and low molecular weight water soluble amines having boiling points of less than 100°C (so they evaporate before the water phase evaporates).

[0044] The coating compositions described herein with the polyamine curing additive also contain a volatile base. Volatile bases are basic substances that are soluble in water, remain in the aqueous coating composition under normal storage conditions, and evaporate from the aqueous coating composition under suitable drying conditions and faster than water at the drying temperature (so as to shift the pH from pH basic towards pH neutral or even pH acidic.

[0045] Generally, one or more volatile bases are incorporated in the composition in an effective amount to maintain the pH of the coating composition in the range of from 7.5 to 12.5 or in the range from 8 or 8.5 to 11. In some embodiments, one or more volatile bases are incorporated in the composition at between 0.1% by weight and 5.0% by weight based on the weight of the coating composition. In certain embodiments, one or more volatile bases are incorporated in the composition at between 0.5% by weight and 2.5% by weight.

[0046] Suitable volatile bases can be selected on the basis of several factors, including their basicity and volatility. Exemplary volatile bases include, but are not limited to, ammonia, lower alkylamines such as dimethylamine, triethylamine, and diethylamine, ethanolamine,

diethanolamine, triethanolamine, morpholine, aminopropanol, 2-amino-2-methyl-1-propanol, 2-dimethylaminoethanol, and combinations thereof. In certain embodiments, the volatile base is ammonia. In some cases, ammonia is the sole volatile base present in the coating composition. Alternatively, ammonia can be incorporated in admixture with other volatile bases, non-volatile bases, such as alkali metal hydroxides, or combinations thereof.

[0047] The volatile base in combination with the polyamine additive of this disclosure is useful to facilitate curing and drying of coating based generally on any polymeric material that uses or can use at least some anionic (e.g., carboxylic) stabilization of the dispersed polymer phase. This includes a variety of acrylic binders (common to many paints) and urethane polymer dispersions (also common to many paints). The amount of anionic based surface active molecules (e.g., surfactant), surface active oligomers or polymers (e.g., support resins), or surface active repeat units incorporated into the polymer of the dispersion/coating is desirably from about 0.5 to about 5 wt.% based on the weight of the dispersed binder and dispersed particulate material in the coating.

[0048] The amine additive herein is useful in ink and coating compositions as component to form aggregated particles at the surface of a coating, so the coating is more hydrophobic and resistance to redispersion or dilution of the polymer, pigment, and fillers by rainwater and other sources of water. The polymer dispersion of the coating desirably has at least some anionic functionality on the surface of the particles that can interact with the amine groups of the amine additive. Preferred anionic functionality is carboxylic acid groups. The amine additive provides coatings that are more quickly resistant to rain, more quickly resistant to smudging, and can be handled or packaged more quickly that equivalent coating formulations without the amine additive. This is because the amine additive facilitates formation of an aggregated polymer/particulate skin on the surface of a film or coating at an earlier time than this would occur in the absence of the amine additive. While some additives for polymers make a less porous film (e.g., due to crosslinking of the binder that sometimes can slow evaporation of water and polar solvents from within the drying film) the amine additive of this disclosure has side chain poly(alkylene oxide chains) that form hydrophilic areas in the surface of the drying film to promote moisture vapor release through the film and from the film surface, allowing final drying of the coating to proceed at normal speed or slightly faster than without the amine additive.

[0049] Having stated what, the amine additive does for a coating, it also does not significantly decrease the final barrier properties of the film or coating to any significant degree, relative to the same film or coating without the amine additive. Therefore, the amine additive (even though it is dispersible or soluble in water at most temperatures above 5°C) does not make the final dry film or coating less resistance to water or most polar or water born staining materials (such as catsup, mustard, etc.). Coatings are often applied to materials to protect the substrate from water and polar staining materials, and thus the coatings containing the amine additive perform substantially equivalently in providing barrier properties to the same compositions less the amine additive. The amine additive just speeds the initial skin formation time (so the coatings are resistant to rain or water in a shorter period of time).

[0050] The amine additive is also useful for some biocidal activity (minimizing biological growth to some extent) in aqueous media. The amine additive can also function as a coagulant for some anionically charged dispersed phases in aqueous media.

[0051] When the amine additive is used in a coating composition, the coating compositions contain one or more anionically colloidally stabilized polymers. The amount of the polyamine additive is from about 0.1 to about 10 wt.% based on the weight of all the other components in the composition (such as the anionically stabilized (co)polymer dispersion, water, fillers, pigments, defoamers, etc.). More desirably, the amount of the polyamine additive is from about 0.2 or 0.5 to about 5, 6 or 8 wt.% of the composition. The amount of the anionically stabilized (co)polymer dispersion is about 10 to about 75 wt.% of the components in the coating; more desirably about 20 to about 65 wt.%. The other components (generally about 15 to 90, 25 to 79 .5 or 80, or 30 to 75, wt.% of the composition) include fillers, pigments, defoamers, biocides, preservatives, etc. common in coating compositions. The anionically colloidally stabilized polymers can be derived from one or more ethylenically-unsaturated monomers, including (meth)acrylate monomers having from 3 to 23 carbon atoms and 2 to 6 oxygen atoms, vinyl aromatic monomers having from 8 to 14 carbon atoms, ethylenically unsaturated aliphatic monomers including dienes having from 2 to 12 carbon atoms, vinyl ester monomers having from 4 to 16 carbons atoms, and assorted other ethylenically unsaturated monomers and combinations thereof. In some embodiments, the anionically colloidally stabilized polymers can include pure acrylic copolymers, styrene acrylic copolymers, vinyl acrylic copolymers, or carboxylated or non-carboxylated styrene butadiene copolymers. In

preferred embodiments, the anionically colloidally stabilized copolymer has a measured Tg of between -70°C and 80°C.

[0052] In some embodiments, the anionically colloidally stabilized polymer includes an acrylic-based copolymer. Acrylic-based copolymers include copolymers derived from one or more (meth)acrylate monomers. The acrylic-based copolymer can be a pure acrylic polymer (i.e., a polymer or copolymer derived exclusively from (meth)acrylate monomers), a styrene-acrylic polymer (i.e., a copolymer derived from styrene and one or more (meth)acrylate monomers), or a vinyl-acrylic polymer (i.e., a copolymer derived from one or more vinyl ester monomers and one or more (meth)acrylate monomers).

[0053] The acrylic-based copolymer can be derived from 50% by weight or greater or 55% by weight or greater of one or more (meth)acrylate monomers (e.g., 65% by weight or greater, 75% by weight or greater, 80% by weight or greater, 85% by weight or greater, 88% by weight or greater, 90% by weight or greater, 91% by weight or greater, 92% by weight or greater, 93% by weight or greater, 94% by weight or greater, or 95% by weight or greater of the (meth)acrylate monomer) based on the total weight of monomers in said anionically colloidally stabilized polymer of said polymer dispersion. In some embodiments, the (meth)acrylate monomer can include esters of a,(3-monoethylenically unsaturated monocarboxylic and dicarboxylic acids having 3 to 6 carbon atoms with alkanols having one to 12 carbon atoms (e.g., esters of acrylic acid, methacrylic acid, maleic acid, fumaric acid, or itaconic acid, with C_1-C_{20}, C_1-C_{12}, C_1-C_8, or C_1-C_4 alkanols).

[0054] The acrylic-based copolymer can be derived from greater than 0% or 0.2% by weight to 5% by weight of one or more carboxylic acid-containing monomers based on the total weight of monomers. Exemplary carboxylic-acid monomers include, but are not limited to, α,β-monoethylenically unsaturated mono- and dicarboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, dimethacrylic acid, ethylacrylic acid, allylacetic acid, vinylacetic acid, mesaconic acid, methylenemalonic acid, citraconic acid, and combinations thereof. In certain embodiments, the acrylic-based copolymer is derived from 0.2% by weight to 5% by weight, or 0.2% by weight to 2.5% by weight, acrylic acid, methacrylic acid, or combinations thereof.

[0055] The anionically colloidally stabilized polymer can have a glass-transition temperature (Tg), as measured by differential scanning calorimetry (DSC) using the mid-point temperature

using as described, for example, in ASTM 3418/82, of between -70°C and 80°C. In certain instances, the anionically colloidally stabilized copolymer has a measured Tg of greater than -70°C (e.g., greater than -60°C, greater than -50°C, greater than -40°C, greater than -30°C, greater than -20°C, greater than -10°C, or greater than 0°C). In some cases, the anionically colloidally stabilized copolymer has a measured Tg of less than 80°C, more desirably less than 70°C and preferably 60°C or less. In some cases, requiring elastomeric coatings, the anionically colloidally stabilized copolymer has a measured Tg of less than 15°C (e.g., less than 10°C, less than 0°C, less than -10°C, less than -20°C, less than -30°C, less than -40°C, less than -50°C. In certain embodiments for elastomeric coatings, the anionically colloidally stabilized copolymer has a measured Tg of between -60°C and 15°C, -55°C and 10°C, or -50°C and 0°C. In some embodiments requiring a hard coating, the anionically colloidally stabilized polymer can have a Tg of from 25°C to 80°C. In these embodiments, the coating composition can further comprise a coalescing agent suitable to depress the Tg of the anionically colloidally stabilized polymer into the film forming range.

[0056] The anionically colloidally stabilized polymer can be prepared by heterophase polymerization techniques, including, for example, free-radical emulsion polymerization, suspension polymerization, and mini-emulsion polymerization. In some examples, the anionically colloidally stabilized polymer is prepared by polymerizing the monomers using free-radical emulsion polymerization. The emulsion polymerization temperature can range from 10°C to 130°C or from 50°C to 90°C. The polymerization medium can include water alone or a mixture of water and water-miscible liquids, such as methanol, ethanol or tetrahydrofuran. In some embodiments, the polymerization medium is free of organic solvents and includes only water, which will mean preferably less than 2 wt.% organic components soluble in the water phase, more desirably less than 1 wt.%, and preferably less than 0.2 wt.% based on the weight of the aqueous phase.

[0057] The emulsion polymerization can be carried out as a batch process, as a semi-batch process, or in the form of a continuous process. In some embodiments, a portion of the monomers can be heated to the polymerization temperature and partially polymerized, and the remainder of the monomer batch can be subsequently fed to the polymerization zone continuously, in steps, or with superposition of a concentration gradient. In some embodiments, the copolymer is produced in a single stage (i.e., does not include separate feeds

having different monomer compositions so as to produce a multistage polymer particle such as a core/shell particle).

[0058] The emulsion polymerization can be performed with a variety of auxiliaries, including water-soluble initiators and regulators. Examples of water-soluble initiators for the emulsion polymerization are ammonium salts and alkali metal salts of peroxodisulfuric acid, e.g., sodium peroxodisulfate, hydrogen peroxide or organic peroxides, e.g., tert-butyl hydroperoxide. Reduction-oxidation (redox) initiator systems are also suitable as initiators for the emulsion polymerization. The redox initiator systems are composed of at least one, usually inorganic, reducing agent and one organic or inorganic oxidizing agent. The oxidizing component comprises, for example, the initiators already specified above for the emulsion polymerization. The reducing components are, for example, alkali metal salts of sulfurous acid, such as sodium sulfite, sodium hydrogen sulfite, alkali metal salts of disulfurous acid such as sodium disulfite, bisulfite addition compounds with aliphatic aldehydes and ketones, such as acetone bisulfite, or reducing agents such as hydroxymethanesulfinic acid and salts thereof, or ascorbic acid. The redox initiator systems can be used in the company of soluble metal compounds whose metallic component is able to exist in a plurality of valence states.

[0059] In the polymerization it is possible to use molecular weight regulators or chain transfer agents, in amounts, for example, of 0 to 0.8 parts by weight, based on 100 parts by weight of the monomers to be polymerized, to reduce the molecular weight of the copolymer. Suitable examples include compounds having a thiol group such as tert-butyl mercaptan, thioglycolic acid ethylacrylic esters, mercaptoethanol, mercaptopropyltrimethoxysilane, and tert-dodecyl mercaptan. Additionally, it is possible to use regulators without a thiol group, such as terpinolene.

[0060] Dispersants, such as surfactants, can also be added during polymerization to help maintain the dispersion of the monomers in the aqueous medium. For example, the polymerization can include less than 3% by weight or less than 1% by weight of surfactants. In some embodiments, the polymerization is substantially free of surfactants and can include less than 0.05% or less than 0.01% by weight of one or more surfactants.

[0061] Anionic and nonionic surfactants can be used during polymerization. Suitable surfactants include ethoxylated C_8 to C_{36} or C_{12} to C_{18} fatty alcohols having a degree of ethoxylation of 3 to 50 or of 4 to 30, ethoxylated mono-, di-, and tri-C_4 to C_{12} or C_4 to C_9

alkylphenols having a degree of ethoxylation of 3 to 50, alkali metal salts of dialkyl esters of sulfosuccinic acid, alkali metal salts and ammonium salts of C_8 to C_{12} alkyl sulfates, alkali metal salts and ammonium salts of C_{12} to C_{18} alkylsulfonic acids, and alkali metal salts and ammonium salts of C_9 to C_{18} alkylarylsulfonic acids.

[0062] The coating compositions described herein further contain one or more polyamine curing additives. The polyamine curing additive functions to help the coating resist solubilization of the binder, pigments, fillers etc. if exposed to water or rain early in the drying/film forming process.

[0063] The coating compositions described herein with the polyamine curing additive also contain a volatile base. Volatile bases are basic substances that are soluble in water, remain in the aqueous coating composition under normal storage conditions, and evaporate from the aqueous coating composition under suitable drying conditions.

[0064] In some embodiments, the composition can further contain one or more additional polymers in the form of a solution or dispersion. These additional polymers can perform a variety of functions in the coating composition or in the final coating. But, the additional polymers are not a required component for the essential features of the disclosure.

[0065] The aqueous coating compositions can further include one or more additives, including pigments, fillers, dispersants, coalescents, pH modifying agents, plasticizers, defoamers, surfactants, thickeners, biocides, co-solvents, and combinations thereof. The choice of additives in the composition will be influenced by a number of factors, including the nature of the anionic polymer dispersion and the intended use of the coating composition.

[0066] Examples of suitable pigments include metal oxides, such as titanium dioxide, zinc oxide, iron oxide, or combinations thereof. In certain embodiments, the composition includes a titanium dioxide pigment. Examples of commercially titanium dioxide pigments are KRONOS® 2101, KRONOS® 2310, available from Kronos WorldWide, Inc. (Cranbury, NJ), TI-PURE® R-900, available from DuPont (Wilmington, DE), or TIONA® AT1 commercially available from Millenium Inorganic Chemicals. Titanium dioxide is also available in concentrated dispersion form. An example of a titanium dioxide dispersion is KRONOS® 4311, also available from Kronos WorldWide, Inc.

[0067] Examples of suitable fillers include calcium carbonate, nepheline syenite, (25% nepheline, 55% sodium feldspar, and 20% potassium feldspar), feldspar (an aluminosilicate),

diatomaceous earth, calcined diatomaceous earth, talc (hydrated magnesium silicate), aluminosilicates, silica (silicon dioxide), alumina (aluminum oxide), clay, (hydrated aluminum silicate), kaolin (kaolinite, hydrated aluminum silicate), mica (hydrous aluminum potassium silicate), pyrophyllite (aluminum silicate hydroxide), perlite, baryte (barium sulfate), Wollastonite (calcium metasilicate), and combinations thereof. In certain embodiments, the composition comprises a calcium carbonate filler.

[0068] Examples of suitable dispersants are polyacid dispersants and hydrophobic copolymer dispersants. Polyacid dispersants are typically polycarboxylic acids, such as polyacrylic acid or polymethacrylic acid, which are partially or completely in the form of their ammonium, alkali metal, alkaline earth metal, ammonium, or lower alkyl quaternary ammonium salts. Hydrophobic copolymer dispersants include copolymers of acrylic acid, methacrylic acid, or maleic acid with hydrophobic monomers. In certain embodiments, the composition includes a polyacrylic acid-type dispersing agent, such as Pigment Disperser N, commercially available from BASF SE.

[0069] Suitable coalescents, which aid in film formation during drying, include ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, ethylene glycol monoethyl ether acetate, ethylene glycol monobutyl ether acetate, diethylene glycol monobutyl ether, diethylene glycol monoethyl ether acetate, dipropylene glycol monomethyl ether, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, and combinations thereof.

[0070] Examples of suitable thickening agents include hydrophobically modified ethylene oxide urethane (HEUR) polymers, hydrophobically modified alkali soluble emulsion (HASE) polymers, hydrophobically modified hydroxyethyl celluloses (HMHECs), hydrophobically modified polyacrylamide, and combinations thereof. HEUR polymers are linear reaction products of diisocyanates with polyethylene oxide end-capped with hydrophobic hydrocarbon groups. HASE polymers are homopolymers of (meth)acrylic acid, or copolymers of (meth)acrylic acid, (meth)acrylate esters, or maleic acid modified with hydrophobic vinyl monomers. HMHECs include hydroxyethyl cellulose modified with hydrophobic alkyl chains. Hydrophobically modified polyacrylamides include copolymers of acrylamide with acrylamide modified with hydrophobic alkyl chains (N-alkyl acrylamide). In certain embodiments, the coating composition includes a hydrophobically modified hydroxyethyl cellulose thickener.

[0071] Defoamers serve to minimize frothing during mixing and/or application of the coating composition. Suitable defoamers include silicone oil defoamers, such as polysiloxanes, polydimethylsiloxanes, polyether modified polysiloxanes, and combinations thereof. Exemplary silicone-based defoamers include BYK®-035, available from BYK USA Inc. (Wallingford, CT), the TEGO® series of defoamers, available from Evonik Industries (Hopewell, VA), and the DREWPLUS® series of defoamers, available from Ashland Inc. (Covington, KY).

[0072] Suitable biocides can be incorporated to inhibit the growth of bacteria and other microbes in the coating composition during storage. Exemplary biocides include 2-[(hydroxymethyl)amino]ethanol, 2-[(hydroxymethyl) amino]2-methyl-1-propanol, o-phenylphenol, sodium salt, 1,2-benzisothiazolin-3-one, 2-methyl-4-isothiazolin-3-one (MIT), 5-chloro2-methyland-4-isothiazolin-3-one (CIT), 2-octyl-4-isothiazolin-3-one (OTT), 4,5-dichloro-2-n-octyl-3-isothiazolone, as well as acceptable salts and combinations thereof. Suitable biocides also include mildewcides that inhibit the growth mildew or its spores in the coating. Examples of mildewcides include 2-(thiocyanomethylthio)benzothiazole, 3-iodo-2-propynyl butyl carbamate, 2,4,5,6-tetrachloroisophthalonitrile, 2-(4-thiazolyl)benzimidazole, 2-N-octyl4-isothiazolin-3-one, diiodomethyl p-tolyl sulfone, as well as acceptable salts and combinations thereof. In certain embodiments, the coating composition contains 1,2-benzisothiazolin-3-one or a salt thereof. Biocides of this type include PROXEL® BD20, commercially available from Arch Chemicals, Inc (Atlanta, GA).

[0073] Exemplary co-solvents and plasticizers include ethylene glycol, propylene glycol, diethylene glycol, and combinations thereof.

[0074] The coating compositions described above can be provided as aqueous dispersions having a solids content of from 30-85% or from 30 or 40-75%.

[0075] Also provided are coatings formed from the coating compositions described herein, as well as methods of forming these coatings. Generally, coatings are formed by applying a coating composition described herein to a surface, and allowing the coating to dry to form a coating. The resultant dry coatings typically comprise, at minimum, an anionically colloidally stabilized polymer and a polyamine curing additive The dry coatings can further comprise one or more additives (e.g., pigments and/or fillers) as described above.

[0076] Coating compositions can be applied to a surface by any suitable coating technique, including spraying, rolling, brushing, or spreading. Coating compositions can be applied in a single coat, or in multiple sequential coats (e.g., in two coats or in three coats) as required. The coating can be co-applied with a setting accelerator to decrease the setting time of the coating on a surface. Suitable setting accelerators include compounds, such as acids, which consume the volatile base and decrease coating setting time. For example, the setting accelerator can be a dilute acid, such as acetic acid or citric acid. Setting accelerators can be applied to a surface prior to coating application, applied simultaneously with the coating composition, or applied to the coating after it has been applied to a surface but prior to drying a particular application. Generally, the coating composition is allowed to dry under ambient conditions. However, in certain embodiments, the coating composition can be dried, for example, by heating and/or by circulating air over the coating.

[0077] Coating thickness can vary depending upon the application of the coating. For example, the coating can have a dry thickness of at least one or 10 mils (e.g., at least 15 mils, at least 20 mils, at least 25 mils, at least 30 mils, or at least 40 mils) for elastomeric coatings, especially where the coating needs to bridge cracks in the substrate. In such elastomeric instances, the coating has a dry thickness of less than 100 mils (e.g., less than 90 mils, less than 80 mils, less than 75 mils, less than 60 mils, less than 50 mils, less than 40 mils, less than 35 mils, or less than 30 mils). In some elastomeric embodiments, the coating has a dry thickness of between 10 mils and 100 mils. In certain embodiments, the coating has a dry thickness of between 10 mils and 40 mils. For less elastomeric coatings, such as metal coatings, and where the Tg can be from 15 or 25 to 80°C, the coating thickness may tend to be thinner such as one to 10 or one to five mils dry thickness.

[0078] In some embodiments, the coating is applied to a road surface as a traffic paint. In these embodiments, the road surface can be, for example, asphalt or concrete. In some cases when the coating is applied as a traffic paint, the coating contains a filler such as a reflective filler.

[0079] In certain embodiments, the coating is applied to a surface to reflect solar radiation. In these cases, the coating will generally contain one or more pigments that reflect solar energy, such as titanium dioxide. By reflecting the sun's heat, the coating can help to cool a surface.

In the case of coatings applied to architectural surfaces such as roofs, the roof coating can help to reduce a building's interior temperatures and cooling costs.

[0080] In certain embodiments, the coating is an elastomeric roof coating. In certain embodiments, the coating will generally satisfy the requirements of ASTM D6083-05, entitled "Standard Specification for Liquid Applied Acrylic Coating Used in Roofing." In particular embodiments, the coating has a tensile strength of greater than 200 psi, and an elongation at break of greater than 100%, according to ASTM D-2370, after 1,000 hours of accelerated weathering.

[0081] Polyamine curing additives can also be incorporated as setting agents in other types of compositions which contain anionically colloidally stabilized polymers or copolymers. In particular, polyamine curing additives may be utilized to decrease the water or rain damage of other compositions where fast setting and/or rain resistance are desirable. For example, polyamine curing additives can be added to conventional adhesives (e.g., construction adhesives), grouts, caulks, sealants, and exterior insulating and finishing systems (EIFS) to provide more water and rain resistant products earlier in the setting or drying process .

[0082] Coating thickness can vary depending upon the application of the coating. For example, the coating can have a dry thickness of at least one or 10 mils (e.g., at least 15 mils, at least 20 mils, at least 25 mils, at least 30 mils, or at least 40 mils) for elastomeric coatings, especially where the coating needs to bridge cracks in the substrate. In such elastomeric instances, the coating has a dry thickness of less than 100 mils (e.g., less than 90 mils, less than 80 mils, less than 75 mils, less than 60 mils, less than 50 mils, less than 40 mils, less than 35 mils, or less than 30 mils). In some elastomeric embodiments, the coating has a dry thickness of between 10 mils and 100 mils. In certain embodiments, the coating has a dry thickness of between 10 mils and 40 mils. For less elastomeric coatings, such as metal coatings, and where the Tg can be from 15 or 25 to 80°C, the coating thickness may tend to be thinner such as one to 10 or one to five mils dry thickness.

[0083] The coating compositions can be applied to a variety of surfaces including, but not limited to metal, asphalt, concrete, stone, ceramic, wood, plastic, polymer, polyurethane foam, glass, and combinations thereof. The coating compositions can be applied to interior or exterior surfaces. In certain embodiments, the surface is an architectural surface, such as a roof, wall, floor, or combination thereof.

EXAMPLES

Ingredients:

DMAPMA – dimethylaminopropyl methacrylamide

HEMA – 2-hydroxyethyl methacrylate

Initiator A – 1.37 g of 70% TBHP in 4.8g of water

TBHP – t-butyl hydrogen peroxide

Reductant A – 0.96 grams of erythorbic acid in 24 grams of water

Iron(II) sulfate heptahydrate

Na4-ETDA – tetrasodium ethylenediaminetetraacetc acid

AMPS™ 2045 – 2-acrylamido-2methylpropanesulfonic acid or its sodium or ammonia salt (AMPS)

SLS – sodium lauryl sulfate

Bisomer™ MPEG 350MA – 350 molecular weight capped polyethylene oxide esterified with methacrylic acid. Available from Geo.

Methacrylamide

Sipomer PAM-100 – phosphate ester of polyethylene glycol methacrylate available from Solvay or Rhodia

MMA – methyl methacrylate

2-EHA – 2-ethylhexylacrylate

VCN – acrylonitrile

MAA – methacrylic acid

Silane A-171 – Vinyltrimethoxysilane

COPS – sodium 1-allyloxy-2-hydroxypropane sulfonate available from Solvay

Styrene

AA – acrylic acid

AE-960 is an acrylic polymer from Lubrizol Advanced Materials, Inc. having anionic colloidal stabilizing group. One could use similar polymers such as Dow Rhoplex™ ED-1791, Rhoplex™ 2885 or BASF Acrynol™ NS 567 and get similar results for viscosity and similar performance as a coating.

Comparative Example I with HEMA

[0084] Monomer composition = 80 DMAPMA/20 HEMA. An aqueous polymer was prepared as follows. A monomer premix was made by mixing 120 grams of water, 96 grams of dimethylaminopropyl methacrylamide (DMAPMA) and 24 grams of 2-hydroxyl ethyl acrylate

(HEMA). Initiator A was made by mixing 1.37 grams of 70% t-butyl hydrogen peroxide (TBHP) in 4.8 grams of water. Reductant A was prepared by dissolving 0.96 grams of erythorbic acid in 24 grams of water. A one-liter reactor was charged with 336 grams of water, 1.68 grams of 0.15% Iron(II) sulfate heptahydrate and 0.48 grams of 1% tetrasodium ethylenediaminetetraacetc acid (Na4-ETDA), and then was heated to 60°C under a nitrogen blanket with proper agitation. At 60°C, Initiator A was added to the reactor. After about 2 minutes, the monomer premix was proportioned to the reaction vessel for over a period of 120 minutes, and reductant A was proportioned to the reactor for over a period of 150 minutes. After completion of reductant A feed, the temperature of the reaction vessel was maintained at 60°C for 60 minutes. The reactor was then cooled to 50°C. A solution of 0.43 grams of 70% TBHP and 0.04 grams of 30% sodium lauryl sulfate (SLS) in 6 grams of water was added to the reactor. After 5 minutes, a solution of 0.25 grams of erythorbic acid in 6 grams of water was added to the reactor. The reactor was maintained at 50°C. After 30 minutes, a solution of 0.43 grams of 70% TBHP and 0.04 grams of 30% sodium lauryl sulfate (SLS) in 6 grams of water was added to the reactor. After 5 minutes, a solution of 0.25 grams of erythorbic acid in 6 grams of water was added to the reactor. The reactor was maintained at 50°C for about 30 minutes. Then, the reactor was cooled to the room temperature. The polymer had a pH 9.5, solids 16.4%, viscosity 15 cps.

Comparative Example II with AMPS 2045

[0085] Monomer composition = 80 DMAPMA/20 AMPS 2045. A polymer was prepared same as Comparative Example I except 48 grams of 50% AMPS 2405 (From Lubrizol) was used instead of HEMA. The polymer had a pH 10.9, solids 17.6%, viscosity 29 cps.

Comparative Example III with Methacrylamide

[0086] Monomer composition = 80 DMAPMA/20 Methacrylamide. A polymer was prepared same as Comparative Example I except 24 grams of methacrylamide was used instead of HEMA. The polymer had a pH 9.9, solids 17.8%, viscosity 24 cps.

Invention Examples of Polyamine Additives

Example 1 with MPEG 350MA

[0087] Monomer composition = 80 DMAPMA/20 MPEG350 MA. A polymer was prepared same as Comparative Example 1 except 24 grams of Bisomer MPEG 350MA (from GEO) was used instead of HEMA. The polymer had a pH 10.3, solids 17.3%, viscosity 31cps.

Example 2 with MPEG 350MA

[0088] Monomer composition = 70 DMAPMA/30 MPEG350 MA. A polymer was prepared same as Comparative Example 1 except a monomer mix contained 84 grams of DMAPMA and 36 grams of Bisomer MPEG 350MA. The polymer had a pH10.4, solids 18.0%, viscosity 11cps.

Table I – Polyamine Additives

Polyamine	DMAPMA	HEMA	MPEG 350MA	AMPS-2405	TS, %	pH	Visc
Comp. # I	80	20	0	0	16.4	9.5	15
Ex. # 1	80	0	20	0	17.3	10.3	31
Comp. # II	80	0	0	20	17.6	10.9	29
Ex. # 2	70	0	30	0	18	10.4	11

Example 3 with MPEG 1005 MA and VA-086

[0089] Monomer composition = 70 DMAPMA/30 MPEG1005 MA. An emulsion polymer was prepared as follows. A monomer premix was made by mixing 153 grams of water, 126 grams of dimethylaminopropyl methacrylamide (DMAPMA) and 108 grams of Visiomer MEG 1005MA W (50% in water, Evonik). Initiator A was made by dissolving 0.9 grams of 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (Azo VA-086 from Wako) in 14.4 grams of water. Initiator B was prepared by dissolving 0.27 grams of Azo VA-086 in 36 grams of water. A one-liter reactor was charged with 324 grams of water, and then was heated to 85°C under a nitrogen blanket with proper agitation. At 85°C, Initiator A was added to the reactor, and then monomer premix was proportioned into the reaction vessel for over a period of 75 minutes. About one minute after the start of monomer premix proportioning, Initiator B was proportioned to the reactor for over a period of 120 minutes. The reaction temperature was kept at 85°C. After completion of Initiator B feed, the temperature of the reaction vessel was maintained at 85°C for 60 minutes. The reactor was then cooled to 50°C. A solution of 0.64 grams of 70% TBHP and 0.06 grams of 30% SLS in 9 grams of water was added to the reactor. After five minutes, a solution of 0.38 grams of erythorbic acid in 9 grams of water was added to the reactor. The reactor was maintained at 50°C. After 30 minutes, a solution of 0.64 grams of 70% TBHP and 0.06 grams of 30% SLS in 9 grams of water was added to the reactor. After five minutes, a solution of 0.38 grams of erythorbic acid in 9 grams of water was added to the reactor. The reactor was maintained at 50°C for about 30 minutes. Then, the reactor was cooled to the room temperature and filtered through 100-micron cloth. The polymer had a pH10.1, solids 22.4%, and viscosity 560 cps.

Example 4 with MPEG 350MA and PAM-100

[0090] Monomer composition = 70 DMAPMA/20 MPEG350 MA/10 PAM-100. A polymer was prepared same as Example 3, except a monomer mix contained 180 grams of water, 18 grams of Sipomer PAM-100 (from Solvay), 8.4 grams of 28% ammonium hydroxide, 126 grams of DMAPMA and 36 grams of Bisomer MPEG 350MA. The polymer had a pH10.1, solids 23.6%, and viscosity 1104 cps.

Example 5 with MPEG 350MA and methacrylamide

[0091] Monomer composition = 70 DMAPMA/10 MPEG350 MA/20 methacrylamide. An emulsion polymer was prepared as follows. A monomer premix was made by mixing 160 grams of water, 32 grams of methacrylamide, 112 grams of dimethylaminopropyl methacrylamide (DMAPMA) and 16 grams of Bisomer MPEG 350MA. Initiator A was made by dissolving 0.8 grams of 2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (Azo VA-086 from Wako) in 20.5 grams of water. Initiator B was prepared by dissolving 0.24 grams of Azo VA-086 in 32 grams of water. A one-liter reactor was charged with 280 grams of water, and then was heated to 85°C under a nitrogen blanket with proper agitation. At 85°C, Initiator A was added to the reactor, and then monomer premix was proportioned into the reaction vessel for over a period of 75 minutes. About one minute after the start of monomer premix proportioning, Initiator B was proportioned to the reactor for over a period of 120 minutes. The reaction temperature was kept at 85°C. After completion of Initiator B feed, the temperature of the reaction vessel was maintained at 85°C for 60 minutes. The reactor was then cooled to 50°C. A solution of 0.57grams of 70% TBHP and 0.05 grams of 30% SLS in 8 grams of water was added to the reactor. After five minutes, a solution of 0.34 grams of erythorbic acid in 8 grams of water was added to the reactor. The reactor was maintained at 50°C. After 30 minutes, a solution of 0.57 grams of 70% TBHP and 0.05 grams of 30% SLS in 8 grams of water was added to the reactor. After five minutes, a solution of 0.34 grams of erythorbic acid in 8 grams of water was added to the reactor. The reactor was maintained at 50°C for about 30 minutes. Then, the reactor was cooled to the room temperature and filtered through 100-micron cloth. The polymer had a pH10.3, solids 22.34%, and viscosity 370 cps.

Example 6 with MPEG 350MA and AMPS-2411

[0092] Monomer composition = 70 DMAPMA/25 MPEG350 MA/5 AMPS-2411. A polymer was prepared same as Example 5 except a monomer mix contained 160 grams of

water, 16 grams of AMPS-2411 (50% in water from Lubrizol), 112 grams of DMAPMA, and 40 grams of Bisomer MPEG 350MA. The polymer had a pH10.0, solids 22.94.0%, viscosity 26 cps.

Example 7 with MPEG 1005 MA

[0093] Monomer composition = 85 DMAEMA/15 MPEG1005 MA. A polymer was prepared same as Example 3, except a monomer mix contained 180 grams of water, 153 grams of dimethyl aminoethyl methacrylate (DMAEMA) and 54 grams of Visiomer MEG 1005MA W. The polymer had a pH 9.1, solids 16.8%, and viscosity 990 cps.

Example 8 with MPEG 350MA and MMA

[0094] Monomer composition = 70 DMAEMA/20 MPEG350 MA/10MMA. A polymer was prepared same as Example 3, except a monomer mix contained 180 grams of water, 126 grams of DMAEMA, 18 grams of methyl methacrylate (MMA), and 36 grams of Bisomer MPEG 350MA. The polymer had a pH 9.2, solids 18.1%, viscosity 8000 cps.

Example 9 with MPEG 350MA and DMAEMA

[0095] Monomer composition = 50 DMAEMA/50 MPEG 350 MA. A polymer was prepared same as Example 3, except a monomer mix contained 180 grams of water, 90 grams of DMAEMA, and 90 grams of Bisomer MPEG 350MA. The polymer had a pH 9.2, solids 19.5%, viscosity 1650 cps.

Example 10 with MPEG 750MA and DMAEMA

[0096] Monomer composition = 80 DMAEMA/20 MPEG 350 MA. A polymer was prepared same as Example 3, except a monomer mix contained 128 grams of water, 128 grams of DMAEMA, and 64 grams of Visiomer MPEG 750MA-W (50% in water, Evonik). The polymer had a pH 9.4, solids 19.03%, viscosity 576 cps.

Example 11 with MPEG 350MA and DMAEMA

[0097] Monomer composition = 75 DMAEMA/15 MPEG 350 MA/10 n-VP. A polymer was prepared same as Example 3, except a monomer mix contained 180 grams of water, 135 grams of DMAEMA, 27 grams of Bisomer MPEG 350MA, and 18 grams of n-vinyl pyrrolidinone. The polymer had a pH 9.3, solids 16.6%, viscosity 1280 cps.

Example 12 with MPEG 350MA

[0098] Monomer composition = 50 DMAPMA/50 MPEG350 MA. A polymer was prepared same as Comparative Example 1 except 60 grams of Bisomer MPEG 350MA and 60 grams of DMAPMA. The polymer had a pH 10.3, solids 16.2% viscosity 10 cps.

Example 13 with MPEG 350MA

[0099] Monomer composition = 30 DMAPMA/70 MPEG350 MA. A polymer was prepared same as Comparative Example 1 except 84 grams of Bisomer MPEG 350MA and 36 grams of DMAPMA. The polymer had a pH 10.0, solids 18.4%, viscosity 40 cps.

Synthesis of Polymers

[0100] Polymers A, B, C, D, E and F were made the same procedure as described in the Example #8 of US Patent 7,931,972 with the monomer compositions as shown in the Table II.

Table II – Polymers

Polymer	2EHA	MMA	BA	VCN	MAA	Sipomer COPS-1	AA	NaSS	pH	TS,%
A	76.7	10	0	10	2	0	0	0	9.3	55.4
B	76.7	10.7	0	10	1.3	0	0	0	9.3	55.5
C	76.7	10.7	0	10	0.65	0.65	0	0	9.3	54.8
D	76.7	10.7	0	10	0	0	1.3	0	9.3	55.2
E	0	3	83.7	10	3	0	0	0	8.1	55.4
F	0	3	83.2	10	3	0	0	0.5	8.1	55.4

Stability of Polyamine Additives in Polymers

[0101] In the stability investigation, polyamine was diluted with 2 times DI water, and then 1 wt.% of polyamine was added to polymer on solid to solid basis under proper agitation. Then, they are aged on 50°C oven for 4 weeks. The results are summarized in Table III.

Table III – Polyamine Stability in Polymer

Polyamine	Polymer	4-week 50°C Oven Stability
Comp. Ex. I	A	Viscosity increase
	B	Viscosity increase
	C	Gelled up
	D	Viscosity increase
Comp. Ex. II	A	Gelled up
	B	Viscosity increase
	C	Gelled up
	D	Okay
Ex. 1	A	Okay
	B	Okay
	C	Viscosity increase
	D	Okay

[0102] Both Polymer E and Polymer F were adjusted to pH 10 with ammonia and mixed with polyamine additives on solid to solid basis. Polyamines were mixed with equal amounts of DI water before adding to each polymer. The polymer and polyamine mixtures were put in over 60°C for stability investigation. The results are listed in the Table IV and V.

Table IV – Viscosity Changes of Polymer E with Various Polyamines

Polymer E Viscosity Results at 60°C (Visc = KU)						
Polyamine	0.4 wt% (24 hrs) 60°C	0.4 wt% (48 hrs) 60°C	0.4 wt% (4 wks) 60°C	0.7 wt% (24 hrs) 60°C	0.7 wt% (48 hrs) 60°C	0.7 wt% (4 wks) oven
Ex. 1	58.1	54.2	60.4	73.1	55.3	60.4
Ex. 2	55.3	57.8	65.7	55	87.3	123.6
Ex. 12	57	92.7	>141	57.6	82.8	124.5
Ex. 13	57.3	64.7	72.2	59.9	63.3	65.7
Comp. Ex. I	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled
Comp. Ex. II	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled
Comp. Ex. III	Gelled	Gelled	Gelled	Gelled	Gelled	Gelled

Table V – Viscosity Changes of Polymer F with Various Polyamines

Polymer F Viscosity Results at 60°C (Visc = KU)						
Polyamine	0.4 wt% (24 hrs)	0.4 wt% (48 hrs)	0.4 wt% (4 wks)	0.7 wt% (24 hrs)	0.7 wt% (48 hrs)	0.7 wt% (4 wks)
Ex. 2	55.9	55.6	61.9	55.3	54.5	58.6
Ex. 12	57	56.2	63.6	55.3	55.3	57
Ex. 13	64	63.3	66.8	64.3	62.1	64.3
Comp. Ex. I	76.4	81.8	>141	86.6	105.9	Gelled
Comp. Ex. II	63.6	62.4	101.8	>141	Gelled	Gelled
Comp. Ex. III	>141	Gelled	Gelled	Gelled	Gelled	Gelled

Dry Time of Coatings

[0103] Polyamine additive formulated with the commercial available polymers from Lubrizol are shown in the Table VI. The final pH of coatings are not adjusted. The leading fast dry polymer in the market is used as comparative purpose and its final pH of the coating is adjusted to above 10 based on the formulation guideline by the polymer supplier. The Competitive Control formulation was based on the recommendation of the resin manufacturer.

Table VI – Coating Formulation

	T141845-50 AE960	**T141845-50 AE960**	**T141846-51 SA850**	**Competitive Control**
Ingredients	**Wt%**			
Water	14.62	14.62	15.16	9.65
KTPP				0.12
Solsperse™ W100	1.29	1.29	1.28	
Tamol™ 850				0.40
Surfynol™ DF-58	0.26	0.26	0.26	
Nopco™ NXZ				0.32
Snowhite™ 12				34.78
Kadox™ 515				3.86
Ti-Pure™ R-960	6.02	6.02	5.96	5.80
Minex™ 2	37.42	37.42	37.06	
Letdown				
Ammonia				0.16
Rhoplex™ EC-1791QS				41.81
Carboset™ AE-960	36.80	36.80		
Carboset™ SA-850			36.77	
Polyamine Ex.10	0.00	2.98	2.92	
Texanol™				0.58
Ethylene Glycol				2.01
Natrosol™ 250 MR	0.26	0.26	0.26	
Natrosol™ 250 MXR				0.35
Skane™ M-8				0.17
Acticide™ MBS	0.09	0.09	0.09	
Airex™ 901w	0.26	0.26	0.26	

[0104] The dry time and stability of viscosity and pH of the formulated paints are listed in the Table VII. As shown in the results, the addition of polyamine additive has reduced the dry time more than two hours. Carboset™ AE-960 and Carboset™ SA-850 are commercially available acrylate emulsions from Lubrizol Advanced Materials, Inc. in the USA. The data shows that the polyamine additive of this disclosure is stable in paints for at least 4 weeks at 60°C, which

we believe is equivalent to over one year of storage at room temperature (25°C). The data shows the polyamine additive decreases dry time. The data shows a competive leading market quick dry product is sold commercially at a pH value about 0.5 pH units than the pH value used with Carboset AE-960 and SA-850. The lower pH storage/retention value is desirable as many consumers and paint appliers are sensitive to ammonia, which is commonly used to adjust the pH of paints with quick dry technology. The data shows the Carboset AE-960 and SA-850 can be stored at pH values around 9.5 or 9.7 for many weeks without viscosity increase and the resulting products dry as faster or faster than the leading market product for fast dry paints.

Table VII – Coating Stability and Dry Time

	Carboset AE-960	Carboset AE-960	Carboset SA-850	Leading Market Product
Polyamine EX.10	0	2.5	2.5	N/A
pH, initial	9.67	9.69	9.49	10.13
pH, 4 wks at 60°C	9.57	9.57	9.48	9.92
KU, Initial Viscosity	108.3	111.3	102.6	97.2
KU, 4 wks at 60°C	107	114.9	104.3	95.2
Film Thickness, mil	20	20	20	20
Dry time, hour	>6	4	3	4

[0105] The polyamine Ex. 10 was also post-added into the commercial paints as shown in the Table VIII to illustrate that the polyamine additive is effective with generally any anionically colloidally stabilized paint composition with carboxyl groups as part of the stabilizing mechanism. The commercial paints were Decaflex™ paint from Sika Liquid Plastics in the UK and the Sikagard™ paint was from Sika in the US. Both paints are known fast dry or fast set coatings. The results show that polyamine additive is effectively reduced the dry time.

Table VIII – Polyamine Additive Post-added in the Commercial Paints				
	Decaflex		Sikagard	
Polyamine Ex. 10, wt.%	0	5	0	5
Film thickness, mil	20	20	20	20
Dry time, hour	>6	4.25	>6	4.5

[0106] Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth

herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0107] As used herein, the transitional term "comprising," which is synonymous with "including," "containing," or "characterized by" is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of "comprising" herein, it is intended that the term also encompass, as alternative embodiments, the phrases "consisting essentially of" and "consisting of," where "consisting of" excludes any element or step not specified and "consisting essentially of" permits the inclusion of additional un-recited elements or steps that do not materially affect the basic and novel characteristics of the composition or method under consideration.

[0108] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims.

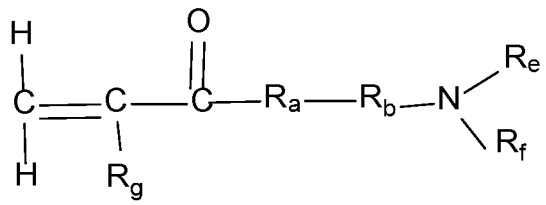
What is claimed is:

1. A polymer dispersion in aqueous media comprising:

a) 10 to 75 wt.% of an anionically colloidally stabilized copolymer dispersion in an aqueous media having a number average particle size via light scattering methods of from 50 to 2000 nanometers in an aqueous media,

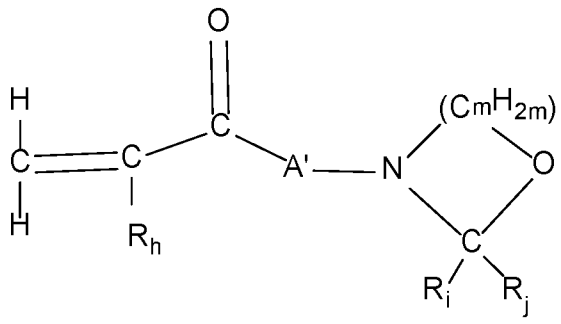
b) 0.1 to 10 wt.% of a water dilutable polyamine additive comprising repeating units from the polymerization product of unsaturated monomers, wherein

(1) about 30-90 wt.% of repeating units are from a free radically polymerizable tertiary amine monomer selected from group consisting of formula A_1 and A_2



Formula A_1

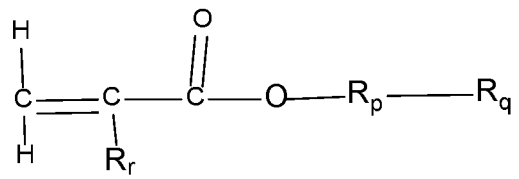
and



Formula A_2

wherein R_a is O or NR_k, R_b is a C_1 to C_6 alkylene, R_e is a C_1-C_4 alkyl, R_f is a C_1-C_4 alkyl, R_g is H or methyl or ethyl and R_h is H or methyl or ethyl, R_k is H, a C_1-C_4 alkyl, or a C_1-C_4 acyl group, A' is poly(oxy-C_2H_4 and/or C_3H_6 alkylene) homopolymer or copolymer of number average molecular weight of 88-348g/mole, m is 2 or 3, Ri is selected from a group comprising hydrogen, phenyl group, benzyl group, and a C_1-C_{12} alkyl group if it is not liked directly to Rj to form an alkylene group, Rj is selected from a group comprising hydrogen, a C_1-C_4 alkyl group, if it is not linked directly to Ri, and optionally Ri and Rj together can covalently bonded to each other to form a C_4 or C_5 alkylene group forming a five or 6 membered ring with the C atom to which they are attached, with

(2) about 10-60 wt.% of repeating units are from polymerizable alkylene oxide monomer B of the formula



B

wherein R_p is a polyalkylene oxide of number average molecular weight from about 88 to about 1200, more desirable from about 132-1100 wherein said polyalkylene oxide has 2 or 3 or 4 carbons per alkylene group (more desirably at least 90 wt.% of the alkylene oxide groups are ethylene oxide), R_q is H or C_1-C_5 alkylene group and more preferably methyl or ethyl; and R_r is H or methyl or ethyl; and

(3) about 0 to about 60 wt.% of the repeating units are from other free radically polymerizable monomers other than monomers A_1, A_2 and B, and

wherein the pH of said polymer dispersion is between 7.5 and 12.5.

2. The polymer dispersion of claim 1, wherein said copolymer comprises at least 50 wt.% of repeating units are derived from polymerizing (meth)acrylate monomers having being esters of alkanols having one to 12 carbon atoms with 3-monoethyleneically unsaturated monocarboxylic and/or unsaturated dicarboxylic acids having 3 to 6 carbon atoms.

3. The polymer dispersion of claim 1 or 2, wherein the dispersion further comprises a pigment or a filler and wherein said polymer dispersion in aqueous media has a pH from 8 to 11.

4. The polymer dispersion of any of claims 1-3, wherein at least 80 wt.% of the repeating units are derived from polymerizing the group consisting of A_1 and A_2 are said A_1 monomer.

5. The polymer dispersion of any of claims 1-4, wherein said copolymer includes from 0.5 to about 2.5 wt.% of a volatile amine (defined as an amine more volatile than water at 25°C) based on the weight of the polymer dispersion.

6. The polymer dispersion of any of claims 1-5, wherein R_2 is methyl or ethyl.

7. The polymer dispersion of any of claims 1-6 used in combination with at titanium dioxide to make an opaque coating.

8. The polymer dispersion of any of claims 1-7, as a roof coating.

9. The polymer dispersion of claim 8, having a film thickness of 10 to 100 mils after air drying.

10. The polymer dispersion of claim 9, having a film thickness of greater than 40 mils after air drying.

11. The polymer dispersion of any of claims 1-7, wherein at least 50 wt.% of the polymer of said polymer dispersion is repeat units from polymerizing a C_4 to C_{12} alky ester of (meth)acrylic acid.

12. The polymer dispersion of claim 11, wherein at least 75 wt.% of said polymer of said polymer dispersion is repeat units from polymerizing a C_4 to C_{12} alky ester of (meth)acrylic acid.

13. The polymer dispersion of any of claims 1-7, wherein at least 60 wt.% of said polymer dispersion is a polyurethane.

14. The polymer dispersion of claim 13, wherein said polymer of said polymer dispersion is a hybrid of polyurethane and polyacrylate.

15. The polymer dispersion of any of claim 1-7, wherein said polymer dispersion has a number average particle size by laser light scattering of 50 to 300 nanometers.

16. The polymer dispersion of claim 15, wherein said dispersion further includes at least 3 parts by weight per hundred parts of polymer dispersion of TiO_2 and a biocide.

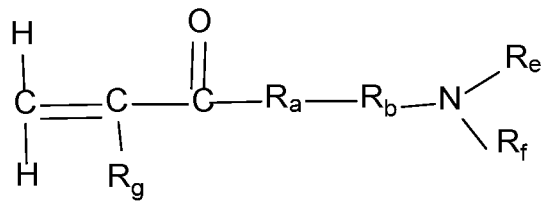
17. The polymer dispersion of claim 15 or 16, wherein at least 50 wt.% of said polymer of said polymer dispersion is repeat units from polymerizing a C_4 to C_{12} alky ester of (meth)acrylic acid.

18. The polymer dispersion of claim 15 or 16, wherein at least 75 wt.% of said polymer of said polymer dispersions is repeat units from polymerizing a C_4 to C_{12} alky ester of (meth)acrylic acid.

19. The polymer dispersion of claim 17 or 18, wherein said water dilutable polyamine comprises 55-85 wt.% of repeating units from a free radically polymerizable tertiary amine monomer selected from group consisting of formula A_1 or A_2; from 15-45 wt.% of repeating units from polymerizable alkylene oxide monomer B; and from 0 to 30 wt.% of repeating units from other free radically polymerizable monomers other than monomers A_1, A_2 and B.

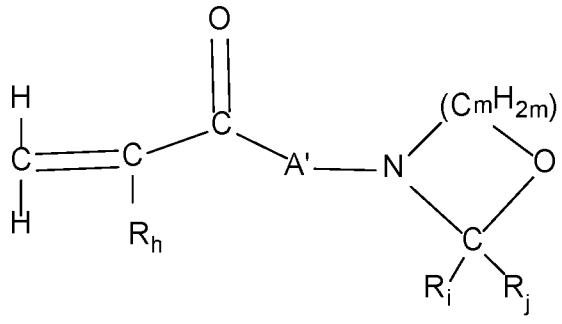
20. The use of a water dilutable polyamine additive to impart water resistance to a coating composition wherein the coating composition comprises an anionically stabilized polymer dispersion, wherein said water dilutable polyamine comprises repeating units from the polymerization product of unsaturated monomers, wherein

a) about 30-90 wt.% of repeating units are from a free radically polymerizable tertiary amine monomer selected from group consisting of formula A_1 and A_2



Formula A_1

and

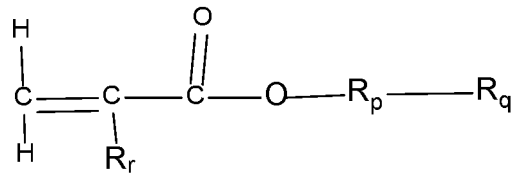


Formula A_2

wherein R_a is O or NR_k, R_b is a C_1 to C_6 alkylene, R_e is a C_1-C_4 alkyl, R_f is a C_1-C_4 alkyl, R_g is H or methyl or ethyl and R_h is H or methyl or ethyl, R_k is H, a C_1-C_4 alkyl, or a C_1-

C_4 acyl group, A' is poly(oxy-C_2H_4 and/or C_3H_6 alkylene) homopolymer or copolymer of number average molecular weight of 88-348g/mole, m is 2 or 3, Ri is selected from a group comprising hydrogen, phenyl group, benzyl group, and a C_1-C_{12} alkyl group if it is not liked directly to Rj to form an alkylene group, Rj is selected from a group comprising hydrogen, a C_1-C_4 alkyl group, if it is not linked directly to Ri, and optionally Ri and Rj together can covalently bonded to each other to form a C_4 or C_5 alkylene group forming a five or 6 membered ring with the C atom to which they are attached, with

b) about 10-60 wt.% of repeating units are from polymerizable alkylene oxide monomer B of the formula



B

wherein R_p is a polyalkylene oxide of number average molecular weight from about 88 to about 1200, more desirable from about 132-1100 wherein said polyalkylene oxide has 2 or 3 or 4 carbons per alkylene group (more desirably at least 90 wt.% of the alkylene oxide groups are ethylene oxide), R_q is H or C_1-C_5 alkylene group and more preferably methyl or ethyl; and R_r is H or methyl or ethyl; and

c) about 0 to about 60 wt.% of the repeating units are from other free radically polymerizable monomers other than monomers A_1, A_2 and B, and

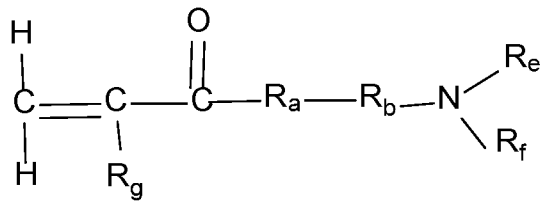
wherein said polyamine imparts into said coating composition earlier water resistance after film formation by said coating composition by including said polyamine additive into said coating composition and homogenizing the polyamine into said coating composition.

21. The use of a water dilutable polyamine additive according to claim 20, wherein said coating composition has a pH of 9.5 or higher when said polyamine is included in said coating composition.

22. A method for enhancing the development of water resistance in a coating composition formed into a film on a substrate, said method comprising incorporating a water dilutable polyamine into said coating composition prior to forming said film and while the coating

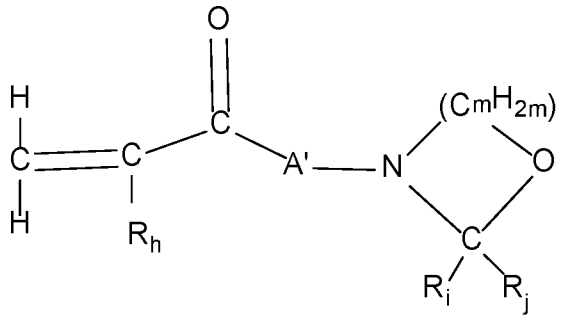
composition has a pH of 9.5 or higher, thereafter maintaining the pH of said coating composition at pH 9.5 or higher until said coating composition is formed into a film on a substrate, and after forming a film on a substrate, allowing the pH of said film on said substrate to fall below pH 9 by volatilization of one or more pH basic components from said coating composition; wherein the coating composition comprises an anionically stabilized polymer dispersion; wherein said water dilutable polyamine comprises repeating units from the polymerization product of unsaturated monomers, wherein

a) about 30-90 wt.% of repeating units are from a free radically polymerizable tertiary amine monomer selected from group consisting of formula A_1 and A_2



Formula A_1

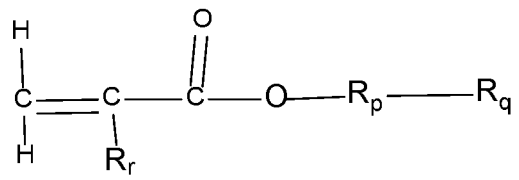
and



Formula A_2

wherein R_a is O or NR_k, R_b is a C_1 to C_6 alkylene, R_e is a C_1-C_4 alkyl, R_f is a C_1-C_4 alkyl, R_g is H or methyl or ethyl and R_h is H or methyl or ethyl, R_k is H, a C_1-C_4 alkyl, or a C_1-C_4 acyl group, A' is poly(oxy-C_2H_4 and/or C_3H_6 alkylene) homopolymer or copolymer of number average molecular weight of 88-348g/mole, m is 2 or 3, Ri is selected from a group comprising hydrogen, phenyl group, benzyl group, and a C_1-C_{12} alkyl group if it is not liked directly to Rj to form an alkylene group, Rj is selected from a group comprising hydrogen, a C_1-C_4 alkyl group, if it is not linked directly to Ri, and optionally Ri and Rj together can covalently bonded to each other to form a C_4 or C_5 alkylene group forming a five or 6 membered ring with the C atom to which they are attached, with

b) about 10-60 wt.% of repeating units are from polymerizable alkylene oxide monomer B of the formula



B

wherein R_p is a polyalkylene oxide of number average molecular weight from about 88 to about 1200, more desirable from about 132-1100 wherein said polyalkylene oxide has 2 or 3 or 4 carbons per alkylene group (more desirably at least 90 wt.% of the alkylene oxide groups are ethylene oxide), R_q is H or C_1-C_5 alkylene group and more preferably methyl or ethyl; and R_r is H or methyl or ethyl; and

about 0 to about 60 wt.% of the repeating units are from other free radically polymerizable monomers other than monomers A_1, A_2 and B.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/052815

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/02 C09D7/65 C04B41/48
ADD.

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)
C09D C08L C04B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 2009/191419 A1 (YUKAWA YOSHIYUKI [JP] ET AL) 30 July 2009 (2009-07-30) paragraphs [0007], [0008], [0046], [0057], [0059] - [0067], [0079] - [0084], [0101], [0102], [0128], [0132]; claims 1-4,8-10,15; examples 2,63; tables 1-5	1-22
Y	US 9 303 183 B1 (GREER ROBERT W [US]) 5 April 2016 (2016-04-05) column 1, lines 14-17; claims 1-18; example 3 column 3, line 14 - column 5, line 41	1-22
A	EP 2 692 753 A1 (ROHM & HAAS [US]; DOW GLOBAL TECHNOLOGIES LLC [US]) 5 February 2014 (2014-02-05) claims 1-6	1-22

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 December 2019	08/01/2020

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Schmitt, Johannes

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/052815

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 2017/132380 A1 (LUBRIZOL ADVANCED MAT INC [US]) 3 August 2017 (2017-08-03) paragraph [0129]; example 6	1-22

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Information on patent family members

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