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(54) Title: ANTI-FREEZE AGENTS

(57) Abstract: There is provided a polymer dispersion comprising: a. a binder component comprising polymer particles dispersed in an aqueous phase; and b. an anti-freeze agent comprising a dendritic polymer or a hyperbranched polymer which is selected from poly (amido) amine (PAMAM), polyglycerol (PGL) or a combination thereof, wherein the PAMAM and/or PGL has a molecular weight of less than 1000 Da. There is also provided a method of lowering the freezing point of a polymer dispersion, the method comprising: mixing the polymer dispersion with an anti-freeze agent selected from dendritic or hyperbranched PAMAM, PGL or a combination thereof, and wherein said PAMAM and/or PGL has a molecular weight of less than 1000 Da, and the use of the PAMAM, PGL or a combination thereof to lower the freezing point of the polymer dispersion.



Description

Title of Invention : Anti-Freeze Agents

Technical Field

[0001] The present invention generally relates to anti-freeze agents, and more specifically to anti-freeze agents for use in aqueous-dispersible polymer compositions or polymeric emulsions. The present invention also relates to methods of lowering the freezing point of aqueous compositions including latex compositions and stabilizing the same under freeze-thaw cycles.

Background Art

10 [0002] Anti-freeze agents or coolants disturb the formation of ice by competing with water-water hydrogen bonds. Anti-freeze agents are commonly employed in mixtures and compositions, such as coating compositions or paint formulations, to improve freeze-thaw stability of the polymer compositions.

[0003] Anti-freeze agents employed in water-based compositions are typically small organic compounds to enable dissolution in the water-based composition. Glycol-based compounds, such as ethylene glycol (EG) and propylene glycol (PG), are a category of anti-freeze agents. However, these known anti-freeze agents are volatile and are prone to escaping, e.g., in engine coolants and in the process of paint manufacturing, storage and the paint coatings after application, resulting in undesirable VOC emissions and causing toxicity to humans and animals. In paint applications, it is generally preferred to provide environmentally friendly and odourless compositions. Additionally, EG may be poisonous to humans and animals. EG is also difficult to detect in the body, and may cause symptoms including intoxication, severe diarrhoea, and vomiting. Therefore, EG is currently banned in many countries and newly developed products are generally free of EG. On the other hand, PG is considerably less toxic than EG, but is still considered a VOC. PG is also less effective as an anti-freeze agent so larger amounts may be needed to achieve the same performance as EG.

[0004] Another category of anti-freeze agents is glycerin, which saw usage mainly in interior combustion engines. However, because of higher cost and weaker anti-freeze capability, glycerin was not as widely adopted as EG. Glycerin is a by-product of the manufacture of biodiesel (fatty acid methyl esters) made by reacting natural vegetable or animal fats with methanol. As biodiesel fuel is becoming increasingly prevalent, the large amount of glycerin generated from the high volume usage of biodiesel fuel has resulted in glycerin becoming cost-competitive with glycols. In the coating and paint industry however, anti-freeze products are still dominated by EG and PG.

[0005] Anti-freeze agents having larger molecular weights, such as block copolymers, are typically employed in organic solvent-based compositions or oil compositions due to the solubility of such compounds. Furthermore, when mixing additives with paint compositions, it is usually required to mitigate the potential adverse effects these additives may exert on coating strength or film forming properties of the paint compositions, e.g., wet time, tack-free time, viscosity, etc.

[0006] Therefore, there is a need to provide anti-freeze agents that are non-volatile, non-toxic and effective for dispersing aqueous polymer compositions, which overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary of Invention

[0007] It is not expected that large molecular weight compounds, such as hyperbranched or dendritic polymers, are able to effectively function as anti-freeze agents in aqueous compositions. This is because it is difficult to maintain such large molecular weight compounds in dispersion in order to disturb the formation of ice.

[0008] Furthermore, small molecular weight compounds, such as EG and PG, are considered most effective as anti-freeze agents in water-based compositions, because such small molecular weight compounds have excellent mobility and high functional group content per unit of molecular weight (number of functional groups/Mw), both of which aid in hydrogen bonding between the anti-freeze agent with water. On the other hand, large unbranched compounds with molecular weights (Mw) of more than 300, such as poly(ethylene glycol) methyl ether

(MPEG350 and MPEG750), are less mobile and have much lower functional group content per unit of molecular weight than the small molecular weight compounds. Thus, large molecular weight compounds are expected to be less effective anti-freeze agents.

5 [0009] It is now discovered that a hyperbranched polymer or dendritic polymer comprising at least one polar functional group is effective in lowering the freezing point of an aqueous composition or stabilizing same under freeze-thaw cycles.

[0010] Accordingly, the present disclosure relates to a polymer dispersion comprising: a. a binder component comprising polymer particles dispersed in an aqueous phase; and b. an anti-freeze agent comprising a dendritic polymer or a hyperbranched polymer, wherein the dendritic polymer or the hyperbranched polymer comprises at least one polar functional group. Advantageously, it has been found that the dendritic or hyperbranched anti-freeze agent may provide comparable, if not superior, anti-freeze capabilities as the relatively smaller anti-freeze agents such as EG or PG. More advantageously, the use of the dendritic or hyperbranched polymer as anti-freeze agent provides additional technical benefits towards the polymer dispersion. For instance, the high density of functional groups occurring on both the nodes and peripheral surface of the dendritic or hyperbranched anti-freeze agent may act to disperse the polymer particles in the dispersion. This may prevent clumping or agglomeration of the polymer particles and improve stability of the polymer dispersion.

[0011] Advantageously, the dendritic or hyperbranched polymer may serve additional functions other than acting as an anti-freeze agent. For instance, it may also replace completely or partially conventional pH buffers (e.g., ethanolamine, diethylamine) used in polymer emulsions. In some embodiments, the use of a dendritic or hyperbranched polymer having peripheral amine functional groups has been found to provide improved stability to polymer emulsions (e.g. latex paint) comprising anti-microbial agents and/or biocides. In particular, the biocide activity of such emulsions may be advantageously maintained over a specific period of time or any reduction was observed to be mitigated by the presence of the disclosed dendritic or hyperbranched anti-freeze agent, compared to formulations which do not contain said dendritic or hyperbranched anti-freeze agent.

[0012] The at least one polar functional group may advantageously improve the solubility of the hyperbranched or dendritic polymer in the aqueous phase. Plural polar functional groups may be provided which may be same or different from each other. Furthermore, the hyperbranched or dendritic polymer may have an average
5 molecular weight of greater than 250, or greater than 500, or greater than 1,000, or greater than 1,400 and up to 8,000, which advantageously reduces its volatility. If provided with a solvent, the hyperbranched or dendritic polymer may exhibit a non-volatile content of more than 95% by weight. The use of an anti-freeze agent comprising a hyperbranched or dendritic polymer may therefore substantially
10 reduce or eliminate VOC emission of the aqueous polymer composition.

[0013] Further advantageously, the hyperbranched or dendritic polymer may act as a rheological additive or modifier to provide a thickening effect to the aqueous composition, such as an aqueous paint formulation, where desired. This may in turn confer a low shear viscosity on the aqueous composition, thereby preventing
15 pigment settling in paint compositions. Compared to the conventional linear structure polymers of prior art anti-freeze agents, the hyperbranched or dendritic polymer provides a much lower viscosity for the same molecular weight, which is beneficial in respect of paint compositions and in particular the ability to be applied as coating films.

[0014] Advantageously, the hyperbranched or dendritic polymer may be modified with one or more, two or more, three or more additional types of functional groups to confer other desirable properties on the disclosed hyperbranched or dendritic polymer. In one embodiment, the functional groups expressed by the dendritic or hyperbranched polymer at its nodes and at its peripheral surface may be the same or
25 different. In embodiments, the dendritic or hyperbranched polymer may comprise one or more additional functional groups different from the polar functional group, either at its nodes or at its peripheral surface. In embodiments, the additional functional group is selected from the group consisting of: hydroxyl group, amine group, amide group, carboxyl group, carboxylate group, carboxylic acid group,
30 epoxy group, glycidol group, acrylate group, carbonyl group, carbamate group, succinamic group, siloxane group and combinations thereof. In particular, the additional functional group may be selected from amidoethanol,

amidoethylethanolamine, sodium carboxylate, diamines, alkanolamine, succinamic acid, trimethoxysilyl, or tris(hydroxymethyl)amidomethane groups. In embodiments, the at least one additional functional group is a hydrophobic functional group.

- 5 [0015] In embodiments, the hyperbranched or dendritic polymer may comprise at least one polar functional group and at least one additional hydrophobic group. Where plural hydrophobic groups are provided, they may be the same or different. The hydrophobic group may also be an oleophobic group, e.g., fluorinated hydrocarbons.
- 10 [0016] In some embodiments, the hyperbranched or dendritic polymer further comprises at least one peripheral hydrophobic functional group. The hydrophobic functional group may be selected from the group consisting of C₂₋₂₀ alkyl group, C₂₋₂₀ hydroxyalkyl group, C₂₋₂₀ alkanolamine group, C₂₋₂₀ aminoalkyl group, C₂₋₂₀ alkanolamide group, C₂₋₂₀ alkoxy group, C₂₋₂₀ alkoxysilyl group and combinations thereof.
- 15

[0017] Advantageously, the at least one hydrophobic functional group provides a stabilizing effect in that the influence of the molecular weight of the hyperbranched or dendritic polymer on its solubility in the aqueous composition is lowered. The disclosed dendritic or hyperbranched polymer comprising hydrophobic groups may

20 improve stability of the polymer dispersion by acting as an amphiphilic surfactant, wherein the polar functional group of the hyperbranched or dendritic polymer interacts with the aqueous solvent molecules and the hydrophobic group of the hyperbranched or dendritic polymer interacts with the binder polymer particles. The hydrophobic group may comprise an aliphatic alkyl group comprising 2 to 20, 4 to

25 20, 6 to 20, 8 to 20, 10 to 20, 12 to 20, 14 to 20, 4 to 18, 8 to 18, 10 to 18, 12 to 18, 14 to 18, 4 to 16, 8 to 16, 10 to 16, 12 to 16 or 14 to 16 carbon atoms. The aliphatic alkyl group may be further substituted with one or more of an amine group, a hydroxyl group, a carboxylate group, a carbonyl group, a cycloalkyl group, a heterocycloalkyl group, and an aryl group.

- 30 [0018] In embodiments, the hyperbranched or dendritic polymer may also comprise cross-linkable peripheral functional groups which may be different from or same as

the polar functional groups or the hydrophobic groups (when present). Exemplary cross-linkable functional groups may include isocyanate groups, hydroxyl groups, carboxylate groups and amine groups.

[0019] In embodiments, the hyperbranched or dendritic polymer may comprise additional functional groups selected to confer properties, such as promoting surface adhesion e.g., by the inclusion of alkoxysilyl functional groups or UV curing e.g., by the inclusion of acrylate functional groups.

[0020] In one aspect, there is provided a polymer dispersion comprising a binder component comprising polymer particles dispersed in an aqueous phase; and an anti-freeze agent selected from poly(amido)amine (PAMAM), polyglycerol (PGL) or a combination thereof, wherein the PAMAM and/or PGL has a molecular weight of less than about 1000 Da. The polymer dispersion may further comprise at least one isothiazolinone, isothiazolinone-derived, benzimidazole, phenylurea biocide or mixtures thereof.

[0021] Advantageously, it has been found that PAMAM or PGL having a molecular weight of less than about 1000 Da according to the present disclosure may provide superior anti-freeze effects when compared to dendritic or hyperbranched polymers outside this weight range. Further advantageously, the PAMAM or PGL may be used in a polymer dispersion composition comprising Isothiazolinone type preservative biocides to achieve enhanced biocidal stability or to preserve/improve their inhibitory effects on the degradation activities of a chemical or microorganism on the dispersion composition.

[0022] The present disclosure is also related to a method for lowering the freezing point of a polymer dispersion, the method comprising: mixing the polymer dispersion with an anti-freeze agent, said anti-freeze agent comprising a dendritic polymer or a hyperbranched polymer, wherein the dendritic polymer or the hyperbranched polymer comprises at least one polar functional group.

[0023] In another aspect, there is provided a method of lowering the freezing point of a polymer dispersion, the method comprising: mixing the polymer dispersion with an anti-freeze agent, said anti-freeze agent selected from PAMAM, PGL or a

combination thereof, and wherein the PAMAM and/or PGL has a molecular weight of less than about 1000 Da.

[0024] The polymer dispersion may be an aqueous-dispersible polymer composition or a polymer dispersion as disclosed herein. In embodiments, the polymer dispersion is a latex composition or a latex emulsion.

[0025] In an embodiment, the present disclosure relates to the use of a hyperbranched polymer or dendritic polymer to lower the freezing point of a polymer dispersion, wherein the hyperbranched or dendritic polymer comprises at least one polar functional group.

[0026] In another aspect, there is provided a method of using a PAMAM, PGL or a combination thereof to lower the freezing point of a polymer dispersion, wherein the PAMAM and/or PGL has a molecular weight of less than about 1000 Da. The method may be employed towards polymer dispersions comprising at least one isothiazolinone, isothiazolinone-derived, benzimidazole, phenylurea biocide or mixtures thereof.

[0027] Advantageously, the interaction of the polar functional group with the water molecules of the polymer dispersion reduces the volatility of the hyperbranched or dendritic polymer, thereby lowering the VOC emission of the polymer dispersion.

[0028] Other embodiments are described in the following description and claims.

Definitions

[0029] The following words and terms used herein shall have the meaning indicated:

[0030] Unless defined otherwise, the term "alkyl" or "alkylene" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group, containing from 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 carbon atoms. In embodiments, an alkyl group may contain a carbon chain length in a range comprising an upper and lower limit from any two integers disclosed above, e.g., C₁₋₂₀, C₄₋₁₆, C₆₋₁₂, etc.

[0031] The term “alkoxy” refers to an alkyl-O- group in which alkyl is as defined herein.

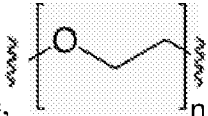

[0032] The term “alkanolamine” refers to an amine group as defined herein having at least one alcohol functional group.

5 [0033] The term “alkoxysilyl” refers to a $-\text{Si}(\text{OR})_n$ group, wherein R is an alkyl as defined herein and n is an integer selected from 1, 2, 3, or 4.

[0034] The term “alkylsilane” refers broadly to $\text{alkyl}(\text{SiH}_4)$, wherein alkyl is as defined above.

10 [0035] The term “glycol ether” refers broadly to alkyl ether, wherein the term “alkyl” is defined above.

[0036] The term “polyethylene glycol” as used herein refers to a chemical moiety

comprising n repeating units of oxy ethylene, , wherein  denotes an attachment point.

15 [0037] The term “cycloalkyl” as used herein refers to a saturated cyclic alkyl group comprising from 3 to 8 ring carbon atoms. The term “heterocycloalkyl” shall refer to a cycloalkyl group as herein defined wherein at least one ring carbon atom has been substituted by one of the following heteroatoms N, O or S. The heterocycloalkyl may contain 1, 2, 3, 4, 5, 6, or 7 heteroatoms.

20 [0038] The term “aryl” as used herein refers to a unsaturated aromatic ring comprising from 3 to 8 ring carbon atoms. The term “heteroaryl” shall refer to an aryl group as herein defined wherein at least one ring carbon atom has been substituted by one of the following heteroatoms N, O or S. The heteroaryl may contain 1, 2, 3, 4, 5, 6, or 7 heteroatoms.

25 [0039] The term “polymer dispersion” as used herein refers to a two-phase system wherein one or more polymers are in the dispersed phase and the dispersing medium is in the continuous phase.

[0040] The term “dendritic polymer” as used herein is intended to describe a repetitively branched, substantially globular molecule having a core moiety

comprising two or more nodes, each node branching into at least two repeating units, each repeating unit having at least two or more branches comprising reactive functional groups; and wherein the reactive functional groups are capable of forming additional layers or generations of the dendritic polymer. Dendritic polymers may be completely and symmetrically branched (“dendrimers”) or may be asymmetrically branched (“hyperbranched polymers”).

[0041] The term “hyperbranched polymer”, in the context of the present specification, refers to a polymer which may be formed via a divergent synthetic method comprising asymmetrical dendritic branching. A hyperbranched polymer may bear resemblance to a symmetrically branched dendrimer and may assume a substantially spherical or globular shape at 4th generation or larger.

[0042] The term “peripheral functionality” or “theoretical peripheral functionality”, when used in the present specification to describe dendrimers, dendritic polymers or hyperbranched polymers, refers to a theoretical amount of reactive functional groups being expressed on the surface of the globular molecule. For instance, if a zero-generation dendritic polymer exhibits a peripheral functionality of 4; a first generation dendritic polymer would exhibit a peripheral functionality of 8; a second generation dendritic polymer would exhibit a peripheral functionality of 16; a third generation dendritic polymer would exhibit a peripheral functionality of 32; and so on.

[0043] The term “biocide” refers to a compound which is inhibitory to degradation activities of a chemical substance or microorganism (e.g. bacteria, algae, fungi) on a product. The term “biocide” when used herein also refers to a compound used in a variety of industry for controlling microbial growth or fouling. The term “biocide” is also to be interpreted broadly to include preservatives, disinfectants, insecticides and pesticides. As used herein, the term “biocide” may preferably refer to thiazolinone-based or isothiazolinone-based biocides. The term may also refer to biocide mixtures comprising at least one thiazolinone-based or an isothiazolinone-based active compound. Exemplary thiazolinone-based biocides may include methylisothiazolinone (MIT), chloromethylisothiazolinone (CMIT), benzisothiazolinone, octylisothiazolinone, dichlorooctylisothiazolinone, butylbenzisothiazolinone or mixtures thereof. The thiazolinone-based or

isothiazolinone-based biocide may also be mixed with other biocides such as imidazole-based biocides (e.g., benzimidazole), phenylurea compounds, etc.

[0044] The term “anti-freeze agent” or “anti-freezing agent” as used herein refers to a compound, composition or mixture added to a liquid medium to reduce the freezing point of water, aqueous phase and/or the bulk medium; or to stabilize the liquid medium when subjected to at least one freeze-thaw cycle (stability can be measured by the changes to viscosity after being subjected to freeze-thaw cycles).

[0045] The term “mol%”, in the context of the present specification and unless otherwise specified, refers to a percentage based on the total number of functional groups per molecule of dendritic or hyperbranched polymer. For example, when a dendritic or hyperbranched molecule comprises 20 mol% of alkyl groups, 20% of the total number of functional groups are alkyl groups.

[0046] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

[0047] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

[0048] As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

[0049] Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range

such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

5 [0050] Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically
10 recited herein.

Detailed Disclosure of Embodiments

[0051] Exemplary, non-limiting embodiments of a polymer dispersion according to the present invention will now be disclosed. An exemplary embodiment of the disclosed polymer dispersion comprises: a) a binder component comprising
15 polymer particles dispersed in an aqueous phase; and b) an anti-freeze agent comprising a dendritic polymer or a hyperbranched polymer, wherein the dendritic polymer or the hyperbranched polymer comprises at least one polar functional group.

[0052] The polymer dispersion comprises polymeric particles dispersed in an
20 aqueous phase. The aqueous phase may comprise an aqueous solvent, e.g., water. The polymer particles may be formed by emulsion polymerization. The binder component may be a polymer emulsion or a latex composition. The binder component may be selected from polyacrylate, polystyrene and co-polymers thereof. In embodiments, the binder component may comprise a polymer formed
25 from monomers such as alkylacrylate (e.g., meth(acrylate), methylacrylate, ethylacrylate, butylacrylate), alkylmethacrylate, vinyl alcohol, vinyl acetate, vinyl acetate-ethylene, styrene, or acrylonitrile, etc. In one embodiment, the polymer composition as disclosed herein may comprise, as the polymeric binder, an acrylate-styrene emulsion polymer. The polymer particles may possess a particle size (or
30 particle diameter) of around 50 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm, 450 nm, or 500 nm. The polymer particles may exhibit a size

distribution wherein the range of the particle diameters may comprise an upper limit and a lower limit selected from the diameters disclosed above. The binder particles may be substantially homogeneously dispersed in deionized water (aqueous solvent).

5 [0053] The polymer dispersion comprises an anti-freeze agent which comprises a dendritic polymer or hyperbranched polymer or a blend thereof. Each dendritic or hyperbranched polymer may express at least one polar functional group in its peripheral functional groups. Alternatively or additionally, each dendritic or hyperbranched polymer may express at least one polar functional group at a
10 branching node. The polymer dispersion may contain no other compound acting to lower the freezing point of the polymer dispersion. In other words, the dendritic or hyperbranched polymer may be used as the sole anti-freeze agent. In embodiments, the disclosed dispersions are substantially free of ethylene glycol, propylene glycol, glycerin, monomeric glycerol, or substituted derivatives thereof. In embodiments,
15 the polymer dispersion may contain no dendritic or hyperbranched polymer other than the disclosed dendritic or hyperbranched polymer. In other words, the disclosed anti-freeze agent may be the sole or only dendritic or hyperbranched polymer in the dispersion. In embodiments, the disclosed dispersions are substantially devoid or free of dendritic or hyperbranched polymers having a
20 theoretical molecular weight of less than 500 Da, less than 450 Da, less than 400 Da, less than 350 Da, less than 300 Da or less than 250 Da.

[0054] The at least one polar functional group may be capable of assisting the hyperbranched or dendritic polymer to remain dispersed in the aqueous phase or composition by non-covalent interactions with the water molecules. Further
25 advantageously, the hyperbranched or dendritic polymer may be a compound having a large molecular weight, e.g. a molecular weight as disclosed herein, and is therefore not as volatile as the small molecular weight compounds known in the art of anti-freeze agents for aqueous compositions, such as ethylene glycol and propylene glycol.

30 [0055] In embodiments, the at least one polar functional group is selected from the group consisting of: hydroxyl group, amine group, amide group, carboxyl group, carboxylate group, carboxylic acid group, epoxy group, glycidol group, acrylate

group, carbonyl group, carbamate group, succinamic group, siloxane group and combinations thereof. In other embodiments, the at least one polar functional group is selected from the group consisting of: hydroxyl group, amine group, amide group, carboxylic acid group, polyethylene glycol group, siloxane group and combinations thereof.

[0056] In an embodiment, the polar functional group is a polyethylene glycol group having about 1 to 20 repeating units of oxyethylene. The polyethylene glycol group may have 1 unit of oxyethylene, or 2 repeating units of oxyethylene, or 3 repeating units of oxyethylene, or 4 repeating units of oxyethylene, or 5 repeating units of oxyethylene, or 6 repeating units of oxyethylene, or 7 repeating units of oxyethylene, or 8 repeating units of oxyethylene, or 9 repeating units of oxyethylene, or 10 repeating units of oxyethylene, or 12 repeating units of oxyethylene, or 14 repeating units of oxyethylene, or 16 repeating units of oxyethylene, or 18 repeating units of oxyethylene, or 20 repeating units of oxyethylene.

[0057] In embodiments, the hyperbranched or dendritic polymer has a non-volatile content of more than 95% by weight. In embodiments, the hyperbranched or dendritic polymer may vaporize or thermally decompose at a temperature higher than that of the polymer dispersion. Advantageously, the inclusion of the hyperbranched or dendritic polymer aids in reducing or substantially eliminating the VOC emission of the aqueous dispersion.

[0058] The dendritic or hyperbranched polymer may comprise non-volatile content of more than 90%, more than 91%, more than 92%, more than 93%, more than 94%, more than 95%, more than 96%, more than 97%, more than 98%, more than 99%, or more than 99.5%, by weight of the polymer.

[0059] The dendritic or hyperbranched anti-freeze agent may be selected as one that exhibits a weight loss of less than 10% when measured according to ASTM D2369-10. The dendritic or hyperbranched anti-freeze agent may exhibit a weight loss of less than 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1% or 0.5% when measured according to ASTM D2369-10. The dendritic or hyperbranched anti-freeze agent may be selected as one that exhibits a weight loss of less than 8% when exposed to

temperature conditions of 110°C, e.g. curing at 110°C. The weight loss refers to the mass of the dendritic or hyperbranched polymer that is lost after a curing/cross-linking procedure as compared to its mass pre-cure. The dendritic or hyperbranched anti-freeze agent may exhibit a weight loss of less than 7%, 6%, 5%, 4%, 3%, 2%, 1% or 0.5% by weight after curing at 110°C. Curing may occur for a duration of at least one hour. Advantageously, this would allow the polymer dispersion to emit a low amount of volatiles upon curing, which may prevent odor or chemical irritation.

[0060] The dendritic or hyperbranched anti-freeze agent may be selected as one that vaporizes at a temperature of at least 250°C or higher, or at least 300°C or higher.

The dendritic or hyperbranched anti-freeze agent may be selected as one that thermally decomposes at a temperature of at least 200°C or higher, or at least 250°C or higher, or at least 300°C or higher.

[0061] The hyperbranched or dendritic polymer may have a pKa (an acid dissociation constant) at 25°C of at least 9.0, or is selected from about 9.0, 9.1, 9.2, 9.3, 9.4 or 9.5. Advantageously, the hyperbranched or dendritic polymer may interact with the water molecules of the aqueous phase or aqueous composition, thereby disrupting the formation of the ice structure and resulting in the lowering of the freezing point of the aqueous composition or polymer dispersion.

[0062] The freezing point of the polymer dispersion may be lowered by 1°C, 2°C, 3°C, 4°C, 5°C, 6°C, 7°C, 8°C, 9°C, 10°C, 11°C, 12°C, 13°C, 14°C, 15°C, 16°C, 17°C, 18°C, 19°C, 20°C or more, as compared to a polymer dispersion without an anti-freeze agent or a polymer dispersion with a monomeric anti-freeze agent such as ethylene glycol and propylene glycol.

[0063] In embodiments, the aqueous composition or dispersion exhibits a change in Krebs Unit (KU) Viscosity of about 10 or less, or 9, 8, 7, 6, 5, 4, 3, 2, 1 or less, upon completion of 1, 2, 3, 4 or 5 freeze-thaw cycles. In embodiments, the polymer dispersion exhibits a change in Krebs Unit Viscosity of about 10 or less, or 9, 8, 7, 6, 5, 4, 3, 2, 1 or less, when measured according to ASTM D562-10. A KU viscosity tolerance of ± 10 units indicates that the consistency of the composition is maintained within the acceptable threshold. In some embodiments, the in-can

appearance of the composition after the freeze-thaw cycles is substantially the same as that before the freeze-thaw test.

[0064] In embodiments, the dendritic or hyperbranched polymer comprises a theoretical peripheral functionality of from about 4 to about 128, or from about 4 to about 8, or from about 4 to about 16, or from about 4 to about 32, or from about 4 to about 64, or from about 16 to about 128, or from about 32 to about 128, or from about 64 to about 128, or from about 16 to about 64, or from about 16 to about 32, or from about 32 to about 64. In one embodiment, a generation-zero dendritic or hyperbranched polymer may be used (i.e., around 4 peripheral functional groups per polymer chain/dendritic molecule). In another embodiment, a first generation dendritic or hyperbranched polymer may be used (i.e., around 8 peripheral functional groups). In yet another embodiment, a second generation dendritic or hyperbranched polymer may be used (i.e., around 16 peripheral functional groups). In yet another embodiment, a third generation dendritic or hyperbranched polymer may be used (i.e., around 32 peripheral functional groups). In yet another embodiment, a fourth generation dendritic or hyperbranched polymer may be used (i.e., around 64 peripheral functional groups). In yet another embodiment, a fifth generation dendritic or hyperbranched polymer may be used (i.e., around 128 peripheral functional groups).

[0065] The hyperbranched or dendritic polymer may comprise at least one, at least two, at least three, at least four, at least five, at least six, at least seven, at least eight, at least nine, at least ten, at least 11, at least 12, at least 13, at least 14, at least 15, at least 16, at least 32, at least 64, or at least 128 polar functional groups. In embodiments, the hyperbranched or dendritic polymer may comprise from about 4 to about 4096 polar functional groups, from about 4 to about 8 polar functional groups, from about 4 to about 16 polar functional groups, from about 4 to about 32 polar functional groups, from about 4 to about 64 polar functional groups, from about 4 to about 128 polar functional groups, from about 4 to about 256 polar functional groups, from about 4 to about 512 polar functional groups, from about 8 to about 16 polar functional groups, from about 8 to about 32 polar functional groups, from about 8 to about 64 polar functional groups, from about 8 to about 128 polar functional groups, from about 8 to about 256 polar functional groups, from

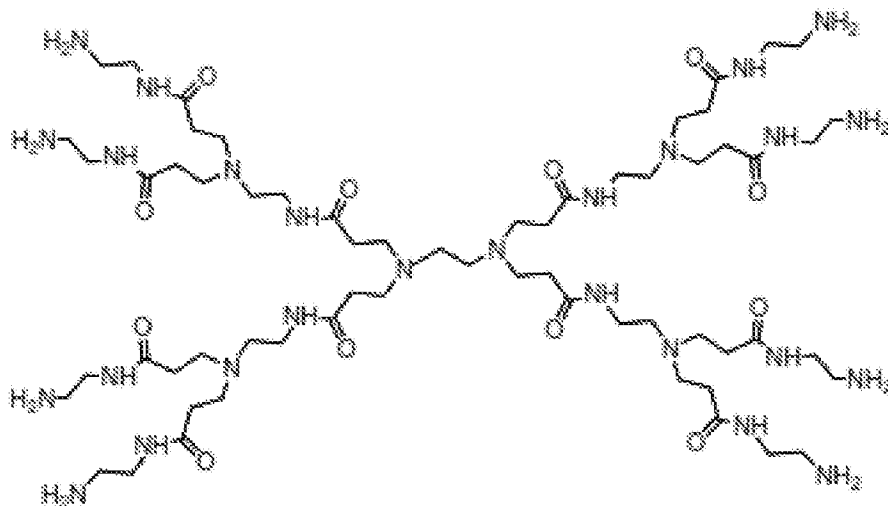
about 8 to about 512 polar functional groups, from about 16 to about 32 polar functional groups, from about 16 to about 64 polar functional groups, from about 16 to about 128 polar functional groups, from about 16 to about 256 polar functional groups, from about 16 to about 512 polar functional groups, from about 32 to about 64 polar functional groups, from about 32 to about 128 polar functional groups, from about 32 to about 256 polar functional groups, or from about 32 to about 512 polar functional groups. In embodiments, the hyperbranched or dendritic polymer may comprise from 4 to 10, 4 to 20, 4 to 30, 4 to 40, 4 to 50, 4 to 60, 4 to 70, 4 to 80, 4 to 90, or 4 to 100 polar functional groups. Where the hyperbranched or dendritic polymer comprises more than one polar functional group, the polar functional groups may be the same or different.

[0066] Due to the high density of the polar functional groups, the hyperbranched or dendritic polymer may advantageously provide an equivalent or near equivalent content of polar functionality as compared to the conventional small molecular anti-freeze compounds when provided at a reduced total molecular weight.

[0067] In embodiments, the polar functional groups of the hyperbranched or dendritic polymer may be located at branching nodes of the polymer and/or at terminal/peripheral ends of the polymer. The peripheral polar functional groups of a previous generation serve as branching nodes for a next generation and thus, polar functional groups may be located at the branching nodes.

[0068] In embodiments, the peripheral functional groups may be partially or fully substituted with one or more, two or more, or three or more additional functional groups as defined herein. The additional functional group(s) may be the same or different as the initial unmodified peripheral functional group. The substitution may for instance include reacting the peripheral functional groups with one or more reactive adducts. The reactive adduct may comprise at least one functional group reactive with the peripheral functional group and at least one functional group intended for grafting onto the hyperbranched or dendritic polymer molecule.

[0069] In an example, the anti-freeze agent may be a poly(amido)amine (“PAMAM”) having the structure illustrated below.



[0070] In the above example, the polar primary amine functional groups are present as peripheral functional groups. Each branching node comprises an amido group. Each dendritic branch comprises at least one amide linkage terminating in an amine functional group. It is being postulated that amido groups, carbonyl groups, and amine functional groups are each individually capable of interacting with the aqueous solvent molecules to prevent or disrupt formation of bonds which may lead to freezing.

[0071] In embodiments, the peripheral -NH_2 functional groups may be partially or fully substituted with one or more additional functional groups. The substitution may for instance include reacting the peripheral amine groups with one or more reactive adducts. The reactive adduct may comprise at least one functional group reactive with the amine group and at least one functional group intended for grafting onto the polyamidoamine molecule. Suitable reactive species may include adducts of polyethyleneglycol (PEG) or polyethylene oxide (PEO).

[0072] The peripheral amine groups may be selected from primary amines (-NH_2), secondary amines (-NHR_1), tertiary amines ($\text{-NR}_1\text{R}_2$), or cyclic amines, wherein R_1 and R_2 may be independently selected from the group consisting of H, alkyl, alkanolamines, alkylamine, alkoxy, alcohol, alkylate, alkylsilane, alkoxysilyl, alkoxysilyl alkylate, amino acid, carbonyl, carboxyl, carboxylate, or esters. Cyclic amines may include heterocycloalkyl ring structures having 3, 4, 5, 6, 7, or 8 ring atoms, wherein at least one heteroatom is N and wherein the ring is saturated or aromatic, and is optionally substituted by one or more functional groups selected

from alkyl, alkanolamines, alkylamine, alkoxy, alcohol, alkylate, alkylsilane, alkoxysilyl, alkoxysilyl alkylate, amino acid, carbonyl, carboxyl, carboxylate, or esters. Cyclic amines may include pyrrolidine, imidazoline, piperidine or piperazine structures. In one embodiment, the peripheral amine group may be an
5 oxo-pyrrolidine group. The amino functional group may be diamines, triamines or tetraamines.

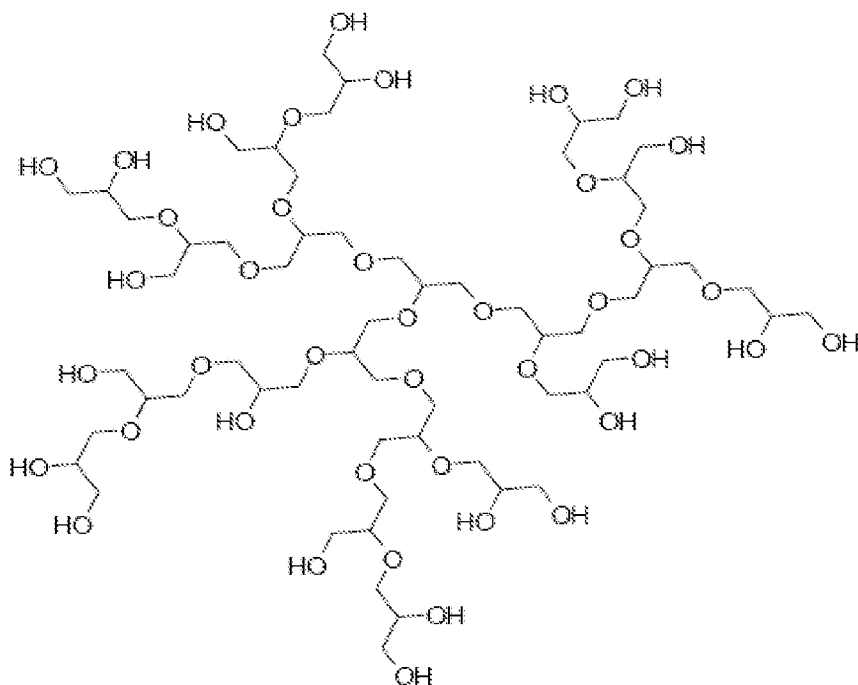
[0073] In some embodiments, the poly(amido)amine may express at least one additional type of functional groups, two additional types of functional groups or three additional types of functional groups selected from the group consisting of:
10 hydroxyl group, amine group, amide group, carboxyl group, carboxylate group, carboxylic acid group, epoxy group, glycidol group, acrylate group, carbonyl group, carbamate group, succinamic group, siloxane group and combinations thereof. In particular, the additional functional group may be selected from amidoethanol, amidoethylethanolamine, sodium carboxylate, diamines, alkanolamine, succinamic
15 acid, trimethoxysilyl, or tris(hydroxymethyl)amidomethane groups. In embodiments, the additional functional group may be distinct from the polar functional group. In embodiments, the additional functional groups may comprise one different type of non-amine functional group, or two different types of non-amine functional groups, or three different types of non-amine functional groups. In
20 embodiments, the poly(amido)amine may express at least one additional type of non-amine peripheral functional group, at least two additional types of non-amine peripheral functional groups, or at least three additional types of non-amine peripheral functional groups.

[0074] In embodiments, the present disclosure provides a latex paint composition,
25 consisting essentially of: a polymeric binder; an aqueous solvent in which said polymeric binder is dispersed therein; at least one additive; and a dendritic / hyperbranched poly(amido)amine present in an amount of from about 0.01 to about 2 wt. % based on the weight of the latex paint composition. In embodiments, the additive is a mixture of additives selected from the group consisting of: biocides,
30 inorganic oxides, and rheological modifiers.

[0075] Where present, the biocide compound may be provided in an amount of about 10 ppm, 15 ppm, 20 ppm, 25 ppm, 30 ppm, 35 ppm, 40 ppm, 45 ppm, 50

ppm, 55 ppm, 60 ppm, 65 ppm, 70 ppm, 75 ppm, 80 ppm, 85 ppm, 90 ppm, 95 ppm, 100 ppm, or may be provided in a range having an upper and lower limit selected from any two values disclosed above. In embodiments, the biocide may be present in an amount from 10 ppm to 50 ppm. The biocide compound may comprise at least one isothiazolinone-based biocide. The biocide may include, but are not limited to, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and mixtures thereof. Advantageously, it is postulated that the buffering properties of the polyamidoamine may stabilize the biocide, allowing the concentrations of the biocide to be maintained or wherein any decrease in biocide concentrations over time is lower compared to a dispersion wherein the polyamidoamine or the polyglycerol anti-freeze agent is absent.

[0076] In another example, the anti-freeze agent may be a hyperbranched or dendritic polymer comprising polar hydroxyl functional groups such as a polyglycerol (“PGL”) having the structure illustrated below.



[0077] In the above example, the polar hydroxyl functional groups are present as peripheral functional groups and the ether functional groups are present at the branching nodes. In one embodiment, the –OH functional groups are not substituted. In other embodiments, the peripheral –OH functional groups may be partially or fully substituted with one or more additional functional groups, other

than –OH. The substitution may for instance include reacting the peripheral hydroxyl groups with one or more reactive adducts. The reactive adduct may comprise at least one functional group reactive with the –OH group and at least one functional group intended for grafting onto the dendritic or hyperbranched polyglycerol. Suitable reactive adducts may include adducts of di-, tri- or poly-isocyanates.

[0078] In some embodiments, the polyglycerol may express at least one additional type of functional groups, two additional types of functional groups or three additional types of functional groups. In embodiments, the additional functional group may be distinct from the polar functional group. In embodiments, the additional functional groups may comprise one different type of non-hydroxyl functional group, or two different types of non-hydroxyl functional groups, or three different types of non-hydroxyl functional groups. In embodiments, the polyglycerol may express at least one additional type of non-hydroxyl peripheral functional group, at least two additional types of non-hydroxyl peripheral functional groups, or at least three additional types of non-hydroxyl peripheral functional groups.

[0079] In embodiments, the additional functional group is selected from the group consisting of: hydroxyl group, amine group, amide group, carboxyl group, carboxylate group, carboxylic acid group, epoxy group, glycidol group, acrylate group, carbonyl group, carbamate group, succinamic group, siloxane group and combinations thereof. In particular, the additional functional group may be selected from amidoethanol, amidoethylethanolamine, sodium carboxylate, diamines, alkanolamine, succinamic acid, trimethoxysilyl, or tris(hydroxymethyl)amidomethane groups. In one embodiment, the polyglycerol comprises a hydroxyl group and a glycidol group.

[0080] Advantageously, the addition of siloxane or alkoxysilyl functional groups as peripheral groups may enable the modified or substituted hyperbranched or dendritic polymer to be used as an adhesion promoter, or to improve cross-linking density. In another example, the addition of acrylate functional groups as peripheral groups may confer UV curability to the hyperbranched or dendritic polymer.

[0081] Where included, the amino functional group may be selected from primary amines (-NH_2), secondary amines (-NHR_1), tertiary amines ($\text{-NR}_1\text{R}_2$), or cyclic amines, wherein R_1 and R_2 may be independently selected from the group consisting of H, alkyl, alkanolamines, alkylamine, alkoxy, alcohol, alkylate, alkylsilane, alkoxysilyl, alkoxysilyl alkylate, amino acid, carbonyl, carboxyl, carboxylate, or esters. Cyclic amines may include heterocycloalkyl ring structures having 3, 4, 5, 6, 7, or 8 ring atoms, wherein at least one heteroatom is N and wherein the ring is saturated or aromatic, and is optionally substituted by one or more function groups selected from alkyl, alkanolamines, alkylamine, alkoxy, alcohol, alkylate, alkylsilane, alkoxysilyl, alkoxysilyl alkylate, amino acid, carbonyl, carboxyl, carboxylate, or esters. Cyclic amines may include pyrrolidine, imidazoline, piperidine or piperazine structures. In one embodiment, the peripheral amine group may be an oxo-pyrrolidine group. The amino functional group may be diamines, triamines or tetraamines.

[0082] Where the polar functional group is a primary amine, the hyperbranched or dendritic polymer may comprise terminal primary amines having a pK_a at 25°C of at least 9.0, or is selected from about 9.0, 9.1, 9.2, 9.3, 9.4 or 9.5.

[0083] Where the polar functional group is a hydroxyl group, the hyperbranched or dendritic polymer may comprise terminal hydroxyl groups having a pK_a at 25°C of at least 9.0, or is selected from about 9.0, 9.1, 9.2, 9.3, 9.4 or 9.5.

[0084] In embodiments, the present disclosure provides a latex paint composition, consisting essentially of: a polymeric binder; an aqueous solvent in which said polymeric binder is dispersed therein; at least one additive; and a dendritic / hyperbranched polyglycerol present in an amount of from about 0.01 to about 2 wt. % based on the weight of the latex paint composition. In embodiments, the additive is a mixture of additives selected from the group consisting of: biocides, inorganic oxides, and rheological modifiers.

[0085] Where present, the biocide compound may be provided in an amount of about 10 ppm, 15 ppm, 20 ppm, 25 ppm, 30 ppm, 35 ppm, 40 ppm, 45 ppm, 50 ppm, 55 ppm, 60 ppm, 65 ppm, 70 ppm, 75 ppm, 80 ppm, 85 ppm, 90 ppm, 95 ppm, 100 ppm, or may be provided in a range having an upper and lower limit

selected from any two values disclosed above. In embodiments, the biocide may be present in an amount from 10 ppm to 50 ppm. The biocide compound may comprise at least one isothiazolinone-based biocide. The biocide may include, but are not limited to, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one, and mixtures thereof. Advantageously, it is postulated that the buffering properties of the polyglycerol may stabilize the biocide, allowing the concentrations of the biocide to be maintained or wherein any decrease in biocide concentrations over time is lower compared to a dispersion wherein the polyamidoamine or the polyglycerol anti-freeze agent is absent.

- 10 [0086] The hyperbranched or dendritic polymer may comprise an unmodified polymer, wherein all the peripheral functional groups are the polar functional groups. The hyperbranched or dendritic polymer may comprise a partially or completed modified polymer. In one embodiment, the dendritic or hyperbranched polymer is unmodified poly(amido)amine (PAMAM). In another embodiment, the
- 15 dendritic or hyperbranched polymer is unmodified polyglycerol (PGL).

[0087] The peripheral functional groups may be neutral or ionic species. For example, carboxylic acid groups may be present as anionic sodium carboxylate, amino groups may be present as cationic species, while hydroxyl groups may be present as neutral species.

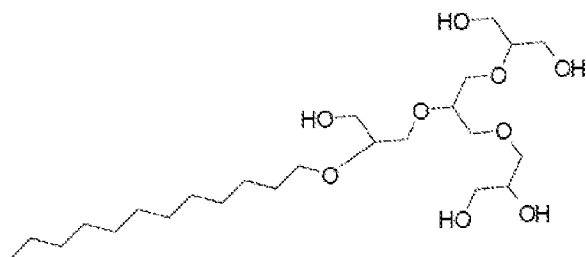
- 20 [0088] The hyperbranched or dendritic polymer may further comprise at least one hydrophobic or oleophobic group selected from the group consisting of C₂₋₂₀ alkyl group, C₂₋₂₀ hydroxyalkyl group, C₂₋₂₀ alkanolamine group, C₂₋₂₀ aminoalkyl group, C₂₋₂₀ alkanolamide group, C₂₋₂₀ alkoxy group, C₂₋₂₀ alkoxysilyl group and combinations thereof.

- 25 [0089] The incorporation of a long hydrocarbon side chain or hydrocarbon tail (e.g., a hydrocarbon side chain having 2-20, 3-20, 4-20, 5-20, 6-20, 7-20, 8-20, 9-20, 10-20, 11-20, 12-20, 13-20, 14-20, or 15-20 carbons) may advantageously stabilize the hyperbranched or dendritic polymer in the polymer dispersion.

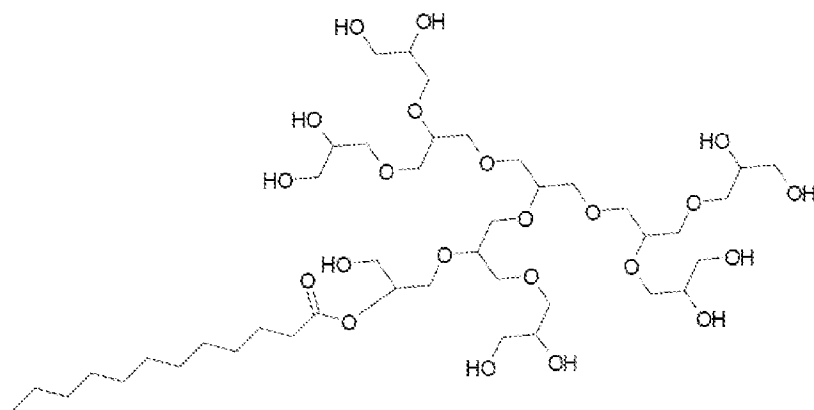
- [0090] The hydrocarbon tail may confer amphiphilicity on the hyperbranched or
- 30 dendritic polymer. The hyperbranched or dendritic polymer may have a hydrophilic-lipophilic balance (HLB) value of between about 10 and 20, indicating

a moderate to complete hydrophilicity of the polymer. The HLB value may be about 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20.

[0091] In an example, the antifreeze agent is a polyglycerol comprising a theoretical peripheral functionality of 6 wherein at least one peripheral –OH group is functionalized by an alkylene oxide group having 12 carbon atoms and a hydrophobic tail, and which is exemplified by the structure illustrated below.

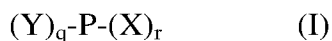


[0092] In another example, the anti-freeze agent may be a polyglycerol having a theoretical peripheral functionality of 12, wherein at least one –OH functional group has been esterified with an aliphatic alkyl group comprising 12 carbon atoms. The anti-freeze agent may have the following structure:



[0093] Additional polar or non-polar functional groups may be expressed, present or located at the branching nodes and/or at the terminal ends of the hyperbranched or dendritic polymer. The peripheral functional groups of a previous generation serve as branching nodes for a next generation and thus, functional groups may be located at the branching nodes.

[0094] The hyperbranched or dendritic polymer may optionally be modified or substituted with one or more substituents X. In one embodiment, a substituted hyperbranched or dendritic polymer may possess the following general formula I:



5 wherein

P is the hyperbranched or dendritic polymer,

Y is the polar functional group,

q is at least 1,

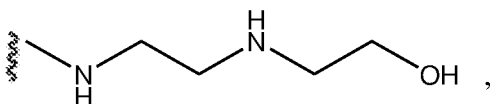
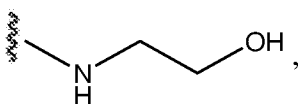
X is an additional functional group as defined herein, which is covalently coupled
10 to said polymer P, and

r is 0 or an integer, wherein $q+r$ represents the total number of surface or peripheral functional groups of polymer P.

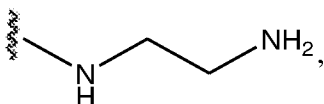
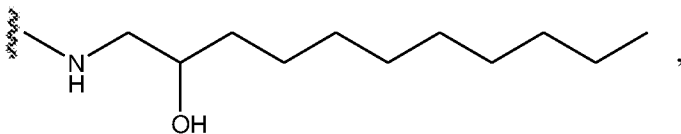
[0095] In specific embodiments, each occurrence of X may be independently selected from:

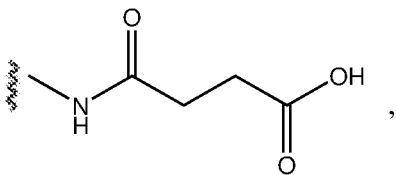
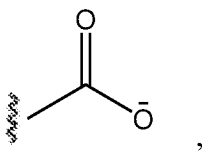
15 -OH,

-polyethylene glycol,

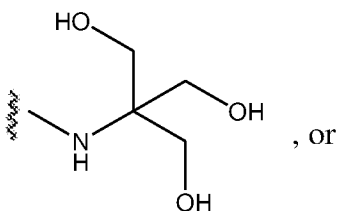
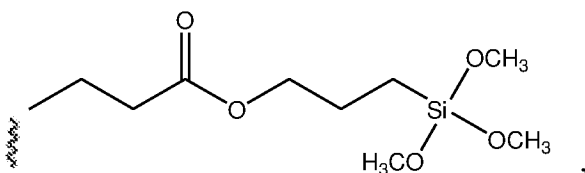


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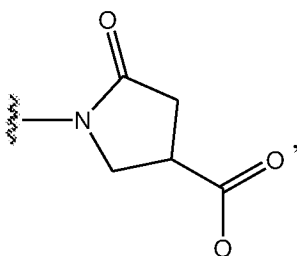





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15 wherein  denotes an attachment point.

[0096] In embodiments, 1 of 10, 1 of 9, 1 of 8, 1 of 7, 1 of 6, 1 of 5, 1 of 4, 1 of 3, 1 of 2, 9 of 10, 8 of 10, 7 of 10, 6 of 10, 5 of 10, 4 of 10, 3 of 10 or 2 of 10, peripheral polar functional groups of the dendritic or hyperbranched polymer may be independently substituted with one or more additional functional groups, which are
20 different from the peripheral polar group.

[0097] The dendritic or hyperbranched polymer may have a ratio of polar functional groups to additional functional groups ($-\text{X}$) of from about 1:9, 1:8, 1:7, 1:6, 1:5, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1 or about 9:1. That is, the ratio of q:r may be from about 1:9, 1:8, 1:7, 1:6, 1:5, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1,
25 7:1, 8:1 or about 9:1.

[0098] For example, where the polar functional group is hydroxyl, the dendritic or hyperbranched polymer may have a ratio of hydroxyl to non-hydroxyl functional groups of from about 1:9, 1:8, 1:7, 1:6, 1:5, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1 or about 9:1.

5 [0099] In another example, where the polar functional group is amine, the dendritic or hyperbranched polymer may have a ratio of amine to non-amine functional groups of from about 1:9, 1:8, 1:7, 1:6, 1:5, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1 or about 9:1.

[00100] The above ratios may also be provided in a range selected from any
10 two ratios herein defined. In other embodiments, the ratio of polar functional groups to additional polar or non-polar functional groups may be from about 99:1 to 1:99.

[00101] The dendritic or hyperbranched polymer may comprise at least 5% of the functional groups as unmodified or native polar functional groups defined
15 herein, at least 10% of the functional groups as unmodified polar functional groups defined herein, at least 20% of the functional groups as unmodified polar functional groups defined herein, at least 30% of the functional groups as unmodified polar functional groups defined herein, at least 40% of the functional groups as unmodified polar functional groups defined herein, at least 50% of the functional
20 groups as unmodified polar functional groups defined herein, at least 60% of the functional groups as unmodified polar functional groups defined herein, at least 70% of the functional groups as unmodified polar functional groups defined herein, at least 80% of the functional groups as unmodified polar functional groups defined herein, at least 90% of the functional groups as unmodified polar functional groups
25 defined herein, at least 95% of the functional groups as unmodified polar functional groups defined herein, or at least 99% of the functional groups as unmodified polar functional groups defined herein; and wherein the remaining functional groups are substituted polar or non-polar functional groups selected from those disclosed herein.

30 [00102] In embodiments, the hyperbranched or dendritic polymer comprises functional groups wherein at least 5% of the functional groups are amine functional

groups. In embodiments, about 5 to 99% of the functional groups of the dendritic or hyperbranched polymer are amine functional groups.

[00103] Where the hyperbranched or dendritic polymer comprises amine functional groups, the average amine number of the hyperbranched or dendritic polymer may be from about 200 mg KOH/g to about 800 mg KOH/g. In some embodiments, the average amine number of the hyperbranched or dendritic polymer may be more than 200 mg KOH/g, more than 250 mg KOH/g, more than 300 mg KOH/g, more than 350 mg KOH/g, more than 400 mg KOH/g, more than 450 mg KOH/g, more than 500 mg KOH/g, more than 550 mg KOH/g, more than 600 mg KOH/g, more than 650 mg KOH/g, more than 700 mg KOH/g, or more than 750 mg KOH/g. As compared to an unbranched or non-hyperbranched polymer, the number of free amine functional groups that can be provided on a hyperbranched or dendritic polymer of the same molecular weight can advantageously be increased. The polar functionality of the disclosed hyperbranched or dendritic polymer is therefore higher than its linear, unbranched or non-hyperbranched counterpart polymers.

[00104] In embodiments, the hyperbranched or dendritic polymer comprises functional groups wherein at least 5% of the functional groups are hydroxyl functional groups. In embodiments, about 5 to 99% of the functional groups of the dendritic or hyperbranched polymer are hydroxyl functional groups.

[00105] Where the hyperbranched or dendritic polymer comprises hydroxyl functional groups, the average hydroxyl number of the hyperbranched or dendritic polymer may be from about 400 mg KOH/g to about 1500 mg KOH/g. In some embodiments, the average hydroxyl number of the hyperbranched or dendritic polymer may be more than 400 mg KOH/g, more than 500 mg KOH/g, more than 600 mg KOH/g, more than 700 mg KOH/g, more than 800 mg KOH/g, more than 900 mg KOH/g, more than 1000 mg KOH/g, more than 1100 mg KOH/g, more than 1200 mg KOH/g, more than 1300 mg KOH/g, or more than 1400 mg KOH/g. As compared to an unbranched or non-hyperbranched polymer, the number of free hydroxyl functional groups that can be provided on a hyperbranched or dendritic polymer of the same molecular weight can advantageously be increased. The polar

functionality of the disclosed hyperbranched or dendritic polymer is therefore higher than its linear, unbranched or non-hyperbranched counterpart polymers.

[00106] In embodiments, the hyperbranched or dendritic polymer comprises hydroxyl groups present at the periphery and/or at the branching nodes, wherein the hydroxyl peripheral groups are partially or fully substituted by glycidol groups. In
5 embodiments, the mol% of glycidol end groups to other end groups (including hydroxyl peripheral groups) comprised in the hyperbranched or dendritic polymer may be from about 100% to about 50%, or any amount therebetween; from about 95% to about 55% or any amount therebetween; from about 90% to about 60% or
10 any amount therebetween; from about 85% to about 65% or any amount therebetween; or from about 80% to about 70% or any amount therebetween. For example, the mol% of glycidol end groups may be 100, 99, 98, 97, 96, 95, 94, 93, 92, 91, 90, 89, 88, 87, 86, 85, 84, 83, 82, 81, 80, 79, 78, 77, 76, 75, 74, 73, 72, 71, 70, 69, 68, 67, 66, 65, 64, 63, 62, 61, 60, 59, 58, 57, 56, 55, 54, 53, 52, 51 or 50
15 mol% or any amount therebetween.

[00107] The disclosed anti-freeze agent may comprise more than one dendritic or hyperbranched polymers as disclosed herein. The anti-freeze agent may comprise one or more dendritic or hyperbranched polymers as disclosed herein and a conventional anti-freeze agent. Exemplary conventional anti-freeze agents
20 include ethylene glycol (EG), propylene glycol (PG), glycerin, monomeric glycerol, or substituted derivatives thereof.

[00108] In some embodiments, the anti-freeze agent consists essentially of the dendritic or hyperbranched polymer as disclosed herein in admixture with one or more components selected from the group consisting of: an additional dendritic or
25 hyperbranched polymer, ethylene glycol and propylene glycol, wherein the additional dendritic or hyperbranched polymer is different from the dendritic or hyperbranched polymer. The additional dendritic or hyperbranched polymer may be a dendritic or hyperbranched polymer as disclosed herein.

[00109] In some embodiments, the anti-freeze agent consists essentially of the dendritic or hyperbranched polymer as disclosed herein. In some embodiments, the
30 disclosed anti-freeze agent may comprise or consist essentially of a dendritic or

hyperbranched polymer as disclosed herein in admixture with a conventional anti-freeze agent, such as EG, to form a blend. The anti-freeze agent may comprise or consist essentially of a mixture having two or more components selected from the group consisting of PAMAM, PGL, PG and EG, provided that at least one of

5 PAMAM or PGL is present in said mixture.

[00110] In an embodiment, the anti-freeze agent may consist essentially of an unmodified, partially modified or fully substituted PAMAM as disclosed herein and an unmodified, partially modified or fully substituted PGL as disclosed herein. In an embodiment, the anti-freeze agent may consist essentially of an unmodified,

10 partially modified or fully substituted PAMAM as disclosed herein and EG. In an embodiment, the anti-freeze agent may consist essentially of an unmodified, partially modified or fully substituted PGL as disclosed herein and EG. In an embodiment, the anti-freeze agent may consist essentially of an unmodified, partially modified or fully substituted PAMAM as disclosed herein and PG. In an

15 embodiment, the anti-freeze agent may consist essentially of an unmodified, partially modified or fully substituted PGL as disclosed herein and PG. In an embodiment, the anti-freeze agent may consist essentially of an unmodified, partially modified or fully substituted PAMAM as disclosed herein, an unmodified, partially modified or fully substituted PGL as disclosed herein and EG. In an

20 embodiment, the anti-freeze agent may consist essentially of an unmodified, partially modified or fully substituted PAMAM as disclosed herein, an unmodified, partially modified or fully substituted PGL as disclosed herein and PG. In an embodiment, the anti-freeze agent may consist essentially of an unmodified, partially modified or fully substituted PAMAM as disclosed herein, an unmodified,

25 partially modified or fully substituted PGL as disclosed herein, EG and PG.

[00111] The wt% ratio between the dendritic or hyperbranched polymer and conventional anti-freeze agent may be about 1:10 to 10:1, or any ratio therebetween, e.g. 1:9, 1:8, 1:7, 1:6, 1:5, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1 or about 9:1.

30 [00112] The hyperbranched or dendritic polymer may comprise functional groups substituted by a hydrophobic group, such as an alkyl chain. The mol% of the substituted alkyl groups may be from about 0% to about 15% or any amount

therebetween. In some embodiments, the mol% of the substituted alkyl groups may be from about 0% to about 15% or any amount therebetween based on the total number of hydroxyl functional groups of unmodified PGL before substitution; from about 1% to about 14% or any amount therebetween; from about 2% to about 13%
5 or any amount therebetween; from about 3% to about 12% or any amount therebetween; from about 4% to about 11% or any amount therebetween; from about 5% to about 10% or any amount therebetween; from about 6% to about 9% or any amount therebetween; or from about 7% to about 8% or any amount therebetween. For example, the mol% of hydrophobic alkyl groups may be 0, 1, 2,
10 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15 mol% or any amount therebetween. For example, where an unmodified PGL is substituted with 20 mol% of alkyl groups, the unmodified PGL has 5 hydroxyl groups, out of which 1 hydroxyl group is substituted by an alkyl group.

[00113] The functional groups may be incorporated onto the hyperbranched
15 or dendritic polymer by any known method in the art. An exemplary method includes grafting a moiety having the desired functional group(s) thereon.

[00114] Another exemplary method includes reacting the hyperbranched or dendritic polymer with a reactive adduct that is linear, branched, hyperbranched or dendritic. The reactive adduct may be reactive with the unmodified dendritic or
20 hyperbranched polymer. The reactive adduct may be reactive with one or more of the functional groups of a modified dendritic or hyperbranched polymer. The reactive adduct may comprise polar functional groups as defined herein.

[00115] Yet another exemplary method includes reacting the dendritic or hyperbranched polymer with monomers comprising the desired functional group(s),
25 such as functional groups defined herein.

[00116] The disclosed dendritic or hyperbranched polymer, e.g. PAMAM or PGL, may have a molecular weight of at least 450 Da. The dendritic or hyperbranched polymer may have a molecular weight of from about 450 to about 8,000 Da, e.g., from about 450 to about 650 Da, from about 450 to about 850 Da,
30 from about 450 to about 1,050 Da, from about 450 to about 1,550 Da, from about 450 to about 2,050 Da, from about 450 to about 2,550 Da, from about 450 to about

3,050 Da, from about 450 to about 3,550 Da, from about 450 to about 4,050 Da, from about 450 to about 4,550 Da, from about 450 to about 5,050 Da, from about 450 to about 5,550 Da, from about 450 to about 6,050 Da, from about 450 to about 6,550 Da, from about 450 to about 7,050 Da, from about 450 to about 7,550 Da, from about 500 to about 600 Da, from about 500 to about 700 Da, from about 500 to about 800 Da, from about 500 to about 900 Da, from about 500 to about 1,000 Da, from about 500 to about 1,200 Da, from about 500 to about 1,400 Da, from about 500 to about 1,600 Da, from about 500 to about 1,800 Da, from about 500 to about 2,000 Da, from about 500 to about 2,200 Da, from about 500 to about 2,500 Da, from about 500 to about 2,700 Da, from about 500 to about 3,000 Da, from about 500 to about 3,250 Da, from about 500 to about 3,500 Da, from about 500 to about 3,750 Da, about 500 to about 4,000 Da, from about 500 to about 4,250 Da, from about 500 to about 4500 Da, from about 500 to about 4,750 Da, from about 500 to about 5,000 Da, from about 500 to about 5,250 Da, from about 500 to about 5,500 Da, from about 500 to about 5,750 Da, from about 500 to about 6,000 Da, from about 500 to about 6,250 Da, from about 500 to about 6,500 Da, from about 500 to about 6,750 Da, from about 500 to about 7,000 Da, from about 500 to about 7,250 Da, from about 500 to about 7,500 Da, from about 500 to about 7,750 Da, or from about 500 to about 8,000 Da. The disclosed dendritic or hyperbranched polymer may have a molecular weight of less than about 6,000 Da, less than about 3,250 Da, less than about 2000 Da, or preferably less than about 1000 Da.

[00117] In an embodiment, the dendritic or hyperbranched polymer, e.g. PAMAM or PGL, may have a molecular weight of from about 450 to about 1,000 Da. Advantageously, it has been found that dendritic or hyperbranched polymer having a molecular weight according to the present disclosure may provide superior anti-freeze effects when compared to dendritic or hyperbranched polymers outside this weight range. Additionally, the dendritic or hyperbranched polymers according to the present disclosure may also provide comparable, if not superior, anti-freeze effects relative to similar-sized but unbranched or non-dendritic or non-hyperbranched compounds, e.g., EG, PG, etc. Further advantageously, the dendritic or hyperbranched polymer may be used in a polymer dispersion composition comprising isothiazolinone type preservative biocides to achieve enhanced biocidal

stability or to preserve/improve their inhibitory effects on the degradation activities of a chemical or microorganism on the dispersion composition.

[00118] The anti-freeze agent may be substantially devoid or free of dendritic or hyperbranched polymers having a molecular weight of less than 500 Da, less than 450 Da, less than 400 Da, less than 350 Da, less than 300 Da or less than 250 Da.

[00119] The anti-freeze agent may be present in the polymer dispersion in an amount of from 0.01 wt.% to about 2 wt.% based on the weight of the polymer dispersion prior to curing. The anti-freeze agent may be present in the polymer dispersion in an amount of from about 0.01 to about 1%, from about 0.01 to about 0.9%, from about 0.01 to about 0.8%, from about 0.01 to about 0.7%, from about 0.01 to about 0.6%, from about 0.01 to about 0.5%, from about 0.01 to about 0.4%, from about 0.01 to about 0.3%, from about 0.01 to about 0.2%, or from about 0.01 to about 0.1%, by weight of the polymer dispersion before curing. Advantageously, the dendritic or hyperbranched polymer requires a substantially small amount (less than about 1 wt. %) to achieve the desirable technical effects disclosed herein.

[00120] The dispersion may further comprise one or more additives selected from the group consisting of: catalysts, reactive diluents, metal silicates, inorganic oxides, clay minerals, talcum powder, kaolin, coalescing solvent, pigment compounds, cross-linkers, surfactants, metal oxide nanoparticles, pH buffers, solvents, corrosion inhibitors, biocides, rheological modifiers, and mixtures thereof.

[00121] Suitable rheological modifiers may be selected from, but are not limited to, hydroxyethylcellulose (HEC), hydrophobically modified alkali soluble emulsion (HASE), hydrophobically modified ethylene oxide urethane (HEUR), or mixtures thereof.

[00122] In some embodiments, the dispersion may not comprise any rheological modifiers/additives. Advantageously, the disclosed anti-freeze agent may act as a rheological additive to provide a thickening effect to the polymer dispersion, where desired. Thus, the aqueous coating composition may advantageously not require further rheological additives to be added.

[00123] The dispersion may further comprise neutralizing or buffering agents, such as 2-amino-2-methy-1-propanol (marketed as AMP-95), triethanolamine (TEA) or dimethylethanolamine (DMEA). Alternatively, the dispersion may not comprise any neutralizing or buffering agents. Advantageously, the disclosed anti-freeze agent provides pH buffering properties to the polymer dispersion, thereby conferring pH stability on the dispersion. Further advantageously, the dispersion may have a pH stability that is comparable to polymer compositions comprising conventional neutralizing agents such as AMP-95, TEA or DMEA.

[00124] Advantageously, the disclosed dispersion may have substantially reduced or negligible VOC emission due to incorporation of the hyperbranched or dendritic polymer, as compared to prior art polymer compositions comprising conventional anti-freeze agents and/or conventional neutralizing agents. The substantially reduced or negligible VOC emission enables the manufacture of substantially odorless paint formulations.

[00125] The disclosed dispersion may further comprise antimicrobial agents and/or biocides. It has been unexpectedly found that when the dispersion comprises antimicrobial agents and/or biocides, the use of the hyperbranched or dendritic polymer leads to improved stability of the antimicrobial agents and biocides. For instance, it has been found that, where the disclosed poly(amido)amine is used, the concentration and/or activity of the biocide compounds are not adversely affected or not as adversely affected relative to coating compositions which employ conventional amine buffers such as a DMEA or AMP-95. In other words, it has been observed that aqueous biocidal compositions may be more stable when mixed with the disclosed hyperbranched or dendritic polymer, as compared to conventional anti-freeze compounds. It is postulated that the biocidal stability is due to the amphiphilicity of the disclosed hyperbranched or dendritic polymer, which can interact with the amphiphilic nature of the antimicrobial agents and/or biocides.

[00126] Advantageously, it has been found that the disclosed hyperbranched or dendritic polymer, when provided in the disclosed amounts, does not impair the stability or film-forming properties of the polymer dispersion.

[00127] The binder component may comprise a polymer emulsion as disclosed herein. In embodiments, the polymer binder comprises polymers selected from the group consisting of polyacrylate, acrylate copolymer, styrene-butadiene polymer, vinyl acetate polymer, polyurethane, urethane copolymer and combinations thereof. The polymer binder may comprise polymer particles dispersed in an aqueous phase, wherein the particle size may be from about 50 nm to about 0.5 μm as determined by electron microscopy. The particle size may be selected to permit dispersion in the aqueous medium and prevent precipitation in the aqueous medium. The polymer emulsion particles may possess a particle size (or particle diameter) of around 50 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm, 450 nm, or 500 nm. The polymer emulsion particles may exhibit a size distribution wherein the range of the particle diameters may comprise an upper limit and a lower limit selected from the diameters disclosed above.

[00128] The polymer dispersion may have a solids content of about 40 to about 60% by weight based on the weight of the dispersion upon curing. When the dispersion is cured or cross-linked, the aqueous and volatile phases are evaporated and lost as a volatile component. The mass of the dispersion remaining upon curing relative to the mass of the dispersion prior to the loss of volatiles is referred to as the “solids content”. Solids content measures the amount of material lost as volatiles during a curing or cross-linking procedure.

[00129] Exemplary, non-limiting embodiments of a method for lowering the freezing point of a polymer dispersion will now be disclosed. The method comprises mixing the polymer dispersion with an anti-freeze agent, said anti-freeze agent comprises a hyperbranched polymer or a dendritic polymer, wherein the hyperbranched polymer or the dendritic polymer comprises at least one polar functional group.

[00130] The polymer dispersion may be any aqueous composition that is required to be maintained in liquid form. That is, the polymer dispersion may be one that requires its freezing point to be lowered in order to be maintained in liquid form. Exemplary aqueous compositions include combustion engine liquids, engine coolants, industrial liquids, biological liquids, paint compositions, etc.

[00131] Other applications may range from cosmetics to medical and biomedical applications, such as nano-carrier compositions and controlled drug release compositions. Advantageously, the disclosed compositions are non-volatile and biocompatible.

5 [00132] In embodiments, the aqueous composition is a coating composition. In embodiments, the aqueous composition is a curable aqueous polymer composition. The aqueous coating composition may be an aqueous-dispersible coating composition. The aqueous coating composition may be a latex paint formulation. In embodiments, the aqueous composition is a polymer emulsion
10 comprising polymer particles selected from polyacrylate, polystyrene and copolymers thereof. In embodiments, the aqueous composition is a polymer dispersion, such as one disclosed herein. In embodiments, the aqueous composition is a paint formulation, such as an emulsion paint formulation. In embodiments, the aqueous composition comprises a polyacrylate composition. In an embodiment, the
15 aqueous composition is a water-based polyacrylate emulsion or an acrylate copolymer emulsion, wherein the primary resin component is a polyacrylate polymer, styrene-butadiene polymer, vinyl acetate polymer, polyurethane dispersion or co-polymer.

[00133] Where the aqueous composition is a coating composition or paint
20 formulation, the composition may be provided as a one-part composition or two-part composition.

[00134] The hyperbranched polymer or dendritic polymer may be one as disclosed herein.

[00135] The hyperbranched polymer or dendritic polymer may comprise a
25 theoretical peripheral functionality of from about 4 to about 128.

[00136] The at least one polar functional group may be selected from the group consisting of: hydroxyl group, amine group, amide group, carboxyl group, carboxylate group, carboxylic acid group, epoxy group, glycidol group, acrylate group, carbonyl group, carbamate group, succinamic group, siloxane group and
30 combinations thereof. In other embodiments, the at least one polar functional group may be selected from the group consisting of: hydroxyl group, amine group, amide

group, carboxylic acid group, polyethylene glycol group, siloxane group and combinations thereof.

[00137] The hyperbranched polymer or dendritic polymer may be an unmodified polymer, wherein all the peripheral functional groups are the polar functional groups. The hyperbranched or dendritic polymer may be a partially or completed modified polymer. The dendritic or hyperbranched polymer may be unmodified poly(amido)amine (PAMAM) or unmodified polyglycerol (PGL).

[00138] The hyperbranched polymer or dendritic polymer may be modified and may comprise at least one additional type of peripheral functional group, two additional types of peripheral functional groups or three additional types of peripheral functional groups. The additional functional groups may be the same or different from each other. Each additional functional group may be the same or distinct from the polar functional group.

[00139] The additional functional groups may be selected from the group consisting of: hydroxyl group, amine group, amide group, carboxyl group, carboxylate group, carboxylic acid group, epoxy group, glycidol group, acrylate group, carbonyl group, carbamate group, succinamic group, siloxane group and combinations thereof.

[00140] The additional functional group may be a hydrophobic functional group. The hydrophobic functional group may be one as disclosed herein.

[00141] The disclosed method may exclude a step of adding amine-functional compounds having a molecular weight of less than 450 Da to the polymer dispersion. The disclosed method may exclude a step of adding dendritic or hyperbranched polymers having a molecular weight of less than 450 Da to the polymer dispersion. The disclosed method may exclude a step of adding ethylene glycol, propylene glycol, glycerin, monomeric glycerol, or substituted derivatives thereof to the polymer dispersion. Alternatively, the disclosed method may comprise a step of adding to the polymer dispersion one or more components selected from the group consisting of: an additional dendritic or hyperbranched polymer, ethylene glycol and propylene glycol, wherein the additional dendritic or hyperbranched polymer is different from the dendritic or hyperbranched polymer.

[00142] The anti-freeze agent may consist essentially of the dendritic or hyperbranched polymer as disclosed herein. In some embodiments, the anti-freeze agent may consist essentially of the dendritic or hyperbranched polymer as disclosed herein in admixture with one or more components selected from the group consisting of: an additional dendritic or hyperbranched polymer, ethylene glycol and propylene glycol, wherein the additional dendritic or hyperbranched polymer is different from the dendritic or hyperbranched polymer.

[00143] The hyperbranched polymer or dendritic polymer may be one which exhibits a weight loss of less than 10% when measured according to ASTM D2369-10.

[00144] The anti-freeze agent may be provided in an amount as disclosed herein. The anti-freeze agent may be provided in an amount of from about 0.01 wt.% to about 2 wt. % based on the weight of the polymer dispersion.

[00145] The disclosed method may further comprise a step of mixing one or more additives with said polymer dispersion. The additives may be chosen from one or more additives as disclosed herein. The additives may be selected from the group consisting of: pigment compounds, cross-linkers, surfactants, solvents, corrosion inhibitors, biocides, rheological modifiers, and mixtures thereof.

[00146] The disclosed dispersion may contain from about 0.1 wt.% to about 2 wt. % of a biocide, e.g. a thiazolinone-based or an isothiazolinone-based biocide. The biocide may be present in the disclosed dispersion in an amount of from about 0.1 wt. % to about 1.8 wt. %, about 0.1 wt. % to about 1.6 wt. %, about 0.1 wt. % to about 1.4 wt. %, about 0.1 wt. % to about 1.2 wt. %, about 0.1 wt. % to about 1 wt. %, about 0.1 wt. % to about 0.8 wt. %, about 0.1 wt. % to about 0.6 wt. %, about 0.1 wt. % to about 0.5 wt. %, about 0.1 wt. % to about 0.4 wt. %, about 0.1 wt. % to about 0.3 wt. %, about 0.1 wt. % to about 0.2 wt. %, about 0.2 wt. % to about 2 wt. %, about 0.3 wt. % to about 2 wt. %, about 0.4 wt. % to about 2 wt. %, about 0.5 wt. % to about 2 wt. %, about 0.6 wt. % to about 2 wt. %, about 0.8 wt. % to about 2 wt. %, about 1 wt. % to about 2 wt. %, about 1.2 wt. % to about 2 wt. %, about 1.4 wt. % to about 2 wt. %, about 1.6 wt. % to about 2 wt. %, or about 1.8 wt. % to about 2 wt. %.

[00147] In embodiments, the hyperbranched polymer or dendritic polymer disclosed herein is used to lower the freezing point of a polymer dispersion, wherein the hyperbranched or dendritic polymer comprises at least one polar functional group.

5 [00148] There is also provided a method of buffering a polymer composition, the method comprising a step of mixing the dendritic or hyperbranched polymer as disclosed herein with a polymer binder in an amount of 0.01 to 1 wt% based on the total weight of the polymer composition. There is further provided a paint formulation comprising polymer emulsion particles, a dendritic or hyperbranched
10 polymer having at least one polar functional group and/or a substituted or non-substituted dendritic or hyperbranched polymer as described hereinabove. There is further provided a paint comprising a coating composition as herein described.

[00149] There is further disclosed a method of improving stability of latex emulsions or paints comprising the addition of dendritic PAMAM and/or dendritic
15 PGL to said latex emulsion in an amount from 0.01 wt. % to about 2 wt. % based on the total weight of the emulsion, wherein the latex emulsion may be substantially free of other dendritic polymers. Preferably, the PAMAM comprises no more than 4 peripheral functional groups and the PGL contains no more than 6 peripheral hydroxyl groups. At least one peripheral –OH group of the PGL may be modified to
20 be coupled to a linear alkylene chain having from 3 to 24 carbon atoms, 6 to 24 carbon atoms, 10 to 24 carbon atoms or 12 to 24 carbon atoms. The method may be employed for acrylate-based emulsions. The method may be employed for latex emulsions or paints comprising at least one thiazolinone-based or isothiazolinone-based biocide. The latex emulsion or paint may also be substantially free of non-
25 dendritic anti-freeze agents such as ethylene glycol and propylene glycol.

Examples

[00150] Non-limiting examples of the invention and comparative examples will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

30 [00151] Raw materials:

[00152] 1. Unsubstituted poly(amido)amine (PAMAM) hyperbranched polymer and dendritic polymers, specified in Table 1 below, from Weihai CY Dendrimer Technology Co., Ltd., China.

[Table 1]

Grade/ Trade name	Type	Generation	NH ₂ per polymer chain (theoretical)	Theoretical Mw	Weight loss at 110°C oven for 1 hr (%wt)
CYD-100A	Dendrimer	0	4	517	1.21
CYD-110A	Dendrimer	1	8	1430	6
CYD-120A	Dendrimer	2	16	3256	3.85
CYD- WU438	Hyperbranched polymer	-	20-50	5942	2.04

5

[00153] 2. Hyperbranched and dendritic polyglycercol (PGL) samples, specified in Table 2 below, from Daicel Corporation Japan.

[Table 2]

Trade Name	Type	Generat ion	Theoretical Mw (Average Hydroxyl number (KOH mg/g))	Weight loss at 110°C oven for 1 hr	
				Non-volatile content (%NVC)	Volatile content (%Volatile)
PGL-06	Dendritic	1	462 (959)	99.81	0.19
PGL-10PSW*	Dendritic	2	759 (822)	96.32	3.68 (H ₂ O)

Trade Name	Type	Generation	Theoretical Mw	Weight loss at 110°C oven for 1 hr	
PGLAL-ML04	Dendritic PGL with one OH group modified with a C ₁₂ alkylene oxide chain	1	457 (581)	99.96	0.4
PGLE -ML10	Dendritic PGL with one OH group esterified with a C ₁₂ alkyl chain	2	942 (634)	97.6	2.4

*A small amount of water was added into PGL-10PSW according to its product brochure.

[00154] 3. 95 % 2-Amino-2-methyl-1-propanol solution (AMP-95) from Angus Chemie GmbH, Germany.

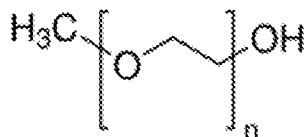
5 [00155] 4. Ethylene glycol (EG) and propylene glycol (PG), specified in Table 3 below, from Sigma-Aldrich, MO, USA.

[Table 3]

Compound	Weight loss at 110°C oven for 1 hr (% wt)
Ethylene glycol	100
Propylene glycol	100

[00156] 5. An acrylic emulsion paint system: "NIPPON PAINT SUPER WEATHERBOND" from Nippon Paint Singapore Co., Ltd.

[00157] 6. MPEG350, MPEG750: poly(ethylene glycol) methyl ether with molecular weight (Mw) 350 and 750 from Sigma-Aldrich, MO, USA, having the



general structure . MPEG350 has an average hydroxyl

number of 154-167 mg KOH/g. MPEG750 has an average hydroxyl number of 71-78 mg KOH/g.

Example 1

[00158] **Preparation of an emulsion paint (named as Paint-X) without**
5 **anti-freeze agent.**

[00159] Paint-X was prepared in-house according to the formulation in Table 4 below.

[Table 4]

No.	Name of the raw material	wt%
1	DI water	15
2	HEC thickener	0.4
3	pH adjuster AMP95	0.1
4	Sodium polycarboxylate-based dispersants	0.8
5	Silicone defoamers	0.5
6	Titanium dioxide	21
7	Talcum	5
8	Kaolin	5
9	Acrylic emulsion (BASF Acronal 7079)	36.5
10	Coalescent (Eastman OE300)	1.5
11	In-can preservative (Lanxess Preventol D7)	0.2
12	Biocide (Lanxess Biox AM 139)	2
13	PU thickener	2
14	DI water	10
	Total	100

10 [00160] Firstly, deionized water was added to a dispersion tank. The mixing speed was controlled at 800-1000 rev / min. Thereafter, raw materials 2 to 8 were sequentially added to the dispersion tank. During addition, an interval of 2 to 3 minutes in between introduction of each raw material was maintained to ensure

adequate mixing. The mixing speed was then raised to 1500-1800 rev / min, kept for 15 to 20 minutes, then reduced to 500-800 rev / min. Raw materials 9 to 14 were then added. During addition, an interval of 2 to 3 minutes in between introduction of each raw material was maintained to ensure adequate mixing.

5 Finally, more water was added, where necessary, to achieve a suitable viscosity.

Example 2

[00161] **Preparation of an emulsion paint (named as Paint-Y) without anti-freeze agent.**

[00162] Paint-Y was prepared in-house according to the formulation in Table
10 5 below.

[Table 5]

No.	Name of the raw material	wt%
1	DI water	25
2	HEC thickener	0.5
3	pH adjuster AMP95	0.1
4	Sodium polycarboxylate-based dispersants	0.8
5	Silicone defoamers	0.4
6	Titanium dioxide	15
7	Kaolin	24
8	Styrene-acrylate copolymer emulsion (BATF, RS998A)	21
9	Coalescent (Eastman Texanol)	1
10	In-can preservative (Lanxess Preventol D7)	0.2
11	Biocide (Lanxess Biox AM 139)	2
12	DI water	10
	Total	100

[00163] The method of preparation is similar to that in Example 1, as follows. Firstly, deionized water was added to a dispersion tank. The mixing speed was

controlled at 800-1000 rev / min. Thereafter, raw materials 2 to 7 were sequentially added to the dispersion tank. During addition, an interval of 2 to 3 minutes in between introduction of each raw material was maintained to ensure adequate mixing. The mixing speed was then raised to 1500-1800 rev / min, kept for 15 to 20 minutes, then reduced to 500-800 rev / min. Raw materials 8 to 12 were then added. During addition, an interval of 2 to 3 minutes in between introduction of each raw material was maintained to ensure adequate mixing. Finally, more water was added, where necessary, to achieve a suitable viscosity.

Example 3

10 [00164] **Determination of the melting point of PGL and PAMAM samples in deionized water (DI water) by differential scanning calorimetry (DSC).**

[00165] Test method is as follows: Samples (5wt%) in DI water solution were cooled from room temperature to -20 °C at 10 °C/min, then held at -50 °C for 10 min, and then heated from -20 °C to 15 °C at 3 °C/min. The results are
15 summarized in the Table 6 below.

[Table 6]

Sample Name	T _{melting} , °C (peak)	Δ, °C (Difference from T _{melting} of DI water
DI water (reference)	4.68	0
PGL		
5%PGL-ML04	2.77	1.91
5%PGL-ML10	2.72	1.96
5%PGL- 10PSW	2.71	1.97
5%PGL-06	2.21	2.47
PAMAM		
5%CYD-WU438	2.3	2.38
5% CYD-100A	3.25	1.43
5% CYD-110A	3.0	1.7

Sample Name	T _{melting} , °C (peak)	Δ , °C (Difference from T _{melting} of DI water)
5% CYD-120A	2.83	1.85

[00166] It is clear that all samples have a positive effect on lowering the melting point of the DI water. The samples comprising PGL-06 and CYD-WU438 (hyperbranched PAMAM) exhibited the largest decrease in melting temperature as compared to the reference DI water, indicating the best anti-freeze properties.

Example 4

[00167] **Determination of the melting point of PGL and PAMAM samples in NIPPON PAINT SUPER WEATHERBOND by DSC.**

[00168] 1.33 g of samples (30% net vol) were added individually into 18.67 g of Nippon paint super weatherbond with about 800-1000 rpm stirring using dispermat.

[00169] The test method is similar to that in Example 3, as follows. The prepared samples were cooled from room temperature to -20 °C at 10 °C/min, then held at -50 °C for 10 min, and then heated from -20 °C to 15 °C at 3 °C/min. The results are summarized in Table 7 below.

[Table 7]

Sample Name	T _{melting} , °C (peak)	Onset melting, °C
“NIPPON PAINT SUPER WEATHERBOND” alone (reference)	-7.17	-6.74
Glycol		
2%(30% net vol of EG in DI water)	-10.42	-10.1
2%(30% net vol of PG in DI water)	-9.75	-9.39

PGL		
2% (30% net vol of PGL-ML10 in DI water)	-13.25	-12.98
2%(30% net vol of PGL-10PSW in DI water)	-10.83	-10.56
2%(30% net vol of PGL-06 in DI water)	-8.75	-8.47
2%(30% net vol of PGL-ML04 in DI water)	-7.42	-7.11
PAMAM		
2% (30% net vol of CYD-100A in DI water)	-13.17	-12.9
2% (30% net vol of CYD-110A in DI water)	-10.42	-12.9
2%(30% net vol of CYD-120A in DI water)	-9.42	-9.08
2%(30% net vol of CYD-WU438 in DI water)	-9.17	-8.86
<i>2% Glycol/PGL/PAMAM = 6.6% solution (30% NV in DI water)</i>		

[00170] It is clear that all samples have a positive effect on lowering the melting point of the paint system. The samples comprising PGL-ML10 and CYD-100A (gen 0 PAMAM dendrimer) exhibited the largest decrease in melting temperature and outperform EG and PG.

[00171] Note that the freezing point could not be accurately measured due to supercooling effect.

Example 5

[00172] **Determination of time taken for freezing of 1% PGL/PAMAM added in NIPPON PAINT SUPER WEATHERBOND.**

[00173] Sample preparation is as follows: 0.68 g of PGL/PAMAM samples or mixtures of PGL/PAMAM with ethylene glycol (30% net vol) were added individually into 19.32 g of Nippon paint super weatherbond with about 800-1000 rpm stirring using dispermat.

[00174] Timer was started upon putting the above prepared samples in a chiller set at -5 °C (actual temperature: -5.2 °C to about -5.6 °C). The results are summarized in Table 8 below.

[Table 8]

PGL set		
Time	No. of hours	Appearance
11:00-13:30	2.5	Nippon paint super weatherbond alone (reference) - Freeze
13:30-14:00	3	PGL-ML04 - Freeze
14:00-15:00	4	PGL-10PSW and -ML10 - Freeze
15:00-17:00	6	EG and PGL-06 - No freeze
PAMAM set		
Time	No. of hours	Appearance
10:30-11:30	3	CYD-110A - Freeze
11:30-16:30	8	EG and CYD-100A - No freeze

[00175] The results show that all additives had a positive effect on extending the freeze time of the NIPPON PAINT SUPER WEATHERBOND paint. PGL-06 offered the best anti-freeze property among the PGL set, while CYD-100A (gen 0 PAMAM dendrimer) provided the best anti-freeze property among the PAMAM set.

Example 6

[00176] **Determination of time taken for freezing of 1% PGL added in paint system (Paint-X).**

[00177] The sample preparation is similar to that of Example 5, as follows: 0.68 g of PGL samples (30% net vol) were added into 19.32 g of Paint-X with about 800-1000 rpm stirring using dispermat.

[00178] Timer was started upon putting the above prepared samples in a chiller set at -5 °C (actual temperature: -5.2 °C to about -5.6 °C). The results are summarized in Table 9 below.

[Table 9]

Time	No. of hours	Appearance
11:00-14:00	3	Paint-X alone -Freeze
11:00-17:00	6	EG and PGL-06 -Freeze ML10 -No freeze

[00179] The results show that all additives had positive effect on extending the freeze time of the paint X. PGL-ML10 offered the better anti-freeze property than PGL-06 in the paint and outperformed EG.

Example 7

[00180] **Characterization of the freeze-thaw stabilizing effect of EG and PAMAM samples in NIPPON PAINT SUPER WEATHERBOND.**

[00181] Sample preparation is as follows: 241.5 g of Nippon paint super weatherbond was accurately weighed. 1 wt% (based on net vol) of EG/PAMAM samples (30% net vol) were post added while being stirred at 800 to 1000 rpm for 10 mins.

[00182] KU viscosity values were recorded on the next day and as the initial viscosity. All samples were frozen at -5°C using chiller for 8 hr starting from 9 am, and then placed at room temperature at 5 pm until 9 am the next day. Three cycles were conducted and then KU viscosity and appearance were checked. The results are summarized in the Table 10.

[00183] In this example, KU tolerance of ± 5 units = good stability.

[Table 10]

Sample Name	Krebs Unit (KU) Viscosity			Appearance
	Initial value before freeze	Final value after 3 cycles	Δ = (Final minus Initial)	
Nippon paint super weatherbond	96.9	102.1	5.2	No colour change
Nippon paint super weatherbond+1%EG	83.5	90.3	6.8	
Nippon paint super weatherbond+1%CYD- 100A	92.3	94.6	2.3	

[00184] The Nippon paint super weatherbond paint had a small amount of EG pre-existing and hence, passed the freeze-thaw stability test. Adding another 1% of EG to the Nippon paint super weatherbond paint did not seem to have a positive effect on the freeze-thaw stability of the paint. However, post adding 1% of CYD-100A (gen 0 PAMAM dendrimer) showed significant improvement of the freeze-thaw stability of the Nippon paint super weatherbond paint, with only $\Delta = 2.3$ KU after three cycles as compared to $\Delta = 5.2$ KU for the standard Nippon paint super weatherbond product. Furthermore, this post addition did not change the appearance of the paint.

Example 8

[00185] **Characterization of the freeze-thaw stabilizing effect of EG, PGL and PAMAM samples in paint system (Paint-X).**

15 [00186] Sample preparation is as follows: 185.25 g of the Paint-X was accurately weighed. 1.5 wt% (based on net vol) of EG/PAMAM samples (9.75 g, 30% net vol) were post added while being stirred at 800 to 1000 rpm for 10 min.

[00187] KU viscosity values were recorded on the next day and as the initial viscosity. All samples were frozen at -5°C using chiller for 8 hrs starting from 9 am, and then placed at room temperature at 5 pm until 9 am the next day. Three

cycles were conducted and then KU viscosity and appearance were checked. The results are summarized in Table 11.

[00188] In this example, KU tolerance of ± 10 units = good stability.

[Table 11]

Sample Name	Krebs Unit (KU) Viscosity			Appearance
	Initial value before freeze	Final value after 3 cycles	Δ = (Final minus Initial)	
Paint-X	100.1	gel	gel	No colour change
Paint-X+1.5%EG	88.7	92	3.3	
Paint-X+1.5%PGL-ML10	82.7	87.3	4.6	
Paint-X+1.5%CYD-100A	85.9	97.6	11.7	
Paint-X+0.8PGL- ML10+0.7%EG	85.4	89.6	4.2	
Paint- X+0.8%CYD100A+0.7%EG	86.1	91.3	5.2	
PaintX+1.5%MPEG350	93.2	gel	gel	
PaintX+1.5%MPEG750	84.3	gel	gel	

5 [00189] Paint-X alone without EG, as well as with conventional large molecular weight linear polymers MPEG350 and MPEG750, failed in the freeze-thaw stability test. It can be seen that the mixtures of Paint-X with MPEG350 or MPEG750 performed worse than the mixture of Paint-X with EG. Accordingly, it is shown that large molecular weight unbranched polymers are less effective as anti-freeze agents as compared to small molecular weight compounds.

[00190] On the other hand, it is shown that large molecular weight hyperbranched or dendritic polymers are unexpectedly more effective as anti-freeze agents as compared to unbranched or non-hyperbranched compounds having comparable or larger molecular weights. The mixture of Paint-X with CYD100A, which has a molecular weight larger than MPEG350, and the mixture of Paint-X with PGL-ML10, which has a molecular weight larger than MPEG750, are more effective as anti-freeze agents as compared to the mixtures with MPEG350 and MPEG750.

[00191] As predicted, both EG and PGL-ML10 alone, as well as the mixture of EG with PGL-ML10 or CYD100A passed the test. Although CYD-100A alone (gen 0 PAMAM dendrimer) marginally failed the test as the required range is within ± 10 KU, CYD-100A indeed evidenced the anti-freeze property as confirmed in Example 7. Due to the complex nature of the chemical structure of CYD-100A as compared to the simple EG, the anti-freeze property could be system-specific and the use of CYD-100A in a paint system like Paint-X should be subjected to further optimization.

[00192] In addition, all the samples did not change the appearance of the paint.

Example 9

[00193] **Characterization of the freeze-thaw stabilizing effect of EG, PGL and PAMAM samples in paint system (Paint-Y).**

[00194] Sample preparation is as follows: 235.86 g of the Paint-Y was accurately weighed. 0.9 wt% (based on net vol) of EG and PGL/PAMAM samples (7.14 g, 30% net vol) were post added while being stirred at 800 to 1000 rpm for 10 min.

[00195] KU viscosity values were recorded on the next day and as the initial viscosity. All samples were frozen at -5°C using chiller for 8 hrs starting from 9 am, and then placed at room temperature at 5 pm until 9 am the next day. Three cycles were conducted and then KU viscosity and appearance were checked. The results are summarized in Table 12.

[00196] In this example, KU tolerance of ± 10 units = good stability.

[Table 12]

Sample Name	Krebs Unit (KU) Viscosity			Appearance
	Initial value before freeze	Final value after 3 cycles	Δ = (Final minus Initial)	
Paint-Y+0.9%EG	96.8	99.4	2.6	No colour change
Paint-Y+0.9%CYD-110A	98.6	120.8	22.2	
Paint-Y+0.9%CYD-120A	98.4	137.2	38.8	
Paint-Y+0.9%CYD-WU438	102.9	123.1	20.2	
Paint-Y+0.9%CYD-100A	102.2	106.6	4.4	
Paint-Y+0.9%PGL-ML04	101	105.8	4.8	
Paint-Y+0.9%PGL-10PSW	100.3	Out of range - too viscous	N.A.	Out of range -too viscous

[00197] Paint-Y without EG (not shown in Table 12) failed in the freeze-thaw stability test. Addition of 0.9% EG showed the best results followed by the same dosage of CYD-100A (gen 0 PAMAM dendrimer) and PGL-ML04.

[00198] The results show that the alkyl chain of the small molecular PGL-ML04 may help to improve the steric hindrance of the dendritic molecule and balance the amphiphilicity.

[00199] The results of CYD-100A shown in Example 7 (test passed), Example 8 (test failed) and this Example 9 (test passed) may indicate that the anti-freeze properties of CYD-100A is colligative and specific to the paint system given a fixed weight percentage.

[00200] As can be seen from Table 12, the use of higher molecular weight PAMAM samples, i.e. CYD-110A ($M_w = 1430$), CYD-120A ($M_w = 3256$) and CYD-WU438 in paint compositions, resulted in higher Δ KU than when low

molecular weight PAMAM sample, CYD-100A ($M_w = 517$), is used. This demonstrates the superior anti-freeze effect of low molecular weight PAMAM when used in polymer emulsion formulations. It is a surprising result that both a generation 0 (4 peripheral functional NH_2 groups) PAMAM and a generation 1 polyglycerol (around 6 peripheral $-\text{OH}$ groups) provided significant improvements to the stability of the paint composition after undergoing three freeze-thaw cycles as described in Example 9.

Example 10

[00201] **Effect of using different pH adjusters on CMIT/MIT stability in white latex paint (Super Weatherbond 00E55).**

[Table 13]

Sample	PH adjuster	Storage duration at RT	MIT/ppm	CMIT/ppm	Storage duration at 50°C	MIT/ppm	CMIT/ppm
	0.1% WU438	initial	24.12	10.53	Initial	24.12	10.53
		1 day	22.6	10.07	1 week	21.65	ND
		2 days	23.29	7.58	2 weeks	23.02	ND
		1 week	23.19	7.54			
		2 weeks	22.71	5.99			
	0.1% CYD120	initial	23.32	6.84	Initial	23.32	6.84
		1 day	22.6	6.03	1 week	24	ND
		2 days	22.79	4.12	2 week	22.40	ND
		1 week	22.42	4.10			
		2 week	22.67	3.88			
	0.1% CYD-100A	initial	27.24	11.58	Initial	27.24	11.58
		1 day	27.77	10.48	1 week	21.94	ND
		2 days	27.51	9.34	2 weeks	19.72	ND
		1 week	27.51	10			
		2 weeks	26.18	9.76			

[00202] Water based paints usually contain high water content and high nutrient level, which in turn provides an environment that is conducive for the proliferation and growth of microbes. Microbes and their metabolic byproducts, on top of being harmful or potentially toxic, can also contribute to the breakdown of

the polymer dispersion, leading to the degradation of the coating or paint. Many factors are affected by the presence of microbes and their metabolic byproducts.

[00203] Table 13 above shows that the addition of a small amount (0.1 wt,%)
5 of a PAMAM dendritic polymer in the paint composition resulted in markedly reduced degradation of CMIT, after 6 days. This is yet another useful and unexpected technical result.

Industrial Applicability

10 [00204] The disclosed hyperbranched or dendritic polymer can be used as a low VOC emissions/VOC-free, non-toxic anti-freeze agent in the field of paint and coatings.

[00205] It is not expected that the disclosed hyperbranched or dendritic
polyglycerol and poly(amido)amine, which are typically used in the bio-medical
15 field, would be suitable for use in coatings or paint formulations. Reasons may include the relatively high cost of the material.

[00206] Compared to conventional linear structure polymers, hyperbranched or dendritic polymers provide much lower viscosity at the same molecular weight, which is beneficial for the manufacture of paint.

20 [00207] The disclosed hyperbranched or dendritic polymer may provide an equivalent or near equivalent content of polar functionality as compared to commonly used small molecular anti-freeze counterparts.

[00208] It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the
25 foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A polymer dispersion comprising:
 - a. a binder component comprising polymer particles dispersed in an aqueous phase; and
 - b. an anti-freeze agent selected from poly(amido)amine (PAMAM), polyglycerol (PGL) or a combination thereof, wherein the PAMAM and/or PGL has a molecular weight of less than 1000 Da.
2. The dispersion of claim 1, wherein said PAMAM or PGL comprises a theoretical peripheral functionality of from about 4 to about 128.
3. The dispersion of any preceding claim, wherein the PAMAM or PGL has a molecular weight of at least 450 Da, or is within a range of 450 Da to 1000 Da.
4. The dispersion of claim 3, wherein the PGL has a hydroxyl number of more than 400 mg KOH /g.
5. The dispersion of claim 3, wherein the PAMAM has an amine number of more than 200 mg KOH /g.
6. The dispersion of any preceding claim, wherein the PAMAM or PGL comprises at least one additional type of peripheral functional group, two additional types of peripheral functional groups or three additional types of peripheral functional groups, and wherein each additional functional group is distinct from the peripheral amine group of PAMAM, or the peripheral hydroxyl group of the PGL.
7. The dispersion of claim 6, wherein the additional functional groups are selected from the group consisting of: hydroxyl group, amine group, amide group, carboxyl group, carboxylate group, carboxylic acid group, epoxy group, glycidol group, acrylate group, carbonyl group, carbamate group, succinamic group, siloxane group and combinations thereof.

8. The dispersion of claim 6, wherein said additional functional group is a hydrophobic functional group.
9. The dispersion of any preceding claim, wherein at least 5% of the total peripheral functional groups of said dendritic or hyperbranched polymer are polar functional groups.
10. The dispersion of any preceding claim, wherein said dendritic or hyperbranched polymer is one which exhibits a weight loss of less than 10% when measured according to ASTM D2369-10.
11. The dispersion of any preceding claim, wherein said anti-freeze agent is present in an amount of from 0.01 wt. % to about 2 wt. % based on the weight of said polymer dispersion prior to curing.
12. The dispersion of any preceding claim, further comprising one or more additives selected from the group consisting of: pigment compounds, cross-linkers, surfactants, solvents, corrosion inhibitors, biocides, rheological modifiers, and mixtures thereof.
13. The dispersion of any preceding claim, wherein said binder component is a polymer emulsion or a latex composition.
14. The dispersion of any preceding claim, wherein said binder is an acrylate-based emulsion.
15. The dispersion of any preceding claim, wherein said dispersion comprises at least one thiazolidinone-based biocide in a concentration of around 0.1 wt. % to 2 wt. %.
16. The dispersion of any one of preceding claims, wherein the anti-freeze agent consists essentially of said PAMAM or PGL; or consists essentially of said PAMAM or PGL in admixture with one or more components selected from

the group consisting of: an additional dendritic or hyperbranched polymer, ethylene glycol and propylene glycol, wherein said additional dendritic or hyperbranched polymer is different from said PAMAM or PGL.

17. A method of lowering the freezing point of a polymer dispersion, the method comprising: mixing the polymer dispersion with an anti-freeze agent, said anti-freeze agent selected from PAMAM, PGL or a combination thereof, and wherein the PAMAM and/or PGL has a molecular weight of less than 1000 Da.
18. The method of claim 15, wherein the hyperbranched or dendritic polymer comprises a theoretical peripheral functionality of from about 4 to about 128.
19. The method of claim 15 or 16, wherein the PAMAM or PGL comprises at least one additional type of peripheral functional group, two additional types of peripheral functional groups or three additional types of peripheral functional groups, and wherein each additional functional group is distinct from the peripheral amine group of PAMAM, or the peripheral hydroxyl group of the PGL.
20. The method of claim 17, wherein the additional functional groups are selected from the group consisting of: hydroxyl group, amine group, amide group, carboxyl group, carboxylate group, carboxylic acid group, epoxy group, glycidol group, acrylate group, carbonyl group, carbamate group, succinamic group, siloxane group and combinations thereof.
21. The method of claim 17, wherein said additional functional group is a hydrophobic functional group.
22. The method of any of claims 15-19, wherein the dendritic or hyperbranched polymer has a molecular weight of at least 450 Da or is within a range of 450 Da to 1000 Da.

23. The method of any of claims 15-20, wherein the dendritic or hyperbranched polymer is selected to be one which exhibits a weight loss of less than 10% when measured according to ASTM D2369-10.
24. The method of any one of claims 15-21, wherein the anti-freeze agent is provided in an amount of from about 0.01 wt.% to about 2 wt. % based on the weight of the polymer dispersion.
25. The method of any one of claims 15 to 22, further comprising a step of mixing one or more additives with said polymer dispersion, wherein the additives are selected from the group consisting of: pigment compounds, cross-linkers, surfactants, solvents, corrosion inhibitors, biocides, rheological modifiers, and mixtures thereof.
26. The method of any one of claims 15 to 23, wherein said polymer dispersion comprises a polymer emulsion or a latex composition.
27. The method of any one of claims 15 to 24, wherein the anti-freeze agent consists essentially of said PAMAM, PGL or a combination thereof or consists essentially of said PAMAM, PGL or a mixture thereof in admixture with one or more components selected from the group consisting of: an additional dendritic or hyperbranched polymer, ethylene glycol and propylene glycol, wherein said additional dendritic or hyperbranched polymer is different from said PAMAM and PGL.
28. Use of a PAMAM, PGL or a combination thereof to lower the freezing point of a polymer dispersion, wherein the PAMAM and/or PGL has a molecular weight of less than 1000 Da.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2017/050308

A. CLASSIFICATION OF SUBJECT MATTER

C09D 7/12 (2006.01) C09D 201/00 (2006.01) C09K 5/20 (2006.01)

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D, C09K

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)

Databases: EPODOC, WPIAP, TXTE, REGISTRY, CAPLUS and Scopus

Keywords: coating, paint, anti-freeze, poly(amido)amine, polyglycerol, hyperbranched, dendritic and other related terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/0063235 A1 (FAHY, G. ET AL.) 30 May 2002 paras [0002], [0027]-[0031], [0036], [0039], [0048] and [0049]; claim 18; and examples 1-14	1, 3, 4, 11-15, 17, 24-26 and 28
X	CN 105368280 A (QINGDAO BAIZHONG CHEMICAL TECH CO LTD) 2 March 2016 abstract; paras [0010]-[0011]; and examples 1-3 of the original non-English language document (a machine translation is enclosed only for your reference)	1-3, 5, 10-16
X	US 2010/0280165 A1 (TERRENOIRE, A. ET AL.) 4 November 2010 Table 2; and paras [0032], [0047]-[0049], [0059], [0063], [0115], [0143], [0204], [0273], [0294], [0297], and [0431]-[0435]	1-28
X	US 2009/0309061 A1 (SEILER, M. ET AL.) 17 December 2009 example 1; and paras [0080]-[0085] and [0091]	1-28

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2017/050308**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2521655 A (NIPSEA TECHNOLOGIES PTE LTD) 1 July 2015 whole document, in particular tables 1 and 4-6	
A	US 2014/0212675 A1 (WANG, S. ET AL.) 31 July 2014 whole document, in particular comparative example 2	
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2017/050308

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

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