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(54) Title: BRANCHED POLYSILOXANE OF REDUCED MOLECULAR WEIGHT AND VISCOSITY

(57) Abstract: The invention relates to a branched polysiloxane composition of reduced molecular weight and viscosity of particular use as mist suppressants in silicone-based paper release coatings. The invention also relates to methods for producing these branched polysiloxane compositions of reduced viscosity.



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BRANCHED POLYSILOXANE OF REDUCED MOLECULAR WEIGHT AND VISCOSITY

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The invention relates to reduced molecular weight branched polysiloxane compositions of particular use as mist suppressants in silicone-based paper release coatings.

Description of the Prior Art

[0002] It is well known that in operations where silicone-based paper release coating formulations are subjected to a high enough rotational or translational motion, e.g., in high speed roll coating of flexible supports and paper, misting and/or aerosoling can become significant problems. These problems become particularly significant when applying these release coatings at roll coating speeds approaching 1000 ft/min, while the trend in the paper coating industry is to use speeds in excess of 1500 ft/min, e.g., 2000-3000 ft/min. In addition to having a deleterious effect on manufacturing operations, these mist and aerosol particles present industrial hygiene and safety issues for those people operating or working in the vicinity of the coating equipment.

[0003] Specialized chemical formulations known generically as "mist suppressants" have commonly been used to reduce the formation of mist in such operations. These mist suppressants are typically branched polysiloxanes of high viscosity, e.g., typically greater than 1,500 centipoise (cPs), where 1cPs = 1 millipascal-second (mPa.s). More typically, the viscosity of the branched polysiloxane is greater than 3,000 cPs or 5,000 cPs. In fact, it is common for the viscosity of the branched polysiloxane to be greater than 50,000 cPs.

[0004] Though it has generally been found that such high viscosity branched polysiloxanes are highly effective mist suppressants, they suffer from the disadvantage of being difficult to handle and process precisely due to their high viscosities. For example, mixing the mist control agent (e.g., in a mixer with the mist-susceptible base formulation) is greatly impeded when using such high viscosity mist control agents. In fact, often, lower viscosity mist control agents are favored, due solely to the above-described technical constraint, over higher viscosity mist control agents, even though higher viscosity mist control agents are generally known to be more effective mist suppressants. Furthermore, lower viscosity mist control agents are preferred to maintain thin and consistent coatings on desired substrates.

[0005] Accordingly, there remains a need for mist suppressant compositions which have at least the same or an improved capability of mist suppression while being easier to handle in transferring and mixing operations.

SUMMARY OF THE INVENTION

[0006] The present invention provides a branched polysiloxane composition which comprises at least one member selected from the group consisting of:

i) branched fragmented polyorganosiloxane, the polysiloxane resulting from reacting under hydrosilylation reaction conditions a mixture comprising:

- a) at least one compound containing on average at least two unsaturated sites per molecule, and
- b) at least one polyorganosiloxane containing on average at least two silylhydride functional groups per molecule,

provided, that at least one of (a) and/or (b) is fragmented by shearing prior to and/or during the hydrosilylation reaction and/or the polyorganosiloxane resulting from the

hydrosilylation reaction is fragmented by shearing to provide the branched fragmented polyorganosiloxane;

ii) branched fragmented polyorganosiloxane, the polysiloxane resulting from equilibrating under equilibration conditions at least two polyorganosiloxanes selected the group consisting of cyclic, linear and branched polyorganosiloxanes, provided, that at least one polyorganosiloxane is fragmented by shearing prior to and/or during equilibrating and/or the polyorganosiloxane resulting from equilibration is fragmented by shearing to provide the branched fragmented polyorganosiloxane; and,

iii) branched fragmented polyorganosiloxane, the polysiloxane resulting from copolymerization under condensation conditions of at least one polyorganosiloxane containing at least two functional groups, provided, that at least one polyorganosiloxane is fragmented by shearing prior to and/or during copolymerization and/or the polyorganosiloxane resulting from copolymerization is fragmented by shearing to provide the branched fragmented polyorganosiloxane.

[0007] In another aspect, the invention provides a method for making a branched polysiloxane which comprises:

i) reacting under hydrosilylation reaction conditions a mixture comprising:

a) at least one compound containing on average at least two unsaturated sites per molecule, and

b) at least one polyorganosiloxane containing on average at least two silylhydride functional groups per molecule, and

ii) fragmenting by shearing at least one of (a) and/or (b) prior to and/or during the hydrosilylation reaction and/or the polyorganosiloxane resulting from the hydrosilylation reaction.

[0008] According to another aspect, the invention provides a method for making a branched polysiloxane which comprises:

i) equilibrating under equilibration conditions at least two polyorganosiloxanes selected the group consisting of cyclic, linear and branched polyorganosiloxanes, and

ii) fragmenting by shearing at least one polyorganosiloxane prior to and/or during equilibration and/or the polyorganosiloxane resulting from equilibration.

[0009] According to yet another aspect, the invention provides a method for making a branched polysiloxane which comprises:

i) copolymerizing under condensation conditions at least one polyorganosiloxane containing at least two functional groups, and

ii) fragmenting by shearing at least one polyorganosiloxane prior to and/or during copolymerization and/or the copolymerized polyorganosiloxane resulting from copolymerization.

[0010] The present invention advantageously provides branched polysiloxane compositions of reduced molecular weight and viscosity. These reduced viscosity polysiloxane compositions provide the same or improved mist suppression as high viscosity mist suppressants known in the art while affording the additional benefits of being easier to handle and process, provide ease of coating, and are economical and simple to make.

DETAILED DESCRIPTION OF THE INVENTION

[0011] According to one embodiment of the invention, a reduced molecular weight polysiloxane composition results from fragmenting a branched polysiloxane composition. According to one specific embodiment of the invention, the branched polysiloxane compositions of reduced molecular weight and viscosity results from

reacting under hydrosilylation reaction conditions, a mixture of: a) at least one compound containing on average at least two unsaturated sites per molecule, and b) at least one polyorganosiloxane containing on average at least two silylhydride function groups per molecule. Provided, that at least one of (a) and/or (b) is fragmented by shearing prior to and/or during the hydrosilylation reaction and/or the polysiloxane resulting from the hydrosilylation reaction is fragmented by shearing to provide the branched fragmented polyorganosiloxane.

[0012] According to another embodiment of the invention, the branched polysiloxane composition of reduced molecular weight and viscosity results from equilibrating under equilibration conditions at least two polyorganosiloxanes selected the group consisting of cyclic, linear and branched polyorganosiloxanes. Provided, that at least one of the polyorganosiloxane is fragmented by shearing prior to and/or during equilibrating and/or the equilibrated polyorganosiloxane is fragmented by shearing to provide the branched fragmented polyorganosiloxane.

[0013] According to yet another embodiment of the invention, the branched polysiloxane composition of reduced molecular weight and viscosity results from copolymerization under condensation conditions of at least one polyorganosiloxane containing at least two functional groups. Provided, that at least one of the polyorganosiloxane is fragmented by shearing prior to and/or during copolymerization and/or the copolymerized polyorganosiloxane is fragmented by shearing to provide the branched fragmented polyorganosiloxane.

[0014] In another embodiment of the invention, the branched polysiloxane composition of reduced molecular weight and viscosity results from reacting under hydrosilylation reaction conditions, a mixture of: a) at least one polyorganosiloxane containing on average at least two unsaturated sites per molecule, and b) at least one polyorganosiloxane containing on average at least two silylhydride function groups per molecule. Provided, that at least one of (a) and/or (b) is fragmented by shearing prior to and/or during the hydrosilylation reaction and/or the polysiloxane resulting from the

hydrosilylation reaction is fragmented by shearing to provide the branched fragmented polyorganosiloxane.

[0015] In yet another embodiment of the invention, the branched polysiloxane composition of reduced molecular weight and viscosity results from copolymerization under condensation conditions at least one polyorganosiloxane containing at least two functional groups and a compound having at least two functional groups capable of reacting with the functional groups of the polyorganosiloxane. Provided, that at least one of the polyorganosiloxane and/or the compound is fragmented by shearing prior to and/or during copolymerization and/or the copolymerized polyorganosiloxane is fragmented by shearing to provide the branched fragmented polyorganosiloxane.

[0016] As used herein, the term “fragmenting” or “fragmented” refers to the breaking of molecular (i.e., chemical) bonds in the branched polysiloxane and/or in one or both of the components from which the branched polysiloxane is derived. Fragmenting can be achieved by any means known in the art. In a particular embodiment, fragmenting is achieved by applying an appropriate shear force, by one or more shear processing steps, on the branched polysiloxane and/or one of the components from which the branched polysiloxane is derived.

[0017] Any means capable of generating an amount of shear force sufficient for breaking chemical bonds can be useful for fragmenting according to the present invention. A fragmenting shear force is more typically provided by use of, but not limited to, a high-speed mixer, high-shear mixer, homogenizer, kneader, mill or extruder. The speed, agitation rate, or screw rate of the equipment must be high enough to cause at least some fragmentation while not rendering the branched polysiloxane substantially ineffective as a mist suppressant. An extruder screw rate of between 75 rpm and 500 rpm has been found to be particularly effective.

[0018] The viscosity of the branched polysiloxane before fragmenting is typically greater than 1,500 centipoise (cPs), where 1cPs = 1 millipascal-second (mPa.s). More

typically, the viscosity of the branched polysiloxane before fragmenting is about or greater than 3,000 cPs, and even more typically about 5,000 cPs. In other embodiments, the viscosity of the non-fragmented branched polysiloxane before fragmenting can be about or greater than 10,000 cPs, 25,000 cPs, 50,000 cPs, 100,000 cPs, or a higher viscosity. By fragmenting, the viscosity is reduced to a desired level, such as, for example, slightly reduced (e.g., 80-95% of the original viscosity), moderately reduced (e.g., 50-80% of the original viscosity), or significantly reduced (e.g., 5-50% of the original viscosity).

[0019] It is most preferable to fragment polysiloxanes in the absence of a diluent. Lack of a diluent allows greater chain entanglement and fragmentation by the shearing apparatus. Diluents reduce the effectiveness of the shear induced fragmentation and thus are minimized or avoided. Higher viscosity diluents aid in fragmentation better than their lower viscosity analogs. Preferred diluents are miscible with the polysiloxane prior to fragmentation and have viscosities above 100 cSt at 25°C. Suitable diluents include, but are not limited to the following: 1) organic compounds, 2) organic compounds containing a silicon atom, 3) mixtures of organic compounds, 4) mixtures of compounds containing a silicon atom, and 5) mixtures of organic compounds and compounds containing a silicon atom. Organic diluents can be, inert aliphatic hydrocarbons such as pentane, hexane, heptane or octane; aromatic hydrocarbons such as benzene, toluene or xylene; alicyclic hydrocarbons such as cyclopentane or cyclohexane; halogenated aliphatic or aromatic hydrocarbons such as dichloromethane, tetrachloroethylene, o-, m- or p-dichlorobenzene or chlorobenzene, and the like can be used

[0020] Branched polysiloxanes as defined herein are materials which are miscible or soluble in an appropriate medium or "good" solvent. Polysiloxane gels or elastomers are defined herein as materials that swell in an appropriate medium or "good" solvent. These materials, i.e., polysiloxane gels and elastomers, are not miscible or soluble in solvents. Specifically, the present invention is focused on the use of branched materials that behave more like liquids rather than gels or elastomers that behave more like solids.

Branched polysiloxanes that contain gel are undesirable because insoluble particulates interfere with the coating integrity. The branched nature of the reduced molecular weight and viscosity polysiloxanes and subsequent chain entanglement provides the unique properties observed. Since gel proportionally consumes a larger amount of the branch points and the gel must be removed prior to use, the properties of the non-gel material are attenuated.

[0021] A critical aspect of this invention is the application of shear, substantial enough to break chemical bonds, during the polymerization. Shearing during the polymerization allows the product to maintain a liquid-like consistency. Reactions performed in the absence of shear will have higher viscosities and possibly gel, see Table 2. Application of shear during the polymerization is postulated to fragment the material keeping the "apparent" crosslink density to very low levels.

[0022] In one embodiment of the invention, the reaction (i.e., hydrosilylation, equilibration and condensation) can be performed in the presence of a diluent. However, according to a specific embodiment of the invention, the reaction (i.e., hydrosilylation, equilibration and condensation) is performed in the absence of a diluent as this aids in better fragmentation of the intermediate polymer. Diluents are more appropriately added after the polymerization-fragmentation step.

[0023] Examples of compounds containing on average at least two unsaturated sites per molecule that are suitable for preparing the branched fragmented polyorganosiloxane resulting from reacting under hydrosilylation reaction conditions include, but are not limited to, unsaturated hydrocarbon containing compounds, e.g., organosilicon compounds containing at least two unsaturated hydrocarbon groups. The unsaturated hydrocarbon groups in the organosilicon compounds of (a) include any straight-chained, branched, or cyclic hydrocarbon groups having at least one carbon-carbon double or triple bond capable of reacting with a silylhydride group under hydrosilylation conditions. More typically, the unsaturated hydrocarbon group contains two to twelve carbon atoms. Some examples of unsaturated hydrocarbon groups include

substituted and unsubstituted vinyl, allyl, 3-butenyl, butadienyl, 4-pentenyl, 2,4-pentadienyl, 5-hexenyl, 6-heptenyl, 7-octenyl, 8-nonenyl, 9 decenyl, 10-undecenyl, 4,7-octadienyl, 5,8-nonadienyl, 5,9-decadienyl, 6,11-dodecadienyl, 4,8-nonadienyl, cyclobutenyl, cyclohexenyl, acryloyl, and methacryloyl.

[0024] Other suitable compounds include materials capable of undergoing a hydrosilylation reaction, such as, for example olefins. Some examples of specific olefins include, but are not limited to: 1,2,4-trivinylcyclohexane, 1,3,5-trivinylcyclohexane, 3,5-dimethyl-4-vinyl-1,6-heptadiene, 1,2,3,4-tetravinylcyclobutane, methytrivinylsilane, tetravinylsilane, and 1,1,2,2-tetraallyloxyethane, and the like.

[0025] Some examples of low molecular weight siloxane compounds suitable for use in preparing branched fragmented polysiloxane resulting from reacting under hydrosilylation reaction conditions include divinyl dimethoxysilane, divinyl diethoxysilane, trivinyl ethoxysilane, diallyl diethoxysilane, triallyl ethoxysilane, vinyl dimethylsiloxyvinyl dimethylcarbinol ($\text{CH}_2=\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2(\text{CH}_2=\text{CH}_2)$), 1,3-divinyl tetramethyl disiloxane, 1,3-divinyl tetraethyl disiloxane, 1,1-divinyl tetramethyl disiloxane, 1,1,3-trivinyl trimethyl disiloxane, 1,1,1-trivinyl trimethyl disiloxane, 1,1,3,3-tetravinyl dimethyl disiloxane, 1,1,1,3-tetravinyl dimethyl disiloxane, 1,3-divinyl tetraphenyl disiloxane, 1,1-divinyl tetraphenyl disiloxane, 1,1,3-trivinyl triphenyl disiloxane, 1,1,1-trivinyl triphenyl disiloxane, 1,1,3,3-tetravinyl diphenyl disiloxane, 1,1,1,3-tetravinyl diphenyl disiloxane, hexavinyl disiloxane, tris(vinyl dimethylsiloxy)methylsilane, tris(vinyl dimethylsiloxy)methoxysilane, tris(vinyl dimethylsiloxy)phenylsilane, and tetrakis(vinyl dimethylsiloxy)silane.

[0026] Some examples of linear siloxane oligomers suitable for use in preparing the branched fragmented polysiloxane of the invention include 1,5-divinyl hexamethyl trisiloxane, 1,3-divinyl hexamethyl trisiloxane, 1,1-divinyl hexamethyl trisiloxane, 3,3-divinyl hexamethyl trisiloxane, 1,5-divinyl hexaphenyl trisiloxane, 1,3-divinyl hexaphenyl trisiloxane, 1,1-

divinylhexaphenyltrisiloxane, 3,3-divinylhexaphenyltrisiloxane, 1,1,1-trivinylpentamethyltrisiloxane, 1,3,5-trivinylpentamethyltrisiloxane, 1,1,1-trivinylpentaphenyltrisiloxane, 1,3,5-trivinylpentaphenyltrisiloxane, 1,1,3,3-tetravinyltetramethyltrisiloxane, 1,1,5,5-tetravinyltetramethyltrisiloxane, 1,1,3,3-tetravinyltetraphenyltrisiloxane, 1,1,5,5-tetravinyltetraphenyltrisiloxane, 1,1,1,3,3-pentavinyltrimethyltrisiloxane, 1,1,3,5,5-pentavinyltrimethyltrisiloxane, 1,1,3,3,5,5-hexavinyldimethyltrisiloxane, 1,1,1,5,5,5-hexavinyldimethyltrisiloxane, 1,1,1,5,5,5-hexavinyldiphenyltrisiloxane, 1,1,1,5,5,5-hexavinyldimethoxytrisiloxane, 1,7-divinyloctamethyltetrasiloxane, 1,3,5,7-tetravinylhexamethyltetrasiloxane, and 1,1,7,7-tetravinylhexamethyltetrasiloxane.

[0027] Some examples of cyclic siloxane oligomers suitable for use in preparing the branched fragmented polysiloxane of the invention include 1,3-divinyltetramethylcyclotrisiloxane, 1,3,5-trivinyltrimethylcyclotrisiloxane, 1,3-divinyltetraphenylcyclotrisiloxane, 1,3,5-trivinyltriphenylcyclotrisiloxane, 1,3-divinyloctamethylcyclotetrasiloxane, 1,3,5-trivinylpentamethylcyclotetrasiloxane, and 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane.

[0028] The polymeric siloxanes (polysiloxanes) suitable for use in preparing the branched fragmented polysiloxane of the invention include any of the linear, branched, and/or crosslinked polymers having any two or more of a combination of M, D, T, and Q groups, wherein, as known in the art, an M group represents a monofunctional group of formula $R_3SiO_{1/2}$, a D group represents a bifunctional group of formula $R_2SiO_{2/2}$, a T group represents a trifunctional group of formula $RSiO_{3/2}$, and a Q group represents a tetrafunctional group of formula $SiO_{4/2}$, and wherein at least two of the R groups are unsaturated hydrocarbon groups and the remainder of the R groups can be any suitable groups including hydrocarbon (e.g., C_1 - C_6), halogen, alkoxy, ester, ether, alcohol, and/or acid groups.

[0029] Some examples of classes of polysiloxanes suitable for use in preparing the branched fragmented polysiloxane of the invention include the MDM, TD, MT,

MDT, MDTQ, MQ, MDQ, and MTQ classes of polysiloxanes, and combinations thereof, having at least two unsaturated hydrocarbon groups.

[0030] In a particular embodiment, the polysiloxane suitable for use in preparing the branched fragmented polysiloxane of the invention is an MD-type of polysiloxane having one or more M and/or M^{vi} groups in combination with one or more D and/or D^{vi} groups, wherein M represents $Si(CH_3)_3O-$, M^{vi} represents $(CH_2=CH)Si(CH_3)_2O-$, D represents $-Si(CH_3)_2O-$, and D^{vi} represents $-Si(CH=CH_2)(CH_3)O-$, “vi” is an abbreviation for “vinyl,” and wherein the MD-type of polysiloxane contains at least two vinyl groups.

[0031] Other suitable MD-type polysiloxanes for use in preparing the branched fragmented polysiloxane of the invention include the $M^{vi}D_nM^{vi}$, $M^{vi}D_n^{vi}M$, $M^{vi}D_n^{vi}D_mM$, $M^{vi}D_n^{vi}M^{vi}$, $M^{vi}D_n^{vi}D_mM^{vi}$, $MD_n^{vi}M$, and $MD_n^{vi}D_mM$ classes of MD-type polysiloxanes, wherein m and n each represent at least 1. Any one or combination of the foregoing types of MD polysiloxanes can be used for polyorganosiloxane of the invention. In various embodiments, m and n can independently represent, for example, a number within the ranges 1-10, 11-20, 50-100, 101-200, 201-500, 501-1500, and higher numbers.

[0032] The D^{vi} groups can also be randomly incorporated (i.e., not as a block) amongst D groups. For example, $M^{vi}D_n^{vi}D_mM$ can represent a polymer wherein n represents 5-20 and m represents 50-1500, and wherein the 5-20 D^{vi} groups are randomly incorporated amongst the 50-1500 D groups.

[0033] In another embodiment of the invention, the M^{vi} and D^{vi} groups can each independently include a higher number of unsaturated functional groups, such as, for example, $(CH_2=CH)_2(CH_3)SiO-$ and $(CH_2=CH)_3SiO-$ groups for M^{vi} or $-Si(CH=CH_2)_2O-$ for D^{vi} .

[0034] The one or more silylhydride-containing compounds for use in preparing the branched fragmented polysiloxane of the invention include any low molecular weight compound, oligomer, or polymer containing at least two silylhydride functional groups

per molecule. Suitable silylhydride-containing compounds for use in the present invention include siloxanes containing at least two silylhydride functional groups, dimethylsilane, diethylsilane, di-(n-propyl)silane, diisopropylsilane, diphenylsilane, methylchlorosilane, dichlorosilane, 1,3-disilapropane, 1,3-disilabutane, 1,4-disilabutane, 1,3-disilapentane, 1,4-disilapentane, 1,5-disilapentane, 1,6-disilahexane, bis-1,2-(dimethylsilyl)ethane, bis-1,3-(dimethylsilyl)propane, 1,2,3-trisilylpropane, 1,4-disilylbenzene, 1,2-dimethyldisilane, 1,1,2,2-tetramethyldisilane, 1,2-diphenyldisilane, 1,1,2,2-tetraphenyldisilane, 1,1,3,3-tetramethyldisiloxane, 1,1,3,3-tetraphenyldisiloxane, 1,1,3,3,5,5-hexamethyltrisiloxane, 1,1,1,5,5,5-hexamethyltrisiloxane, 1,3,5-trimethylcyclotrisiloxane, 1,3,5,7-tetramethylcyclotetrasiloxane, and 1,3,5,7-tetraphenylcyclotetrasiloxane, and the like.

[0035] Examples of silylhydride-containing oligomers and polymers of the invention include any of the linear, branched, and/or crosslinked polymers having any two or more of a combination of M, D, T, and Q groups, as described above, and having at least two silylhydride functional groups in the oligomer or polymer.

[0036] According to one embodiment of the invention, silylhydride-containing compounds for preparing the branched fragmented polysiloxane of the invention are an MD-type of polysiloxane having one or more M and/or M^H groups in combination with one or more D and/or D^H groups, wherein M represents $\text{Si}(\text{CH}_3)_3\text{O}-$, M^H represents $\text{HSi}(\text{CH}_3)_2\text{O}-$, D represents $-\text{Si}(\text{CH}_3)_2\text{O}-$, and D^H represents $-\text{Si}(\text{H})(\text{CH}_3)\text{O}-$, and wherein the MD-type of polysiloxane contains at least two silylhydride groups.

[0037] Examples of suitable MD-type polysiloxanes include the $M^H D_n M^H$, $M^H D^H_n M$, $M^H D^H_n D_m M$, $M^H D^H_n M^H$, $M^H D^H_n D_m M^H$, $MD^H_n M$, and $MD^H_n D_m M$ classes of MD-type polysiloxanes, and combinations thereof, wherein m and n each represent at least 1 and can have any of the numerical values as described above.

[0038] The D^H groups can also be randomly incorporated (i.e., not as a block) amongst D groups. For example, $M^H D^H_n D_m M$ can represent a polymer wherein n

represents 5-20 and m represents 50-1500, and wherein the 5-20 D^H groups are randomly incorporated amongst the 50-1500 D groups.

[0039] In one embodiment, M^H and D^H groups can each independently have a higher number of silylhydride functional groups, such as, for example, $H_2Si(CH_3)O-$ and H_3SiO- groups for M^H or $-Si(H)_2O-$ for D^H .

[0040] Examples of siloxane-containing oligomers and polymers for preparing the branched fragmented polysiloxanes via equilibration of the invention include the linear, branched, and/or crosslinked polymers having any two or more of a combination of M, D, T, and Q groups, as described above in the oligomer or polymer.

[0041] In a particular embodiment of the invention, the siloxane used for equilibrating under equilibration conditions is an MD-type of polysiloxane having one or more M groups in combination with one or more D groups, wherein M represents $Si(CH_3)_3O-$, D represents $-Si(CH_3)_2O-$.

[0042] Examples of suitable MD-type polysiloxanes include the MD_nM , MD_nM , MD_nD_mM , MD_nM , MD_nD_mM , MD_nM , and MD_nD_mM classes of MD-type polysiloxanes, and combinations thereof, wherein m and n each represent at least 1 and can have any of the numerical values as described above.

[0043] Some examples of silylhalide-containing oligomers and polymers suitable for copolymerization under condensation conditions include any of the linear, branched, and/or crosslinked polymers having any two or more of a combination of M, D, T, and Q groups, as described above, and having at least two silylhalide functional groups in the oligomer or polymer. The halide present can be any suitable for condensation, for example, chloride, bromide, iodide or any mixture.

[0044] In a particular embodiment of the invention, the polyorganosiloxane used for copolymerizing under condensation conditions is the MD-type of polysiloxane having one or more M and/or M^X groups in combination with one or more D and/or D^X groups,

wherein M represents $\text{Si}(\text{CH}_3)_3\text{O}-$, M^{X} represents $\text{XSi}(\text{CH}_3)_2\text{O}-$, D represents $-\text{Si}(\text{CH}_3)_2\text{O}-$, and D^{X} represents $-\text{Si}(\text{X})(\text{CH}_3)\text{O}-$, and wherein the MD-type of polysiloxane contains at least two silylhalide groups. The X group being a halide suitable for condensation, for example, chloride, bromide, iodide or any mixture.

[0045] Examples of suitable MD-type polysiloxanes include the $\text{M}^{\text{X}}\text{D}_n\text{M}^{\text{X}}$, $\text{M}^{\text{X}}\text{D}_n^{\text{X}}\text{M}$, $\text{M}^{\text{X}}\text{D}_n^{\text{X}}\text{D}_m\text{M}$, $\text{M}^{\text{X}}\text{D}_n^{\text{X}}\text{M}^{\text{X}}$, $\text{M}^{\text{X}}\text{D}_n^{\text{X}}\text{D}_m\text{M}^{\text{X}}$, $\text{MD}_n^{\text{X}}\text{M}$, and $\text{MD}_n^{\text{X}}\text{D}_m\text{M}$ classes of MD-type polysiloxanes, and combinations thereof, wherein m and n each represent at least 1 and can have any of the numerical values as described above.

[0046] The D^{X} groups can also be randomly incorporated (i.e., not as a block) amongst D groups. For example, $\text{M}^{\text{X}}\text{D}_n^{\text{X}}\text{D}_m\text{M}$ can represent a polymer wherein n represents 5-20 and m represents 50-1500, and wherein the 5-20 D^{X} groups are randomly incorporated amongst the 50-1500 D groups.

[0047] In other embodiments of the invention, M^{X} and D^{X} groups can each independently have a higher number of silylhalide functional groups, such as, for example, $\text{X}_2\text{Si}(\text{CH}_3)\text{O}-$ and $\text{X}_3\text{SiO}-$ groups for M^{X} or $-\text{Si}(\text{X})_2\text{O}-$ for D^{X} .

[0048] Examples of silanol-containing oligomers and polymers for use in preparing the branched fragmented polyorganosiloxane resulting from copolymerization under condensation conditions include any of the linear, branched, and/or crosslinked polymers having any two or more of a combination of M, D, T, and Q groups, as described above, and having at least two silanol functional groups in the oligomer or polymer.

[0049] The silanols can be homopolymers, copolymers or mixtures thereof. It is preferred that the silanol contain on average at least two organic radicals in a molecule per silicon atom. Examples of suitable silanols include hydroxyl end-blocked polydimethylsiloxane, hydroxyl end-blocked polydiorganosiloxane having siloxane units of dimethylsiloxane and phenylmethylsiloxane, hydroxyl end-blocked polymethyl-3,3,3-trifluoropropylsiloxane and hydroxyl end-blocked polyorganosiloxane having siloxane

units of monomethylsiloxane, dimethylsiloxane, with the monomethylsiloxane units supplying "on-chain" hydroxyl groups. The silanol also includes mixtures of hydroxylated organosiloxane polymers, such as mixture of hydroxyl end-blocked polydimethylsiloxane and diphenylmethylsilanol.

[0050] In a particular embodiment of the invention, the polyorganosiloxane used in preparing the branched fragmented polyorganosiloxane resulting from copolymerization under condensation conditions is an MD-type of polysiloxane having one or more M and/or M^{OH} groups in combination with one or more D and/or D^{OH} groups, wherein M represents $Si(CH_3)_3O-$, M^{OH} represents $HOSi(CH_3)_2O-$, D represents $-Si(CH_3)_2O-$, and D^{OH} represents $-Si(OH)(CH_3)O-$, and wherein the MD-type of polysiloxane contains at least two silanol groups.

[0051] Examples of suitable MD-type polysiloxanes include the $M^{OH}D_nM^{OH}$, $M^{OH}D_n^{OH}M$, $M^{OH}D_n^{OH}D_mM$, $M^{OH}D_n^{OH}M^{OH}$, $M^{OH}D_n^{OH}D_mM^{OH}$, $MD_n^{OH}M$, and $MD_n^{OH}D_mM$ classes of MD-type polysiloxanes, and combinations thereof, wherein m and n each represent at least 1 and can have any of the numerical values as described above.

[0052] The D^{OH} groups can also be randomly incorporated (i.e., not as a block) amongst D groups. For example, $M^{OH}D_n^{OH}D_mM$ can represent a polymer wherein n represents 5-20 and m represents 50-1500, and wherein the 5-20 D^{OH} groups are randomly incorporated amongst the 50-1500 D groups.

[0053] In yet another embodiment of the invention, M^{OH} and D^{OH} groups can each independently have a higher number of silanol functional groups, such as, for example, $(HO)_2Si(CH_3)O-$ and $(HO)_3SiO-$ groups for M^{OH} or $-Si(OH)_2O-$ for D^{OH} .

[0054] Examples of alkoxysilane-containing oligomers and polymers for use in preparing the branched fragmented polyorganosiloxane resulting from copolymerization under condensation conditions include any of the linear, branched, and/or crosslinked polymers having any two or more of a combination of M, D, T, and Q groups, as

described above, and having at least two alkoxysilane functional groups in the oligomer or polymer.

[0055] In a particular embodiment of the invention, the polyorganosiloxane used in preparing the branched fragmented polyorganosiloxane resulting from copolymerization under condensation conditions is an MD-type of polysiloxane having one or more M and/or M^{OR} groups in combination with one or more D and/or D^{OR} groups, wherein M represents $Si(CH_3)_3O-$, M^{OR} represents $ROSi(CH_3)_2O-$, D represents $-Si(CH_3)_2O-$, and D^{OR} represents $-Si(OR)(CH_3)O-$, and wherein the MD-type of polysiloxane contains at least two alkoxysilanes wherein R may be independently chosen from methyl, ethyl, or propyl groups.

[0056] Examples of suitable MD-type polysiloxanes include the $M^{OR}D_nM^{OR}$, $M^{OR}D^{OR}_nM$, $M^{OR}D^{OR}_nD_mM$, $M^{OR}D^{OR}_nM^{OR}$, $M^{OR}D^{OR}_nD_mM^{OR}$, MD^{OR}_nM , and $MD^{OR}_nD_mM$ classes of MD-type polysiloxanes, and combinations thereof, wherein m and n each represent at least 1 and can have any of the numerical values as described above.

[0057] The D^{OR} groups can also be randomly incorporated (i.e., not as a block) amongst D groups. For example, $M^{OR}D^{OR}_nD_mM$ can represent a polymer wherein n represents 5-20 and m represents 50-1500, and wherein the 5-20 D^{OR} groups are randomly incorporated amongst the 50-1500 D groups.

[0058] In still another embodiment of the invention, M^{OR} and D^{OR} groups can each independently have a higher number of alkoxy functional groups, such as, for example, $(RO)_2Si(CH_3)O-$ and $(RO)_3SiO-$ groups for M^{OR} or $-Si(OR)_2O-$ for D^{OR} .

[0059] Examples of silylester-containing oligomers and polymers the used in preparing the branched fragmented polyorganosiloxane resulting from copolymerization under condensation conditions include any of the linear, branched, and/or crosslinked polymers having any two or more of a combination of M, D, T, and Q groups, as described above, and having at least two silylester functional groups in the oligomer or polymer. Wherein the R group of the ester moiety is 1 to 6, 7 to 12, 13 to 30 carbon

monovalent hydrocarbon radical, e.g., methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, phenyl, benzyl, and mesityl.

[0060] According to one embodiment of the invention, the polyorganosiloxane used in preparing the branched fragmented polyorganosiloxane resulting from copolymerization under condensation conditions is an MD-type of polysiloxane having one or more M and/or $M^{O(CO)R}$ groups in combination with one or more D and/or $D^{O(CO)R}$ groups, wherein M represents $Si(CH_3)_3O-$, $M^{O(CO)R}$ represents $R(CO)OSi(CH_3)_2O-$, D represents $-Si(CH_3)_2O-$, and $D^{O(CO)R}$ represents $-Si(O(CO)R)(CH_3)O-$, and wherein the MD-type of polysiloxane contains at least two silylester groups wherein R may contain between 1-6, 7-12, 13-30 carbon atoms.

[0061] Examples of suitable MD-type polysiloxanes include the $M^{O(CO)R}D_nM^{O(CO)R}$, $M^{O(CO)R}D^{O(CO)R}_nM$, $M^{O(CO)R}D^{O(CO)R}_nD_mM$, $M^{O(CO)R}D^{O(CO)R}_nM^{O(CO)R}$, $M^{O(CO)R}D^{O(CO)R}_nD_mM^{O(CO)R}$, $MD^{O(CO)R}_nM$, and $MD^{O(CO)R}_nD_mM$ classes of MD-type polysiloxanes, and combinations thereof, wherein m and n each represent at least 1 and can have any of the numerical values as described above.

[0062] The $D^{O(CO)R}$ groups can also be randomly incorporated (i.e., not as a block) amongst D groups. For example, $M^{O(CO)R}D^{O(CO)R}_nD_mM$ can represent a polymer wherein n represents 5-20 and m represents 50-1500, and wherein the 5-20 $D^{O(CO)R}$ groups are randomly incorporated amongst the 50-1500 D groups.

[0063] In another embodiment of the invention, $M^{O(CO)R}$ and $D^{O(CO)R}$ groups can each independently have a higher number of silylester functional groups, such as, for example, $(R(CO)O)_2Si(CH_3)O-$ and $(R(CO)O)_3SiO-$ groups for $M^{O(CO)R}$ or $-Si(O(CO)R)_2O-$ for $D^{O(CO)R}$.

[0064] According to another embodiment of the invention, when preparing the branched polysiloxane composition of the invention, the number of unsaturated sites per molecule of compound (a) (alternatively, the number of functional groups possessed by compound(a)) and the number of silylhydride functional groups per polyorganosiloxane

(b) can vary in any combination to each other so long as there are at least two per molecule, respectively. Furthermore, the number of functional groups per polyorganosiloxane(s) and compound(s) undergoing copolymerization under condensation conditions can vary in any combination to each other so long as there are at least two per molecule, respectively.

[0065] For example, compound (a) can have two, or any number unsaturated sites per molecule while polyorganosiloxane (b) can have the same or different number of functional groups per molecule and are in any molar ratio with respect to each other, including equal or similar molar amounts. Similarly, the polyorganosiloxane(s) and compound(s) undergoing copolymerization under condensation conditions can contain an equal or different number of functional groups and are in any molar ratio with respect to each other, including equal or similar molar amounts provided that the polyorganosiloxane and compound each have at least two functional groups per molecule.

[0066] In yet another embodiment, the branched polysiloxane follows a branching pattern similar to a star polymer wherein when either compound (a) or polyorganosiloxane (b) has a higher number unsaturated sites or functional groups, respectively, (i.e., crosslinkers) they are present in a lower molar amount than the molecule of either compound (a) or polyorganosiloxane (b) having a lower number of unsaturated sites or functional groups, respectively, (i.e., extenders). As such, the above-described star polymer pattern is distinct from a dendritic pattern in which branching predominates.

[0067] For example, (a) or (b) can have at least four, five, six, seven, eight, nine, ten, or a higher number of unsaturated sites/functional groups, respectively, and be in a lower molar amount than (a) or (b) containing two or three unsaturated sites/functional groups, respectively, per molecule.

[0068] The unsaturated sites of compound (a) can be in any suitable molar ratio to silylhydride functional groups of polyorganosiloxane (b), e.g., 100:1, 50:1, 25:1, 20:1, 10:1, 1:10, 1:20, 1:25, 1:50, 1:100, and any range of ratios therebetween. Likewise, the functional groups of polyorganosiloxane(s) undergoing copolymerization under condensation conditions with a compound(s) having at least two functional groups can be in any suitable molar ratio, e.g., 100:1, 50:1, 25:1, 20:1, 10:1, 1:10, 1:20, 1:25, 1:50, 1:100, and any range of ratios therebetween.

[0069] In a particular embodiment, the unsaturated sites of compound (a) are in a molar ratio to silylhydride functional groups of polyorganosiloxane (b) within a range according to the formula $(6-s):1$ or $1:(1+t)$ wherein s represents a number equal to or greater than 0 and less than 5, and t represents a number greater than 0 and equal to or less than 5. Some examples of such molar ratios of unsaturated sites of compound (a) to functional groups of polyorganosiloxane (b) include 6:1, 5.5:1, 5:1, 4.5:1, 4:1, 3.5:1, 3:1, 2.5:1, 2:1, 1.5:1, 1.4:1, 1.2:1, 1:1.2, 1:1.4, 1:1.5, 1:2, 1:2.5, 1:3, 1:3.5, 1:4, 1:4.5, 1:5, 1:5.5, and 1:6, and any range of ratios therebetween. The ratios within the range according to the formula $(6-s):1$ or $1:(1+t)$ can apply to the functional groups of polyorganosiloxane(s) and compound(s) undergoing copolymerization under condensation conditions as well and can be depicted by the examples of molar ratios described herein, i.e., 6:1, 5.5:1, 5:1, 4.5:1, 4:1, 3.5:1, 3:1, 2.5:1, 2:1, 1.5:1, 1.4:1, 1.2:1, 1:1.2, 1:1.4, 1:1.5, 1:2, 1:2.5, 1:3, 1:3.5, 1:4, 1:4.5, 1:5, 1:5.5, and 1:6, and any range of ratios therebetween.

[0070] For example, in one embodiment, the unsaturated sites of compound (a) are in a molar ratio to silylhydride functional groups of polyorganosiloxane (b) within a range according to the formula $(4.6-s):1$ or $1:(1+s)$ wherein s represents a number greater than 0 and less than 3.6. In another embodiment, the unsaturated sites of compound (a) are in a molar ratio to silylhydride functional groups of polyorganosiloxane (b) within a range according to the formula $(4.25-s):1$ or $1:(1+t)$ wherein s represents a number equal to or greater than 0 and less than 3.25, and t represents a number greater than 0 and equal

to or less than 3.25. In yet another embodiment, the unsaturated sites of compound (a) are in a molar ratio to silylhydride functional groups of polyorganosiloxane (b) within a range of about 4.5:1 to about 2:1. The ratios within the ranges according to the formulae $(4.6-s):1$ or $1:(1+s)$ wherein s represents a number greater than 0 and less than 3.6 and $(4.25-s):1$ or $1:(1+t)$ wherein s represents a number equal to or greater than 0 and less than 3.25, and t represents a number greater than 0 and equal to or less than 3.25, apply to the functional groups of functional groups of polyorganosiloxane(s) and compound(s) undergoing copolymerization under condensation conditions as well.

[0071] The phrase “hydrosilylation conditions” is defined herein as the conditions known in the art for hydrosilylation reaction between compounds containing unsaturated groups and compounds containing silylhydride groups.

[0072] As known in the art, a hydrosilylation catalyst is required to promote or effect the hydrosilylation reaction between compound (a) and polyorganosiloxane (b) either during or after mixing of the components at a suitable temperature. The hydrosilylation catalyst typically contains one or more platinum-group metals or metal complexes. For example, the hydrosilylation catalyst can be a metallic or complexed form of ruthenium, rhodium, palladium, osmium, iridium, or platinum. More typically, the hydrosilylation catalyst is platinum-based. The platinum-based catalyst can be, for example, platinum metal, platinum metal deposited on a carrier (e.g., silica, titania, zirconia, or carbon), chloroplatinic acid, or a platinum complex wherein platinum is complexed to a weakly binding ligand such as divinyltetramethyldisiloxane. The platinum catalyst can be included in a concentration range of, for example, 1-100 ppm, but is more typically included in a concentration of about 5 to 40 ppm.

[0073] Equilibration and condensation conditions herein are those conditions known in the art for equilibration and condensation reactions, which optionally include the use of appropriate catalysts. A condensation reaction being defined as a reaction that produces a “condensate” molecule from the reaction of two functional groups. An

equilibration reaction is redistribution of chain lengths based on kinetic and/or thermodynamics.

[0074] The equilibration catalysts of the present include: acids, bases, tetralkyl ammonium salts and the like. Examples include various metal hydroxides, i.e., sodium hydroxide, potassium hydroxide, cesium hydroxide, or an appropriate silanolate, (i.e., the product of silanol and hydroxide). Acids may include any strong acid such as sulfuric, hydrochloric, hydrobromic, linear phosphonitirilic chloride (LPNC), ethylsulfuric, chlorosulfonic, selenic, nitric, phosphoric, pyrophosphoric, and boric acid. Acids can also be present as supported catalysts on solid supports such as fullers' earth and the like. Lewis acids are also effective for equilibrations: iron (III) chloride, aluminum (III) chloride, iron (III) oxide, boron trifluoride, zinc chloride and tin (IV) chloride.

[0075] Condensation catalysts contemplated herein include various tin (IV) compounds that are soluble in the medium. For example dibutyltindilaurate, dibutyltindiacetate, dibutyltindimethoxide, tinooctoate, isobutyltintriceroate, dibutyltinoxide, dibutyltin bis-diisooctylphthalate, bis-tripropoxysilyl dioctyltin, dibutyltin bis-acetylacetone, silylated dibutyltin dioxide, carbomethoxyphenyl tin tris-uberate, isobutyltin triceroate, dimethyltin dibutyrate, dimethyltin di-neodecanoate, triethyltin tartarate, dibutyltin dibenzoate, tin oleate, tin naphthenate, butyltintri-2-ethylhexylhexoate, and tinbutyrate. In one embodiment, tin compounds and $(C_8H_{17})_2SnO$ dissolved in $(n-C_3H_7O)_4Si$ are used. In another embodiment, diorganotin bis β -diketonates are used. Other examples of tin compounds may be found in US 5,213,899, US 4,554,338, US 4,956,436, and US 5,489,479, the teachings of which are herewith and hereby specifically incorporated by reference. In yet another embodiment, chelated titanium compounds, for example, 1,3-propanedioxytitanium bis(ethylacetoacetate); di-isopropoxytitanium bis(ethylacetoacetate); and tetra-alkyl titanates, for example, tetra n-butyl titanate and tetra-isopropyl titanate, are used.

[0076] Other examples of condensation catalysts include titanium compounds such as tetrabutyl titanate, titanium diisopropoxy-bis-ethylacetoacetate, and

tetraisopropoxy titanate; carboxylates of bismuth; carboxylates of lead; carboxylates of zirconium; amines such as triethylamine, ethylenetriamine, butylamine, octylamine, dibutylamine, monoethanolamine, diethanolamine, triethanolamine, diethylenetriamine, triethylenetetramine, cyclohexylamine, benzylamine, diethylaminopropylamine, xylylenediamine, triethylenediamine, guanidine, diphenylguanidine, and morpholine.

[0077] In one embodiment, tetravalent $\text{SiO}_{4/2}$ groups (i.e., Q groups) are excluded from the branched polysiloxane composition.

[0078] In another embodiment, unsaturated hydrocarbon compounds, such as, e.g., alpha-olefins, are excluded from the component mixture from which the branched polysiloxane is derived. Some examples of such unsaturated hydrocarbon compounds include alpha-olefins of the formula $\text{CH}_2=\text{CHR}^1$ wherein R^1 is selected from halogen, hydrogen, or a heteroatom-substituted or unsubstituted hydrocarbon group having one to sixty carbon atoms. Some heteroatoms include oxygen (O) and nitrogen (N) atoms.

[0079] In yet another embodiment, oxy-substituted hydrocarbon compounds, such as oxyalkylene-containing and/or ester-containing saturated or unsaturated compounds, are excluded from the branched polysiloxane composition.

[0080] Auxiliary and other components can be included, as necessary, to the component mixture for making the above-described branched polysiloxanes of reduced molecular weight and viscosity. Some types of auxiliary components include catalyst inhibitors, surfactants, and diluents. Some examples of catalyst inhibitors for addition polymerizations (i.e., hydrosilylations) include maleates, fumarates, unsaturated amides, acetylenic compounds, unsaturated isocyanates, unsaturated hydrocarbon diesters, hydroperoxides, nitriles, amines, and diaziridines. Some examples of diluents include the hydrocarbons (e.g., pentanes, hexanes, heptanes, octanes), aromatic hydrocarbons (e.g., benzene, toluene, and the xylenes), ketones (e.g., acetone, methylethylketone), and halogenated hydrocarbons (e.g., trichloroethene and perchloroethylene).

[0081] Examples have been set forth below for the purpose of illustration. The

scope of the invention is not to be in any way limited by the examples set forth herein.

[0082] In the following examples, the component referred to as Component A is a commercially available difunctional vinyl-terminated polysiloxane of the formula $M^{vi}D_{110}M^{vi}$ having a viscosity of 200-300cPs. The component referred to as Component B is an industrially produced hexafunctional silylhydride-containing polysiloxane of the formula $MD_{500}D^{H}_{6.5}M$ having a viscosity of 6,000 to 15,000 cPs and hydride content of 155 to 180 ppm, where 6.5 represents an average number of D^H groups randomly incorporated amongst D groups. The component referred to as Component C is a commercially available catalyst formulation containing 10% by weight platinum. The component referred to as Component D is a commercially available catalyst formulation containing 1000 ppm platinum concentration in Component A. The component referred to as Component E is a commercially available solventless anti-mist additive containing a branched polysiloxane composition containing a Q resin and alpha olefin and has a viscosity of ca. 25000 cPs. The component referred to as Component F is a commercially available solventless anti-mist additive containing a branched polysiloxane composition containing a Q resin and alpha olefin and has a viscosity of ca. 300000 cPs.

EXAMPLE 1

Synthesis of a Reduced Molecular Weight Polysiloxane Composition by Application of Shear

[0083] In accordance with the invention, Example 1 is a branched polysiloxane composition of reduced molecular weight and viscosity that was prepared by a continuous process as follows: Component A and Component B were pumped into a static mixer maintained at ambient temperature at 11.2 and 3.58 lb/h, respectively. The mixed polymer stream was added to barrels 1/2 of a 30mm co-rotating twin screw extruder (450 rpm). Component D was added to barrel 1/2 at 0.15 lb/h. The first three barrels of the extruder were maintained at ambient temperature; the next 7 barrels were heated at 150°C and contained a variety of different mixing elements to ensure

homogeneity of the reaction mass. Component A was added to the reaction mixture at barrel 9 at 16.6 lb/h. Cooling of the product, i.e., Example 1, occurred in barrels 11-15.

[0084] Comparative Example 1 is a batch synthesized non-fragmented branched polysiloxane composition that was prepared as follows: To a 1L reactor equipped with an overhead stirrer, GN2 inlet, thermometer, and oil bath was added 168.7g (ca. 20.2mmol) of Component A, and ca. 0.05g of Component C. The mixture was agitated for one hour under ambient conditions. Next, 54.4g (ca. 1.4mmol) of Component B was separately cooled to 4°C and then added to the components above with stirring. The mixture was agitated for 15 minutes under ambient conditions and then slowly heated to 90°C. After 30 minutes, some gelling was observed. To the reaction mixture was added 255.5g of Component A at 90°C. The mixture was stirred for two hours at 90°C, cooled to room temperature (~25°C), and discharged from the kettle. The amount of product, i.e., Comparative Example 4, was 430.9g, which corresponds to a 90% yield. The shear viscosity and shear modulus were measured at 12 Hz to be 2.813 Pa.s and 201.2 Pa, respectively.

[0085] Table 1 below illustrates the physical property differences between Example 1 and Comparative Example 1. As presented in Table 1, the continuous process produced a polysiloxane composition with a substantially lower gel content than the batch process of Comparative Example 1. Gel particulates do not promote mist reduction, and in addition, are capable of causing problems during the coating process. Accordingly, the polysiloxane composition produced by the batch process required filtration while the polysiloxane composition produced by the continuous process, i.e., Example 1, did not require filtration.

[0086] In addition, the lower shear viscosity (η') and modulus (G') of the polysiloxane composition of Example 1 allowed for easier handling than the polysiloxane composition of the batch process of Comparative Example 1.

[0087]

TABLE 1

Examples	η' (cPs)	G' (Pa)	Gel (%)
Example 1	1.875	44.34	0.12
Comparative Example 1	2.813	201.2	20

EXAMPLE 2

Synthesis of a Reduced Molecular Weight Polysiloxane Composition by Application of Shear

[0088] Example 2 was prepared as follows: Component E was added to barrel 6 of the extruder at a temperature of 45°C and a screw rate of 400rpm. The sheared product, i.e., Example 2, was collected and used at 1% loading in misting trials and compare to Comparative Example 2 (i.e., Component E without shearing). The results of the misting trials are displayed in Table 2 below.

EXAMPLE 3

Synthesis of a Reduced Molecular Weight Polysiloxane Composition by Application of Shear

[0089] Example 3 was prepared as follows: Component F was added to barrel 6 of the extruder at a temperature of 45°C and a screw rate of 400rpm. The sheared product, i.e., Example 3, was collected and used at 1% loading in misting trials and compare to Comparative Example 3 (i.e., Component F without shearing). The results of the misting trials are displayed in Table 2 below.

[0090] The mist suppressant properties of Examples 2 and 3 was measured in a conventional silicone-based coating formulation and compared to a silicone-based

coating formulation containing Comparative Examples 2 and 3 (i.e., Component E and F without shearing, respectively). Misting suppression was determined by roll coating the coating formulations using an 18-inch wide, five-roll pilot coater at line speeds from 1,500-3,000 feet per minute onto Nicolet NG241 paper or equivalent. The target coat weight was 0.6 – 0.9 pounds per ream. Mist was measured using Model 8520 DustTrak Aerosol Monitor manufactured by TSI Corporation. The monitor was positioned where the highest concentration of mist was visually perceived.

[0091] The coating formulation for Examples 2-3 and Comparative Examples 2-3 was prepared as follows: to a two-gallon plastic pail was charged with 99 parts (1980 g) of a commercially available $M^{Vi}D_{110}M^{Vi}$ solution (containing 100 ppm Pt and 0.4% diallylmaleate inhibitor). The anti-mist composition was charged to the pail in the amount of 1 part (20g) and mixed with a drill-mounted agitator. The crosslinker, a commercially available hydride ($MD_{30}D_{15}M^H$) was added to the pail in the amount of 5.5 parts (110g). The mixture was mixed thoroughly with a drill-mounted agitator.

[0092] TABLE 2

Examples	Shear Rate (rpm)	η' (cPs, 12Hz)	G' (Pa, 12Hz)	Viscosity (cPs)	Mist* (mg/m ³)
Comparative Example 2	0	3,273	151	25,250	2.08
Example 2	400	3,033	133	9,950	2.22
Comparative Example 3	0		431	300,000	1.02
Example 3	400	7,589	384	34,000	1.43

* Mist values are particulates measured at 3000 ft/min. The concentration of anti-mist additive is 1% (w/w) of the formulation.

[0093] Thus, whereas there have been described what are presently believed to be the preferred embodiments of the present invention, those skilled in the art will realize

that other and further embodiments can be made without departing from the spirit of the invention, and it is intended to include all such further modifications and changes as come within the true scope of the claims set forth herein.

CLAIMS:

1. A branched polysiloxane composition which comprises at least one member selected from the group consisting of:

i) branched fragmented polyorganosiloxane, the polysiloxane resulting from reacting under hydrosilylation reaction conditions a mixture comprising:

a) at least one compound containing on average at least two unsaturated sites per molecule, and

b) at least one polyorganosiloxane containing on average at least two silylhydride functional groups per molecule,

provided, that at least one of (a) and/or (b) is fragmented by shearing prior to and/or during the hydrosilylation reaction and/or the polyorganosiloxane resulting from the hydrosilylation reaction is fragmented by shearing to provide the branched fragmented polyorganosiloxane;

ii) branched fragmented polyorganosiloxane, the polysiloxane resulting from equilibrating under equilibration conditions at least two polyorganosiloxanes selected from the group consisting of cyclic, linear and branched polyorganosiloxanes, provided, that at least one polyorganosiloxane is fragmented by shearing prior to and/or during equilibrating and/or the polyorganosiloxane resulting from equilibration is fragmented by shearing to provide the branched fragmented polyorganosiloxane; and,

iii) branched fragmented polyorganosiloxane, the polysiloxane resulting from copolymerization under condensation conditions of at least one polyorganosiloxane containing at least two functional groups, provided, that at least one polyorganosiloxane is fragmented by shearing prior to and/or during copolymerization and/or the polyorganosiloxane resulting from copolymerization is fragmented by shearing to provide the branched fragmented polyorganosiloxane.

2. The branched polysiloxane composition of Claim 1 wherein compound (a) is at least one polyorganosiloxane containing on average at least two unsaturated sites per molecule.
3. The branched polysiloxane composition of Claim 1 wherein branched fragmented polyorganosiloxane iii) results from copolymerization under condensation conditions of at least one polyorganosiloxane containing at least two functional groups and at least one compound with at least two functional groups, provided, that at least one polyorganosiloxane and/or compound is fragmented by shearing prior to and/or during copolymerization and/or the copolymerized polyorganosiloxane is fragmented by shearing to provide the branched fragmented polyorganosiloxane.
4. The branched polysiloxane composition of Claim 1 wherein at least one compound (a) or polyorganosiloxane (b) contains at least six functional groups per molecule.
5. The branched polysiloxane composition of Claim 3 wherein at least one polyorganosiloxane or compound contains at least six functional groups per molecule.
6. The branched polysiloxane composition of Claim 1 wherein at least one compound (a) or polyorganosiloxane (b) has more functional groups than the other and is present in a molar amount equal to or lower than the molar amount of the other.
7. The branched polysiloxane composition of Claim 3 wherein at least one polyorganosiloxane or compound has more functional groups than the other and is present in a molar amount equal to or lower than the molar amount of the other.
8. The branched polysiloxane composition of Claim 1 wherein the unsaturated sites of (a) are in a molar ratio to silylhydride functional groups of (b) within a range of about

(6-s):1 or about 1:(1+t) where s represents a number equal to or greater than 0 and less than 5, and t represents a number greater than 0 and equal to or less than 5.

9. The branched polysiloxane composition of Claim 3 wherein the functional groups of the polyorganosiloxane are in a molar ratio to the functional groups of the compound within a range of about (6-s):1 or about 1:(1+t) where s represents a number equal to or greater than 0 and less than 5, and t represents a number greater than 0 and equal to or less than 5.

10. The branched polysiloxane composition of Claim 1 wherein the unsaturated sites of (a) are in a molar ratio to silylhydride functional groups of (b) within a range according to a formula (4.6-s):1 or 1:(1+s) where s represents a number greater than 0 and less than 3.6.

11. The branched polysiloxane composition of Claim 3 wherein the functional groups of polyorganosiloxane are in a molar ratio to the functional groups of the compound within a range according to a formula (4.6-s):1 or 1:(1+s) where s represents a number greater than 0 and less than 3.6.

12. The branched polysiloxane composition of Claim 1 wherein the unsaturated sites of (a) are in a molar ratio to silylhydride functional groups of (b) within a range according to a formula (4.25-s):1 or 1:(1+t) where s represents a number equal to or greater than 0 and less than 3.25, and t represents a number greater than 0 and equal to or less than 3.25.

13. The branched polysiloxane composition of Claim 3 wherein the functional groups of polyorganosiloxane are in a molar ratio to the functional groups of the compound within a range according to a formula (4.25-s):1 or 1:(1+t) where s represents a number equal to or greater than 0 and less than 3.25, and t represents a number greater than 0 and equal to or less than 3.25.

14. The branched polysiloxane composition of Claim 1 wherein the unsaturated sites of (a) are in a molar ratio to silylhydride functional groups of (b) within a range according to a formula $(4.6-s):1$ where s represents a number greater than 0 and less than 3.6.
15. The branched polysiloxane composition of Claim 3 wherein the functional groups of polyorganosiloxane are in a molar ratio to the functional groups of the compound within a range according to a formula $(4.6-s):1$ where s represents a number greater than 0 and less than 3.6.
16. The branched polysiloxane composition of Claim 1 wherein the unsaturated sites of (a) are in a molar ratio to silylhydride functional groups of (b) within a range of about 4.5:1 to about 2:1.
17. The branched polysiloxane composition of Claim 3 wherein the functional groups of polyorganosiloxane are in a molar ratio to the functional groups of the compound within a range of about 4.5:1 to about 2:1.
18. The branched polysiloxane composition of Claim 1 wherein the shearing is performed, optionally, with a diluent possessing a viscosity greater than about 100 cSt.
19. The branched polysiloxane composition of Claim 1 having reduced molecular weight and viscosity as compared to polysiloxane not fragmented by shearing.
20. A method for making a branched polysiloxane which comprises:
- i) reacting under hydrosilylation reaction conditions a mixture comprising:
 - a) at least one compound containing on average at least two unsaturated sites per molecule, and
 - b) at least one polyorganosiloxane containing on average at least two silylhydride functional groups per molecule, and

ii) fragmenting by shearing at least one of (a) and/or (b) prior to and/or during the hydrosilylation reaction and/or the polyorganosiloxane resulting from the hydrosilylation reaction.

21. The method of Claim 20 wherein compound (a) is at least one polyorganosiloxane containing on average at least two unsaturated sites per molecule.

22. The method of Claim 20 wherein at least one compound (a) or polyorganosiloxane (b) has more functional groups than the other and is present in a molar amount equal to or lower than the molar amount of the other.

23. The method of Claim 20 wherein the unsaturated sites of (a) are in a molar ratio to silylhydride functional groups of (b) within a range of about (6-s):1 or about 1:(1+t) where s represents a number equal to or greater than 0 and less than 5, and t represents a number greater than 0 and equal to or less than 5.

24. The method of Claim 20 wherein the unsaturated sites of (a) are in a molar ratio to silylhydride functional groups of (b) within a range of about 4.5:1 to about 2:1.

25. The method of Claim 20 wherein the shear processing steps are performed, optionally, with diluent possessing a viscosity greater than about 100 cSt.

26. A method for making a branched polysiloxane which comprises:

i) equilibrating under equilibration conditions at least two polyorganosiloxanes selected the group consisting of cyclic, linear and branched polyorganosiloxanes, and

ii) fragmenting by shearing at least one polyorganosiloxane prior to and/or during equilibration and/or the polyorganosiloxane resulting from equilibration.

27. The method of Claim 26 wherein the shear processing steps are performed, optionally, with diluent possessing a viscosity greater than about 100 cSt.

28. A method for making a branched polysiloxane which comprises:

i) copolymerizing under condensation conditions at least one polyorganosiloxane containing at least two functional groups, and

ii) fragmenting by shearing at least one polyorganosiloxane prior to and/or during copolymerization and/or the copolymerized polyorganosiloxane resulting from copolymerization.

29. The method of Claim 28 wherein at least one polyorganosiloxane containing at least two functional groups and at least one compound with at least two functional groups are copolymerized under condensation conditions, provided, that at least one polyorganosiloxane and/or compound is fragmented by shearing prior to and/or during copolymerization and/or the copolymerized polyorganosiloxane is fragmented by shearing to provide the branched fragmented polyorganosiloxane.

30. The method of Claim 29 wherein at least one polyorganosiloxane or compound has more functional groups than the other and is present in a molar amount equal to or lower than the molar amount of the other.

31. The method of Claim 29 wherein the functional groups of the polyorganosiloxane are in a molar ratio to the functional groups of the compound within a range of about $(6-s):1$ or about $1:(1+t)$ where s represents a number equal to or greater than 0 and less than 5, and t represents a number greater than 0 and equal to or less than 5.

32. The method of Claim 29 wherein the functional groups of polyorganosiloxane are in a molar ratio to the functional groups of the compound within a range of about 4.5:1 to about 2:1.