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(54) Titre : COMPOSITIONS ADHESIVES
(54) Title: ADHESIVE COMPOSITIONS

(57) **Abrégé/Abstract:**

The present disclosure generally relates to adhesive compositions and articles including at least one of polydiorganosiloxane polyoxamide copolymer and/or silicone polyurea block copolymer and a silicate tackifying resin. Some embodiments of the adhesive composition include at least one of a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%.

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(54) Title: ADHESIVE COMPOSITIONS

(57) Abstract: The present disclosure generally relates to adhesive compositions and articles including at least one of polydiorganosiloxane polyoxamide copolymer and/or silicone polyurea block copolymer and a silicate tackifying resin. Some embodiments of the adhesive composition include at least one of a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%.

ADHESIVE COMPOSITIONS

Technical Field

5 The present disclosure generally relates to adhesive compositions and articles including at least one of polydiorganosiloxane polyoxamide copolymer and/or silicone polyurea block copolymer and a silicate tackifying resin.

Background

10 Siloxane polymers have unique properties derived mainly from the physical and chemical characteristics of the siloxane bond. These properties include low glass transition temperature, thermal and oxidative stability, resistance to ultraviolet radiation, low surface energy and hydrophobicity, high permeability to many gases, and biocompatibility. The siloxane polymers, however, often lack tensile strength.

15 The low tensile strength of the siloxane polymers can be improved by forming block copolymers. Some block copolymers contain a “soft” siloxane polymeric block or segment and any of a variety of “hard” blocks or segments. Polydiorganosiloxane polyamides and polydiorganosiloxane polyureas are exemplary block copolymers.

20 Polydiorganosiloxane polyamides have been prepared by condensation reactions of amino terminated silicones with short-chained dicarboxylic acids. Alternatively, these copolymers have been prepared by condensation reactions of carboxy terminated silicones with short-chained diamines. Because polydiorganosiloxanes (*e.g.*, polydimethylsiloxanes) and polyamides often have significantly different solubility parameters, it can be difficult to find reaction conditions for production of siloxane-based polyamides that result in high degrees of polymerization, particularly with larger homologs of the polyorganosiloxane segments. Many of the known siloxane-based polyamide copolymers contain
25 relatively short segments of the polydiorganosiloxane (*e.g.*, polydimethylsiloxane) such as segments having no greater than about 30 diorganosiloxy (*e.g.*, dimethylsiloxy) units or the amount of the polydiorganosiloxane segment in the copolymer is relatively low. That is, the fraction (*i.e.*, amount based on weight) of polydiorganosiloxane (*e.g.*, polydimethylsiloxane) soft segments in the resulting copolymers tends to be low.

30 Polydiorganosiloxane polyureas are another type of block copolymer. This type of block copolymer has been included in adhesive compositions. Although these block copolymers have many desirable characteristics, some of them tend to degrade when subjected to elevated temperatures such as 250 °C or higher.

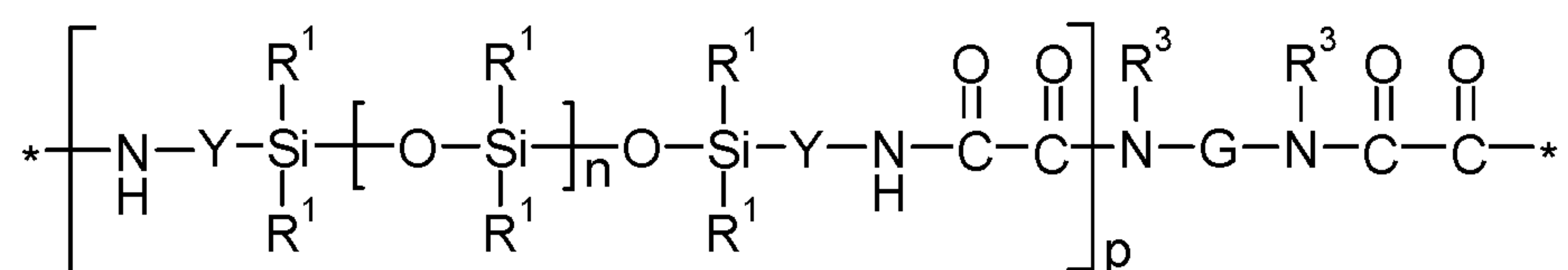
Summary

35 The inventors of the present disclosure recognized that an adhesive composition or article including at least one of (1) a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or (2) a silicone polyurea block

copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt% had various advantage or benefits.

Adhesive compositions, adhesive articles, and methods of making the adhesive articles are provided. The polydiorganosiloxane polyoxamide copolymers can contain a relatively large fraction of polydiorganosiloxane compared to many known polydiorganosiloxane polyamide copolymers. The adhesive compositions can be formulated as either a pressure sensitive adhesive or as a heat activated adhesive.

In a first aspect, an adhesive composition is provided that includes at least one of (1) a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or (2) a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%. In some embodiments, the polydiorganosiloxane polyoxamide contains at least two repeat units of Formula I.



I

In this formula, each R^1 is independently an alkyl, haloalkyl, aralkyl, alkenyl, aryl, or aryl substituted with an alkyl, alkoxy, or halo, wherein at least 50 percent of the R^1 groups are methyl. Each Y is independently an alkylene, aralkylene, or a combination thereof. Subscript n is independently an integer of 40 to 1500 and subscript p is an integer of 1 to 10. Group G is a divalent group that is the residue unit that is equal to a diamine of formula $\text{R}^3\text{HN-G-NHR}^3$ minus the two -NHR^3 groups (*i.e.*, amino groups). Group R^3 is hydrogen or alkyl or R^3 taken together with G and with the nitrogen to which they are both attached forms a heterocyclic group. Each asterisk (*) indicates a site of attachment of the repeat unit to another group in the copolymer such as, for example, another repeat unit of Formula I.

In a second aspect, an article is provided that includes a substrate and an adhesive layer adjacent to at least one surface of the substrate. The adhesive layer includes at least one of (1) a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or (2) a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%

In a third aspect, a method of making an article is provided. The method includes providing a substrate and applying an adhesive composition to at least one surface of the substrate. The adhesive composition includes including at least one of (1) a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or (2) a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%.

The above summary of the present disclosure is not intended to describe each disclosed embodiment or every implementation of the present disclosure. The description that follows more particularly exemplifies illustrative embodiments. In several places throughout the application, guidance is provided through lists of examples, which can be used in various combinations. In each instance, the recited list serves only as a representative group and should not be interpreted as an exclusive list.

Detailed Description of the Disclosure

Adhesive compositions and articles are provided that include at least one of (1) a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or (2) a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%. The adhesive compositions can be either pressure sensitive adhesives or heat activated adhesives.

Definitions

The terms “a”, “an”, and “the” are used interchangeably with “at least one” to mean one or more of the elements being described.

The term “alkenyl” refers to a monovalent group that is a radical of an alkene, which is a hydrocarbon with at least one carbon-carbon double bond. The alkenyl can be linear, branched, cyclic, or combinations thereof and typically contains 2 to 20 carbon atoms. In some embodiments, the alkenyl contains 2 to 18, 2 to 12, 2 to 10, 4 to 10, 4 to 8, 2 to 8, 2 to 6, or 2 to 4 carbon atoms. Exemplary alkenyl groups include ethenyl, n-propenyl, and n-butenyl.

The term “alkyl” refers to a monovalent group that is a radical of an alkane, which is a saturated hydrocarbon. The alkyl can be linear, branched, cyclic, or combinations thereof and typically has 1 to 20 carbon atoms. In some embodiments, the alkyl group contains 1 to 18, 1 to 12, 1 to 10, 1 to 8, 1 to 6, or 1 to 4 carbon atoms. Examples of alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, cyclohexyl, n-heptyl, n-octyl, and ethylhexyl.

The term “alkylene” refers to a divalent group that is a radical of an alkane. The alkylene can be straight-chained, branched, cyclic, or combinations thereof. The alkylene often has 1 to 20 carbon atoms. In some embodiments, the alkylene contains 1 to 18, 1 to 12, 1 to 10, 1 to 8, 1 to 6, or 1 to 4 carbon atoms. The radical centers of the alkylene can be on the same carbon atom (*i.e.*, an alkylidene) or on different carbon atoms.

The term “alkoxy” refers to a monovalent group of formula -OR where R is an alkyl group.

The term “alkoxycarbonyl” refers to a monovalent group of formula -(CO)OR where R is an alkyl group and (CO) denotes a carbonyl group with the carbon attached to the oxygen with a double bond.

The term “aralkyl” refers to a monovalent group of formula -R^a-Ar where R^a is an alkylene and Ar is an aryl group. That is, the aralkyl is an alkyl substituted with an aryl.

The term “aralkylene” refers to a divalent group of formula $-R^a-Ar^a-$ where R^a is an alkylene and Ar^a is an arylene (*i.e.*, an alkylene is bonded to an arylene).

The term “aryl” refers to a monovalent group that is aromatic and carbocyclic. The aryl can have one to five rings that are connected to or fused to the aromatic ring. The other ring structures can be aromatic, non-aromatic, or combinations thereof. Examples of aryl groups include, but are not limited to, phenyl, biphenyl, terphenyl, anthryl, naphthyl, acenaphthyl, anthraquinonyl, phenanthryl, anthracenyl, pyrenyl, perylenyl, and fluorenyl.

The term “arylene” refers to a divalent group that is carbocyclic and aromatic. The group has one to five rings that are connected, fused, or combinations thereof. The other rings can be aromatic, non-aromatic, or combinations thereof. In some embodiments, the arylene group has up to 5 rings, up to 4 rings, up to 3 rings, up to 2 rings, or one aromatic ring. For example, the arylene group can be phenylene.

The term “aryloxy” refers to a monovalent group of formula $-OAr$ where Ar is an aryl group.

The term “carbonyl” refers to a divalent group of formula $-(CO)-$ where the carbon atom is attached to the oxygen atom with a double bond.

The term “halo” refers to fluoro, chloro, bromo, or iodo.

The term “haloalkyl” refers to an alkyl having at least one hydrogen atom replaced with a halo. Some haloalkyl groups are fluoroalkyl groups, chloroalkyl groups, or bromoalkyl groups.

The term “heteroalkylene” refers to a divalent group that includes at least two alkylene groups connected by a thio, oxy, or $-NR-$ where R is alkyl. The heteroalkylene can be linear, branched, cyclic, or combinations thereof and can include up to 60 carbon atoms and up to 15 heteroatoms. In some embodiments, the heteroalkylene includes up to 50 carbon atoms, up to 40 carbon atoms, up to 30 carbon atoms, up to 20 carbon atoms, or up to 10 carbon atoms. Some heteroalkylenes are polyalkylene oxides where the heteroatom is oxygen.

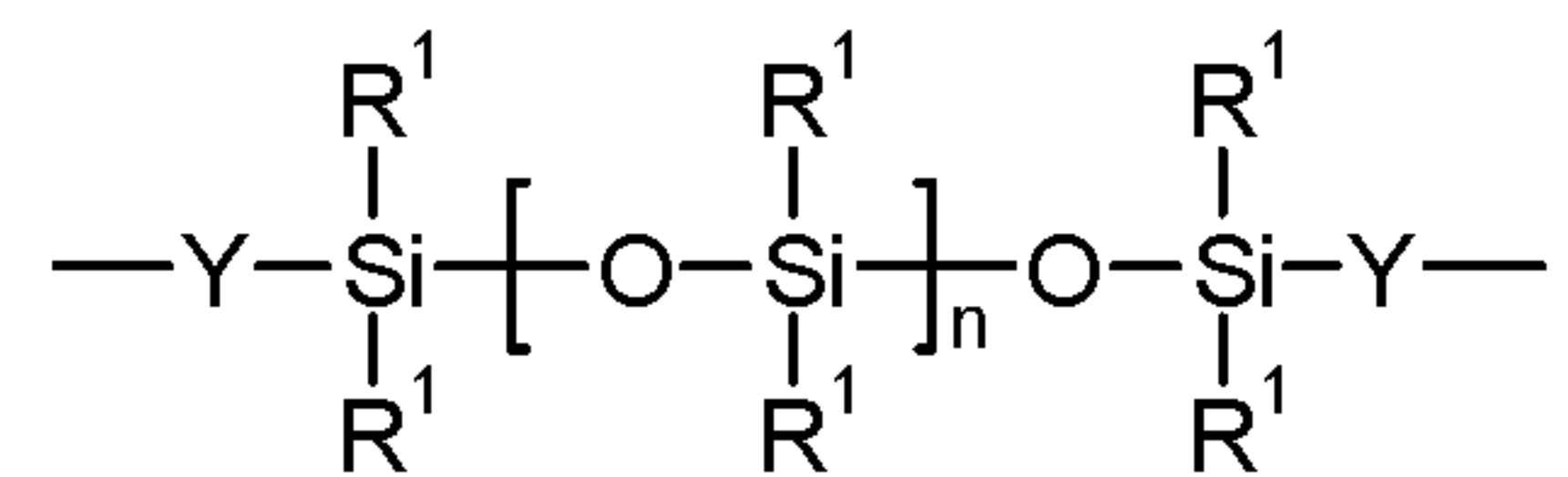
The term “oxalyl” refers to a divalent group of formula $-(CO)-(CO)-$ where each (CO) denotes a carbonyl group.

The terms “oxalylamino” and “aminoxalyl” are used interchangeably to refer to a divalent group of formula $-(CO)-(CO)-NH-$ where each (CO) denotes a carbonyl.

The term “aminoxalylamino” refers to a divalent group of formula $-NH-(CO)-(CO)-NR^d-$ where each (CO) denotes a carbonyl group and R^d is hydrogen, alkyl, or part of a heterocyclic group along with the nitrogen to which it is attached. In most embodiments, R^d is hydrogen or alkyl. In many embodiments, R^d is hydrogen.

The terms “polymer” and “polymeric material” refer to both materials prepared from one monomer such as a homopolymer or to materials prepared from two or more monomers such as a copolymer, terpolymer, or the like. Likewise, the term “polymerize” refers to the process of making a polymeric material that can be a homopolymer, copolymer, terpolymer, or the like. The terms “copolymer” and “copolymeric material” refer to a polymeric material prepared from at least two monomers.

The term “polydiorganosiloxane” refers to a divalent segment of formula



where each R¹ is independently an alkyl, haloalkyl, aralkyl, alkenyl, aryl, or aryl substituted with an alkyl, alkoxy, or halo; each Y is independently an alkylene, aralkylene, or a combination thereof; and subscript n is independently an integer of 40 to 1500.

The term “adjacent” means that a first layer is positioned near a second layer. The first layer can contact the second layer or can be separated from the second layer by one or more additional layers.

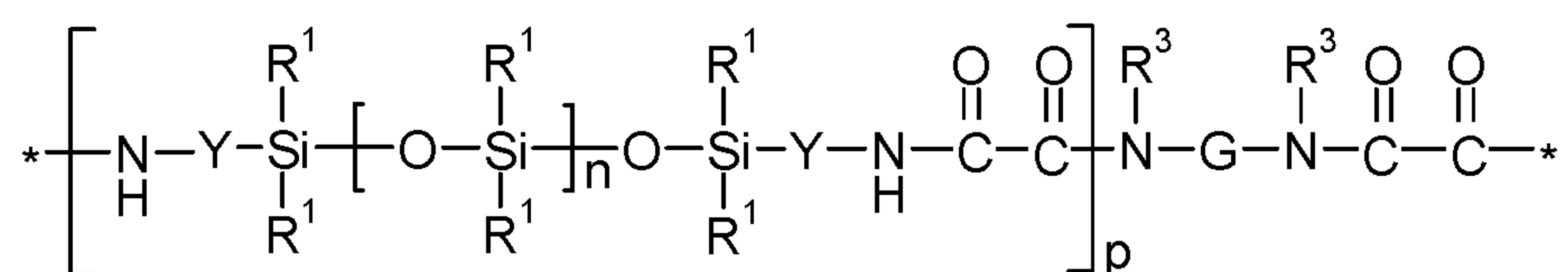
The terms “room temperature” and “ambient temperature” are used interchangeably to mean a temperature in the range of 20 °C to 25 °C.

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numbers set forth are approximations that can vary depending upon the desired properties using the teachings disclosed herein.

Adhesive compositions

In some embodiments, the adhesive composition including at least one of (1) a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or (2) a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%.

In some embodiments, the block polydiorganosiloxane polyoxamide copolymer contains at least two repeat units of Formula I.



I

In this formula, each R¹ is independently an alkyl, haloalkyl, aralkyl, alkenyl, aryl, or aryl substituted with an alkyl, alkoxy, or halo, wherein at least 50 percent of the R¹ groups are methyl. Each Y is independently an alkylene, aralkylene, or a combination thereof. Subscript n is independently an integer of 40 to 1500 and the subscript p is an integer of 1 to 10. Group G is a divalent group that is the residue unit that is equal to a diamine of formula R³HN-G-NHR³ minus the two –NHR³ groups. Group R³ is hydrogen or alkyl (*e.g.*, an alkyl having 1 to 10, 1 to 6, or 1 to 4 carbon atoms) or R³ taken together with G and with the nitrogen to which they are both attached forms a heterocyclic group (*e.g.*, R³HN-G-NHR³ is piperazine or the like). Each asterisk (*) indicates a site of attachment of the repeat unit to another group in the copolymer such as, for example, another repeat unit of Formula I.

Suitable alkyl groups for R¹ in Formula I typically have 1 to 10, 1 to 6, or 1 to 4 carbon atoms. Exemplary alkyl groups include, but are not limited to, methyl, ethyl, isopropyl, n-propyl, n-butyl, and iso-butyl. Suitable haloalkyl groups for R¹ often have only a portion of the hydrogen atoms of the corresponding alkyl group replaced with a halogen. Exemplary haloalkyl groups include chloroalkyl and fluoroalkyl groups with 1 to 3 halo atoms and 3 to 10 carbon atoms. Suitable alkenyl groups for R¹ often have 2 to 10 carbon atoms. Exemplary alkenyl groups often have 2 to 8, 2 to 6, or 2 to 4 carbon atoms such as ethenyl, n-propenyl, and n-butenyl. Suitable aryl groups for R¹ often have 6 to 12 carbon atoms. Phenyl is an exemplary aryl group. The aryl group can be unsubstituted or substituted with an alkyl (*e.g.*, an alkyl having 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms), an alkoxy (*e.g.*, an alkoxy having 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms), or halo (*e.g.*, chloro, bromo, or fluoro). Suitable aralkyl groups for R¹ usually have an alkylene group having 1 to 10 carbon atoms and an aryl group having 6 to 12 carbon atoms. In some exemplary aralkyl groups, the aryl group is phenyl and the alkylene group has 1 to 10 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms (*i.e.*, the structure of the aralkyl is alkylene-phenyl where an alkylene is bonded to a phenyl group).

In some embodiments, at least 50 percent of the R¹ groups are methyl. For example, at least 60 percent, at least 70 percent, at least 80 percent, at least 90 percent, at least 95 percent, at least 98 percent, or at least 99 percent of the R¹ groups can be methyl. The remaining R¹ groups can be selected from an alkyl having at least two carbon atoms, haloalkyl, aralkyl, alkenyl, aryl, or aryl substituted with an alkyl, alkoxy, or halo.

Each Y in Formula I is independently an alkylene, aralkylene, or a combination thereof. Suitable alkylene groups typically have up to 10 carbon atoms, up to 8 carbon atoms, up to 6 carbon atoms, or up to 4 carbon atoms. Exemplary alkylene groups include methylene, ethylene, propylene, butylene, and the like. Suitable aralkylene groups usually have an arylene group having 6 to 12 carbon atoms bonded to an alkylene group having 1 to 10 carbon atoms. In some exemplary aralkylene groups, the arylene portion is phenylene. That is, the divalent aralkylene group is phenylene-alkylene where the phenylene is bonded to an alkylene having 1 to 10, 1 to 8, 1 to 6, or 1 to 4 carbon atoms. As used herein with reference to group Y, “a combination thereof” refers to a combination of two or more groups selected from an alkylene and aralkylene group. A combination can be, for example, a single aralkylene bonded to a single alkylene (*e.g.*, alkylene-arylene-alkylene). In one exemplary alkylene-arylene-alkylene combination, the arylene is phenylene and each alkylene has 1 to 10, 1 to 6, or 1 to 4 carbon atoms.

Each subscript n in Formula I is independently an integer of 40 to 1500. For example, subscript n can be an integer up to 1000, up to 500, up to 400, up to 300, up to 200, up to 100, up to 80, or up to 60. The value of n is often at least 40, at least 45, at least 50, or at least 55. For example, subscript n can be in the range of 40 to 1000, 40 to 500, 50 to 500, 50 to 400, 50 to 300, 50 to 200, 50 to 100, 50 to 80, or 50 to 60.

The subscript p is an integer of 1 to 10. For example, the value of p is often an integer up to 9, up to 8, up to 7, up to 6, up to 5, up to 4, up to 3, or up to 2. The value of p can be in the range of 1 to 8, 1 to 6, or 1 to 4.

Group G in Formula I is a residual unit that is equal to a diamine compound of formula $R^3HN-G-NHR^3$ minus the two amino groups (*i.e.*, $-NHR^3$ groups). Group R^3 is hydrogen or alkyl (*e.g.*, an alkyl having 1 to 10, 1 to 6, or 1 to 4 carbon atoms) or R^3 taken together with G and with the nitrogen to which they are both attached forms a heterocyclic group (*e.g.*, $R^3HN-G-NHR^3$ is piperazine). The diamine can have primary or secondary amino groups. In most embodiments, R^3 is hydrogen or an alkyl. In many embodiments, both of the amino groups of the diamine are primary amino groups (*i.e.*, both R^3 groups are hydrogen) and the diamine is of formula $H_2N-G-NH_2$.

In some embodiments, G is an alkylene, heteroalkylene, polydiorganosiloxane, arylene, aralkylene, or a combination thereof. Suitable alkylens often have 2 to 10, 2 to 6, or 2 to 4 carbon atoms. Exemplary alkylene groups include ethylene, propylene, butylene, and the like. Suitable heteroalkylens are often polyoxyalkylens such as polyoxyethylene having at least 2 ethylene units, polyoxypropylene having at least 2 propylene units, or copolymers thereof. Suitable polydiorganosiloxanes include the polydiorganosiloxane diamines of Formula III, which are described below, minus the two amino groups. Exemplary polydiorganosiloxanes include, but are not limited to, polydimethylsiloxanes with alkylene Y groups. Suitable aralkylene groups usually contain an arylene group having 6 to 12 carbon atoms bonded to an alkylene group having 1 to 10 carbon atoms. Some exemplary aralkylene groups are phenylene-alkylene where the phenylene is bonded to an alkylene having 1 to 10 carbon atoms, 1 to 8 carbon atoms, 1 to 6 carbon atoms, or 1 to 4 carbon atoms. As used herein with reference to group G, "a combination thereof" refers to a combination of two or more groups selected from an alkylene, heteroalkylene, polydiorganosiloxane, arylene, and aralkylene. A combination can be, for example, an aralkylene bonded to an alkylene (*e.g.*, alkylene-arylene-alkylene). In one exemplary alkylene-arylene-alkylene combination, the arylene is phenylene and each alkylene has 1 to 10, 1 to 6, or 1 to 4 carbon atoms.

In some embodiments, the polydiorganosiloxane polyoxamide tends to be free of groups having a formula $-R^a-(CO)-NH-$ where R^a is an alkylene. All of the carbonylamino groups along the backbone of the copolymeric material are part of an oxalylamino group (*i.e.*, the $-(CO)-(CO)-NH-$ group). That is, any carbonyl group along the backbone of the copolymeric material is bonded to another carbonyl group and is part of an oxalyl group. More specifically, the polydiorganosiloxane polyoxamide has a plurality of aminoxalylamino groups.

In some embodiments, the polydiorganosiloxane polyoxamide is a linear, block copolymer and can be an elastomeric material. Unlike many of the known polydiorganosiloxane polyamides that are generally formulated as brittle solids or hard plastics, the polydiorganosiloxane polyoxamides can be formulated to include greater than 50 weight percent polydiorganosiloxane segments based on the weight of the copolymer. The weight percent of the diorganosiloxane in the polydiorganosiloxane polyoxamides can be increased by using higher molecular weight polydiorganosiloxanes segments to provide greater

than 60 weight percent, greater than 70 weight percent, greater than 80 weight percent, greater than 90 weight percent, greater than 95 weight percent, or greater than 98 weight percent of the polydiorganosiloxane segments in the polydiorganosiloxane polyoxamides. Higher amounts of the polydiorganosiloxane can be used to prepare elastomeric materials with lower modulus while maintaining reasonable strength.

Some of the polydiorganosiloxane polyoxamides can be heated to a temperature up to 200 °C, up to 225 °C, up to 250 °C, up to 275 °C, or up to 300 °C without noticeable degradation of the material. For example, when heated in a thermogravimetric analyzer in the presence of air, the copolymers often have less than a 10 percent weight loss when scanned at a rate 50 °C per minute in the range of 20 °C to about 350 °C. Additionally, the copolymers can often be heated at a temperature such as 250 °C for 1 hour in air without apparent degradation as determined by no detectable loss of mechanical strength upon cooling.

The polydiorganosiloxane polyoxamide copolymers have many of the desirable features of polysiloxanes such as low glass transition temperatures, thermal and oxidative stability, resistance to ultraviolet radiation, low surface energy and hydrophobicity, and high permeability to many gases. Additionally, the copolymers exhibit good to excellent mechanical strength.

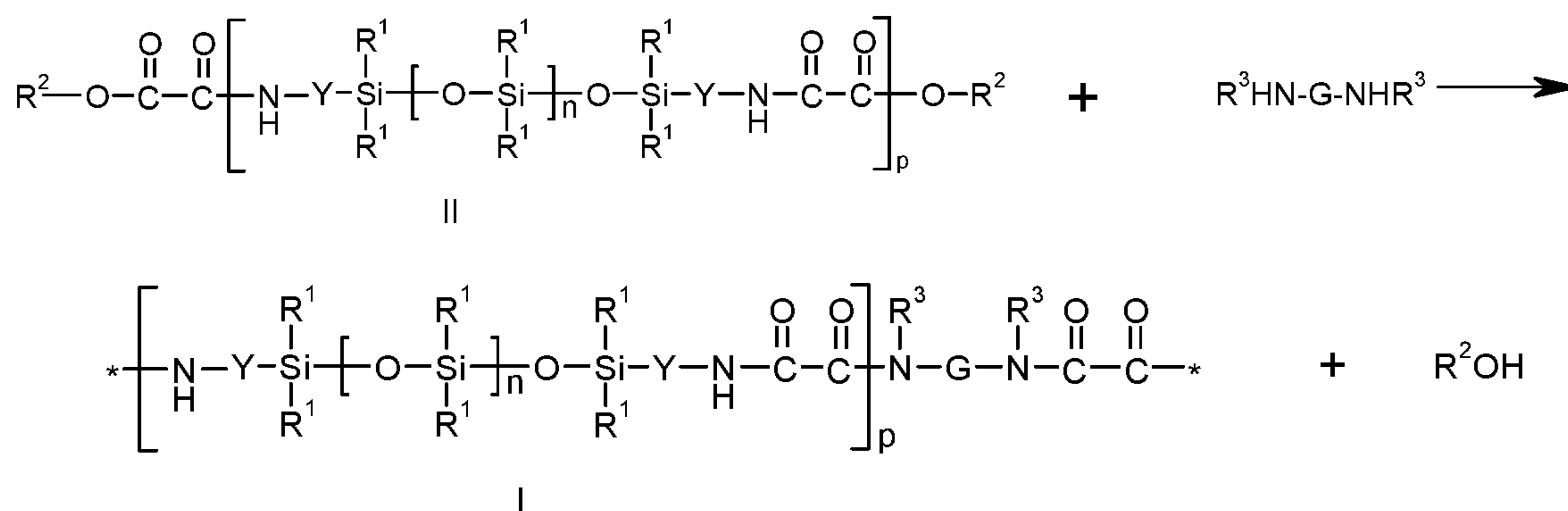
The copolymeric material of Formula I can be optically clear. As used herein, the term “optically clear” refers to a material that is clear to the human eye. An optically clear copolymeric material often has a luminous transmission of at least about 90 percent, a haze of less than about 2 percent, and opacity of less than about 1 percent in the 400 to 700 nm wavelength range. Both the luminous transmission and the haze can be determined using, for example, the method of ASTM-D 1003-95.

Additionally, the copolymeric material of Formula I can have a low refractive index. As used herein, the term “refractive index” refers to the absolute refractive index of a material (*e.g.*, copolymeric material or adhesive composition) and is the ratio of the speed of electromagnetic radiation in free space to the speed of the electromagnetic radiation in the material of interest. The electromagnetic radiation is white light. The index of refraction is measured using an Abbe refractometer, available commercially, for example, from Fisher Instruments of Pittsburgh, PA. The measurement of the refractive index can depend, to some extent, on the particular refractometer used. The copolymeric material usually has a refractive index in the range of about 1.41 to about 1.50.

The polydiorganosiloxane polyoxamides are soluble in many common organic solvents such as, for example, toluene, tetrahydrofuran, dichloromethane, aliphatic hydrocarbons (*e.g.*, alkanes such as hexane), or mixtures thereof.

The linear block copolymers having repeat units of Formula I can be prepared, for example, as represented in Reaction Scheme A.

Reaction Scheme A



5 In this reaction scheme, a precursor of Formula II is combined under reaction conditions with a diamine having two primary amino groups, two secondary amino groups, or one primary amino group and one secondary amino group. The diamine is usually of formula $\text{R}^3\text{HN-G-NHR}^3$. The R^2OH by-product is typically removed from the resulting polydiorganosiloxane polyoxamide.

10 The diamine $\text{R}^3\text{HN-G-NHR}^3$ in Reaction Scheme A has two amino groups (*i.e.*, -NHR^3). Group R^3 is hydrogen or alkyl (*e.g.*, an alkyl having 1 to 10, 1 to 6, or 1 to 4 carbon atoms) or R^3 taken together with G and with the nitrogen to which they are both attached forms a heterocyclic group (*e.g.*, the diamine is piperazine or the like). In most embodiments, R^3 is hydrogen or alkyl. In many embodiments, the diamine has two primary amino groups (*i.e.*, each R^3 group is hydrogen) and the diamine is of formula $\text{H}_2\text{N-G-NH}_2$. The portion of the diamine exclusive of the two amino groups is referred to as group G in Formula I.

15 The diamines are sometimes classified as organic diamines or polydiorganosiloxane diamines with the organic diamines including, for example, those selected from alkylene diamines, heteroalkylene diamines, arylene diamines, aralkylene diamines, or alkylene-aralkylene diamines. The diamine has only two amino groups so that the resulting polydiorganosiloxane polyoxamides are linear block copolymers that are often elastomeric, hot melt processible (*e.g.*, the copolymers can be processed at elevated temperatures such as up to 250 °C or higher without apparent degradation of the composition), and soluble in some common organic solvents. The diamine is free of a polyamine having more than two primary or secondary amino groups. Tertiary amines that do not react with the precursor of Formula II can be present. Additionally, the diamine is free of any carbonylamino group. That is, the diamine is not an amide.

25 Exemplary polyoxyalkylene diamines (*i.e.*, G is a heteroalkylene with the heteroatom being oxygen) include, but are not limited to, those commercially available from Huntsman, The Woodlands, TX under the trade designation JEFFAMINE D-230 (*i.e.*, polyoxypropylene diamine having an average molecular weight of about 230 g/mole), JEFFAMINE D-400 (*i.e.*, polyoxypropylene diamine having an average molecular weight of about 400 g/mole), JEFFAMINE D-2000 (*i.e.*, polyoxypropylene diamine having an average molecular weight of about 2,000 g/mole), JEFFAMINE HK-511 (*i.e.*, polyetherdiamine with both oxyethylene and oxypropylene groups and having an average molecular

weight of about 220 g/mole), JEFFAMINE ED-2003 (*i.e.*, polypropylene oxide capped polyethylene glycol with an average molecular weight of about 2,000 g/mole), and JEFFAMINE EDR-148 (*i.e.*, triethyleneglycol diamine).

Exemplary alkylene diamines (*i.e.*, G is a alkylene) include, but are not limited to, ethylene diamine, propylene diamine, butylene diamine, hexamethylene diamine, 2-methylpentamethylene 1,5-diamine (*i.e.*, commercially available from DuPont, Wilmington, DE under the trade designation DYTEK A), 1,3-pentane diamine (commercially available from DuPont under the trade designation DYTEK EP), 1,4-cyclohexane diamine, 1,2-cyclohexane diamine (commercially available from DuPont under the trade designation DHC-99), 4,4'-bis(aminocyclohexyl)methane, and 3-aminomethyl-3,5,5-trimethylcyclohexylamine.

Exemplary arylene diamines (*i.e.*, G is an arylene such as phenylene) include, but are not limited to, m-phenylene diamine, o-phenylene diamine, and p-phenylene diamine. Exemplary aralkylene diamines (*i.e.*, G is an aralkylene such as alkylene-phenyl) include, but are not limited to 4-aminomethyl-phenylamine, 3-aminomethyl-phenylamine, and 2-aminomethyl-phenylamine. Exemplary alkylene-aralkylene diamines (*i.e.*, G is an alkylene-aralkylene such as alkylene-phenylene-alkylene) include, but are not limited to, 4-aminomethyl-benzylamine, 3-aminomethyl-benzylamine, and 2-aminomethyl-benzylamine.

The precursor of Formula II in Reaction Scheme A has at least one polydiorganosiloxane segment and at least two oxalylamino groups. Group R¹, group Y, subscript n, and subscript p are the same as described for Formula I. Each group R² is independently an alkyl, haloalkyl, aryl, or aryl substituted with an alkyl, alkoxy, halo, or alkoxycarbonyl.

Suitable alkyl and haloalkyl groups for R² often have 1 to 10, 1 to 6, or 1 to 4 carbon atoms. Although tertiary alkyl (*e.g.*, tert-butyl) and haloalkyl groups can be used, there is often a primary or secondary carbon atom attached directly (*i.e.*, bonded) to the adjacent oxy group. Exemplary alkyl groups include methyl, ethyl, n-propyl, iso-propyl, n-butyl, and iso-butyl. Exemplary haloalkyl groups include chloroalkyl groups and fluoroalkyl groups in which some, but not all, of the hydrogen atoms on the corresponding alkyl group are replaced with halo atoms. For example, the chloroalkyl or a fluoroalkyl groups can be chloromethyl, 2-chloroethyl, 2,2,2-trichloroethyl, 3-chloropropyl, 4-chlorobutyl, fluoromethyl, 2-fluoroethyl, 2,2,2-trifluoroethyl, 3-fluoropropyl, 4-fluorobutyl, and the like. Suitable aryl groups for R² include those having 6 to 12 carbon atoms such as, for example, phenyl. An aryl group can be unsubstituted or substituted with an alkyl (*e.g.*, an alkyl having 1 to 4 carbon atoms such as methyl, ethyl, or n-propyl), an alkoxy (*e.g.*, an alkoxy having 1 to 4 carbon atoms such as methoxy, ethoxy, or propoxy), halo (*e.g.*, chloro, bromo, or fluoro), or alkoxycarbonyl (*e.g.*, an alkoxycarbonyl having 2 to 5 carbon atoms such as methoxycarbonyl, ethoxycarbonyl, or propoxycarbonyl).

The precursor of Formula II can include a single compound (*i.e.*, all the compounds have the same value of p and n) or can include a plurality of compounds (*i.e.*, the compounds have different values for p, different values for n, or different values for both p and n). Precursors with different n values have

siloxane chains of different length. Precursors having a p value of at least 2 are chain extended. Different amounts of the chain-extended precursor of Formula II in the mixture can affect the final properties of the elastomeric material of Formula I. That is, the amount of the second compound of Formula II (*i.e.*, p equal to at least 2) can be varied advantageously to provide elastomeric materials with a range of properties. For example, a higher amount of the second compound of Formula II can alter the melt rheology (*e.g.*, the elastomeric material can flow easier when molten), alter the softness of the elastomeric material, lower the modulus of the elastomeric material, or a combination thereof.

In some embodiments, the precursor is a mixture of a first compound of Formula II with subscript p equal to 1 and a second compound of Formula II with subscript p equal to at least 2. The first compound can include a plurality of different compounds with different values of n. The second compound can include a plurality of compounds with different values of p, different values of n, or different values of both p and n. Mixtures can include at least 50 weight percent of the first compound of Formula II (*i.e.*, p is equal to 1) and no greater than 50 weight percent of the second compound of Formula II (*i.e.*, p is equal to at least 2) based on the sum of the weight of the first and second compounds in the mixture. In some mixtures, the first compound is present in an amount of at least 55 weight percent, at least 60 weight percent, at least 65 weight percent, at least 70 weight percent, at least 75 weight percent, at least 80 weight percent, at least 85 weight percent, at least 90 weight percent, at least 95 weight percent, or at least 98 weight percent based on the total amount of the compounds of Formula II. The mixtures often contain no greater than 50 weight percent, no greater than 45 weight percent, no greater than 40 weight percent, no greater than 35 weight percent, no greater than 30 weight percent, no greater than 25 weight percent, no greater than 20 weight percent, no greater than 15 weight percent, no greater than 10 weight percent, no greater than 5 weight percent, or no greater than 2 weight percent of the second compound.

Reaction Scheme A can be conducted using a plurality of precursors of Formula II, a plurality of diamines, or a combination thereof. A plurality of precursors having different average molecular weights can be combined under reaction conditions with a single diamine or with multiple diamines. For example, the precursor of Formula II may include a mixture of materials with different values of n, different values of p, or different values of both n and p. The multiple diamines can include, for example, a first diamine that is an organic diamine and a second diamine that is a polydiorganosiloxane diamine. Likewise, a single precursor can be combined under reaction conditions with multiple diamines.

The molar ratio of the precursor of Formula II to the diamine is often about 1:1. For example the molar ratio is often less than or equal to 1: 0.90, less than or equal to 1: 0.92, less than or equal to 1: 0.95, less than or equal to 1: 0.98, or less than or equal to 1: 1. The molar ratio is often greater than or equal to 1: 1.02, greater than or equal to 1: 1.05, greater than or equal to 1: 1.08, or greater than or equal to 1: 1.10. For example, the molar ratio can be in the range of 1: 0.90 to 1: 1.10, in the range of 1: 0.92 to 1: 1.08, in the range of 1: 0.95 to 1: 1.05, or in the range of 1: 0.98 to 1: 1.02. Varying the molar ratio can be used, for example, to alter the overall molecular weight, which can affect the rheology of the resulting

copolymers. Additionally, varying the molar ratio can be used to provide oxalylamino-containing end groups or amino end groups, depending upon which reactant is present in molar excess.

The condensation reaction of the precursor of Formula II with the diamine (*i.e.*, Reaction Scheme A) are often conducted at room temperature or at elevated temperatures such as at temperatures up to about 250 °C. For example, the reaction often can be conducted at room temperature or at temperatures up to about 100 °C. In other examples, the reaction can be conducted at a temperature of at least 100 °C, at least 120 °C, or at least 150 °C. For example, the reaction temperature is often in the range of 100 °C to 220 °C, in the range of 120 °C to 220 °C, or in the range of 150 °C to 200 °C. The condensation reaction is often complete in less than 1 hour, in less than 2 hours, in less than 4 hours, in less than 8 hours, or in less than 12 hours.

Reaction Scheme A can occur in the presence or absence of a solvent. Suitable solvents usually do not react with any of the reactants or products of the reactions. Additionally, suitable solvents are usually capable of maintaining all the reactants and all of the products in solution throughout the polymerization process. Exemplary solvents include, but are not limited to, toluene, tetrahydrofuran, dichloromethane, aliphatic hydrocarbons (*e.g.*, alkanes such as hexane), or mixtures thereof.

Any solvent that is present can be stripped from the resulting polydiorganosiloxane polyoxamide at the completion of the reaction. Solvents that can be removed under the same conditions used to remove the alcohol by-product are often preferred. The stripping process is often conducted at a temperature of at least 100 °C, at least 125 °C, or at least 150 °C. The stripping process is typically at a temperature less than 300 °C, less than 250 °C, or less than 225 °C.

Conducting Reaction Scheme A in the absence of a solvent can be desirable because only the volatile by-product, R²OH, needs to be removed at the conclusion of the reaction. Additionally, a solvent that is not compatible with both reactants and the product can result in incomplete reaction and a low degree of polymerization.

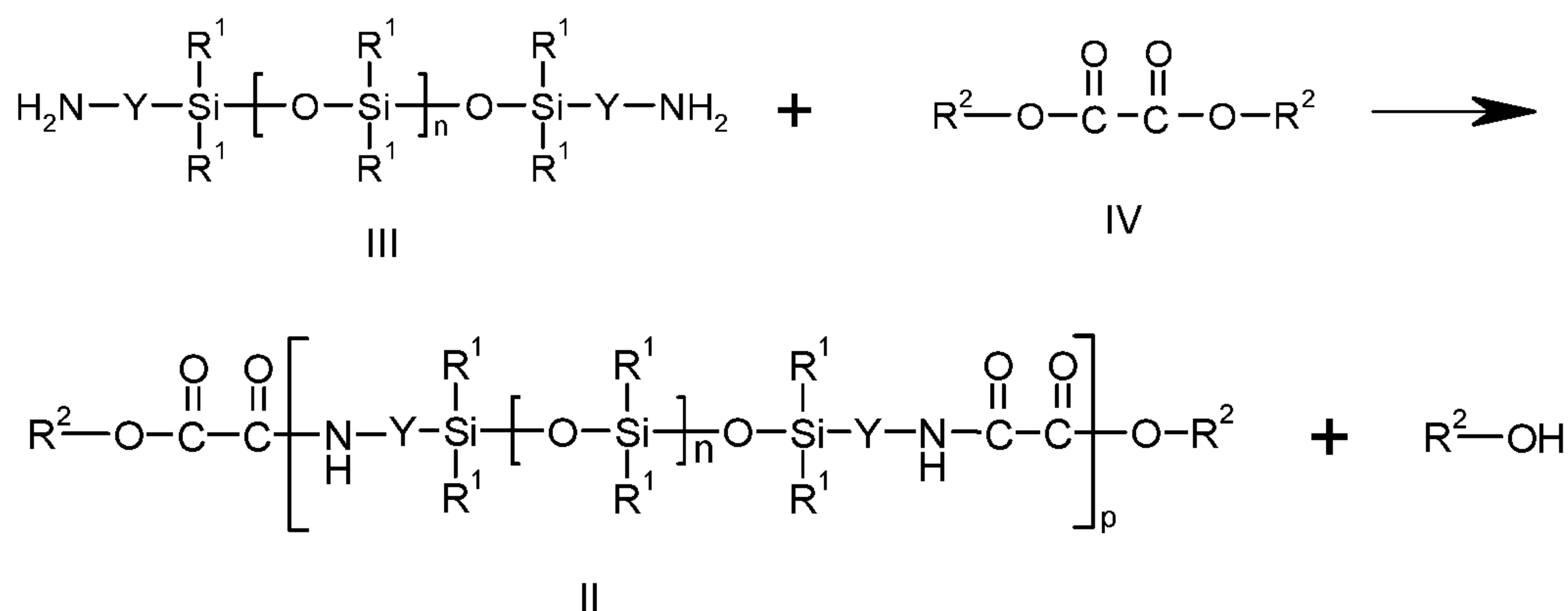
Any suitable reactor or process can be used to prepare the copolymeric material according to Reaction Scheme A. The reaction can be conducted using a batch process, semi-batch process, or a continuous process. Exemplary batch processes can be conducted in a reaction vessel equipped with a mechanical stirrer such as a Brabender mixer, provided the product of the reaction is in a molten state has a sufficiently low viscosity to be drained from the reactor. Exemplary semi-batch process can be conducted in a continuously stirred tube, tank, or fluidized bed. Exemplary continuous processes can be conducted in a single screw or twin screw extruder such as a wiped surface counter-rotating or co-rotating twin screw extruder.

In many processes, the components are metered and then mixed together to form a reaction mixture. The components can be metered volumetrically or gravimetrically using, for example, a gear, piston or progressing cavity pump. The components can be mixed using any known static or dynamic method such as, for example, static mixers, or compounding mixers such as single or multiple screw extruders. The reaction mixture can then be formed, poured, pumped, coated, injection molded, sprayed,

sputtered, atomized, stranded or sheeted, and partially or completely polymerized. The partially or completely polymerized material can then optionally be converted to a particle, droplet, pellet, sphere, strand, ribbon, rod, tube, film, sheet, coextruded film, web, non-woven, microreplicated structure, or other continuous or discrete shape, prior to the transformation to solid polymer. Any of these steps can be conducted in the presence or absence of applied heat. In one exemplary process, the components can be metered using a gear pump, mixed using a static mixer, and injected into a mold prior to solidification of the polymerizing material.

The polydiorganosiloxane-containing precursor of Formula II in Reaction Scheme A can be prepared by any known method. In some embodiments, this precursor is prepared according to Reaction Scheme B.

Reaction Scheme B

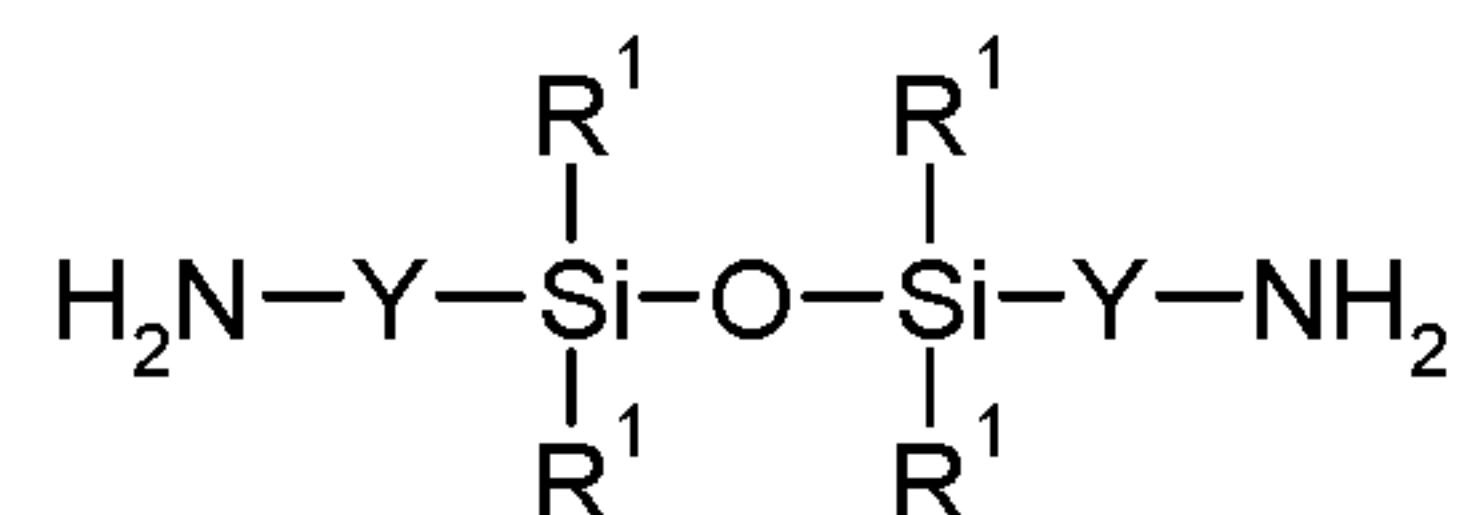


A polydiorganosiloxane diamine of Formula III (p moles) is reacted with a molar excess of an oxalate of Formula IV (greater than p + 1 moles) under an inert atmosphere to produce the polydiorganosiloxane-containing precursor of Formula II and R²-OH by-product. In this reaction, R¹, Y, n, and p are the same as previously described for Formula I. Each R² in Formula IV is independently an alkyl, haloalkyl, aryl, or aryl substituted with an alkyl, alkoxy, halo, or alkoxycarbonyl. The preparation of the precursor of Formula II according to Reaction Scheme B is further described in U.S. Publication No. 2007/0149745 (Leir et al.)

The polydiorganosiloxane diamine of Formula III in Reaction Scheme B can be prepared by any known method and can have any suitable molecular weight, such as an average molecular weight in the range of 700 to 150,000 g/mole. Suitable polydiorganosiloxane diamines and methods of making the polydiorganosiloxane diamines are described, for example, in U.S. Patent Nos. 3,890,269 (Martin), 4,661,577 (Jo Lane et al.), 5,026,890 (Webb et al.), 5,276,122 (Aoki et al.), 5,214,119 (Leir et al.), 5,461,134 (Leir et al.), 5,512,650 (Leir et al.), and 6,355,759 (Sherman et al.), incorporated herein by reference in their entirety. Some polydiorganosiloxane diamines are commercially available, for example, from Shin Etsu Silicones of America, Inc., Torrance, CA and from Gelest Inc., Morrisville, PA.

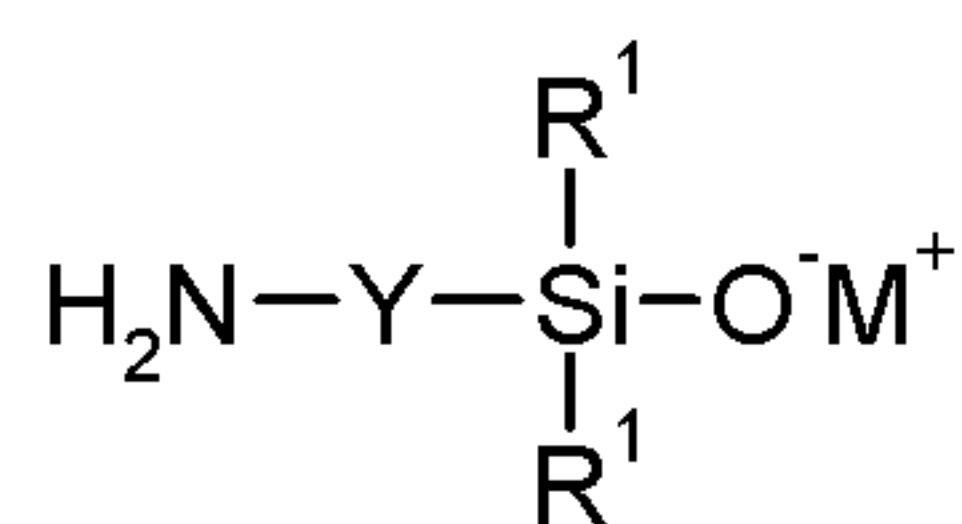
A polydiorganosiloxane diamine having a molecular weight greater than 2,000 g/mole or greater than 5,000 g/mole can be prepared using the methods described in U.S. Patent Nos. 5,214,119 (Leir et

al.), 5,461,134 (Leir et al.), and 5,512,650 (Leir et al.). One of the described methods involves combining under reaction conditions and under an inert atmosphere (a) an amine functional end blocker of the following formula



V

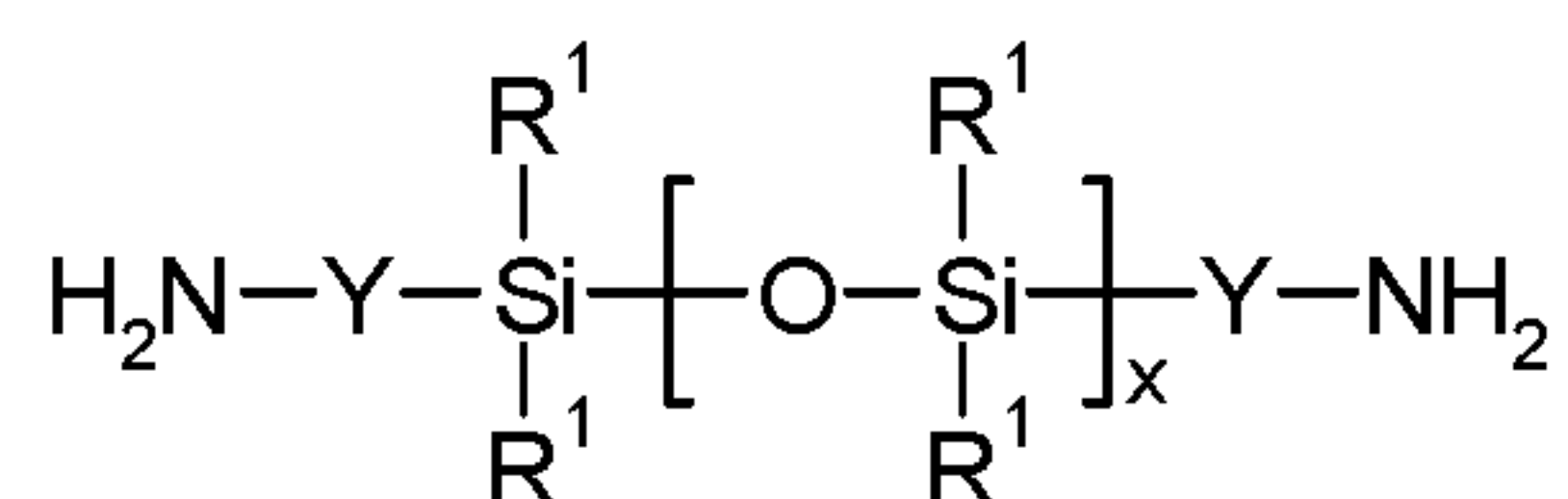
where Y and R¹ are the same as defined for Formula I; (b) sufficient cyclic siloxane to react with the amine functional end blocker to form a polydiorganosiloxane diamine having a molecular weight less than 2,000 g/mole; and (c) an anhydrous aminoalkyl silanolate catalyst of the following formula



VI

where Y and R¹ are the same as defined in Formula I and M⁺ is a sodium ion, potassium ion, cesium ion, rubidium ion, or tetramethylammonium ion. The reaction is continued until substantially all of the amine functional end blocker is consumed and then additional cyclic siloxane is added to increase the molecular weight. The additional cyclic siloxane is often added slowly (*e.g.*, drop wise). The reaction temperature is often conducted in the range of 80 °C to 90 °C with a reaction time of 5 to 7 hours. The resulting polydiorganosiloxane diamine can be of high purity (*e.g.*, less than 2 weight percent, less than 1.5 weight percent, less than 1 weight percent, less than 0.5 weight percent, less than 0.1 weight percent, less than 0.05 weight percent, or less than 0.01 weight percent silanol impurities). Altering the ratio of the amine end functional blocker to the cyclic siloxane can be used to vary the molecular weight of the resulting polydiorganosiloxane diamine of Formula III.

Another method of preparing the polydiorganosiloxane diamine of Formula III includes combining under reaction conditions and under an inert environment (a) an amine functional end blocker of the following formula

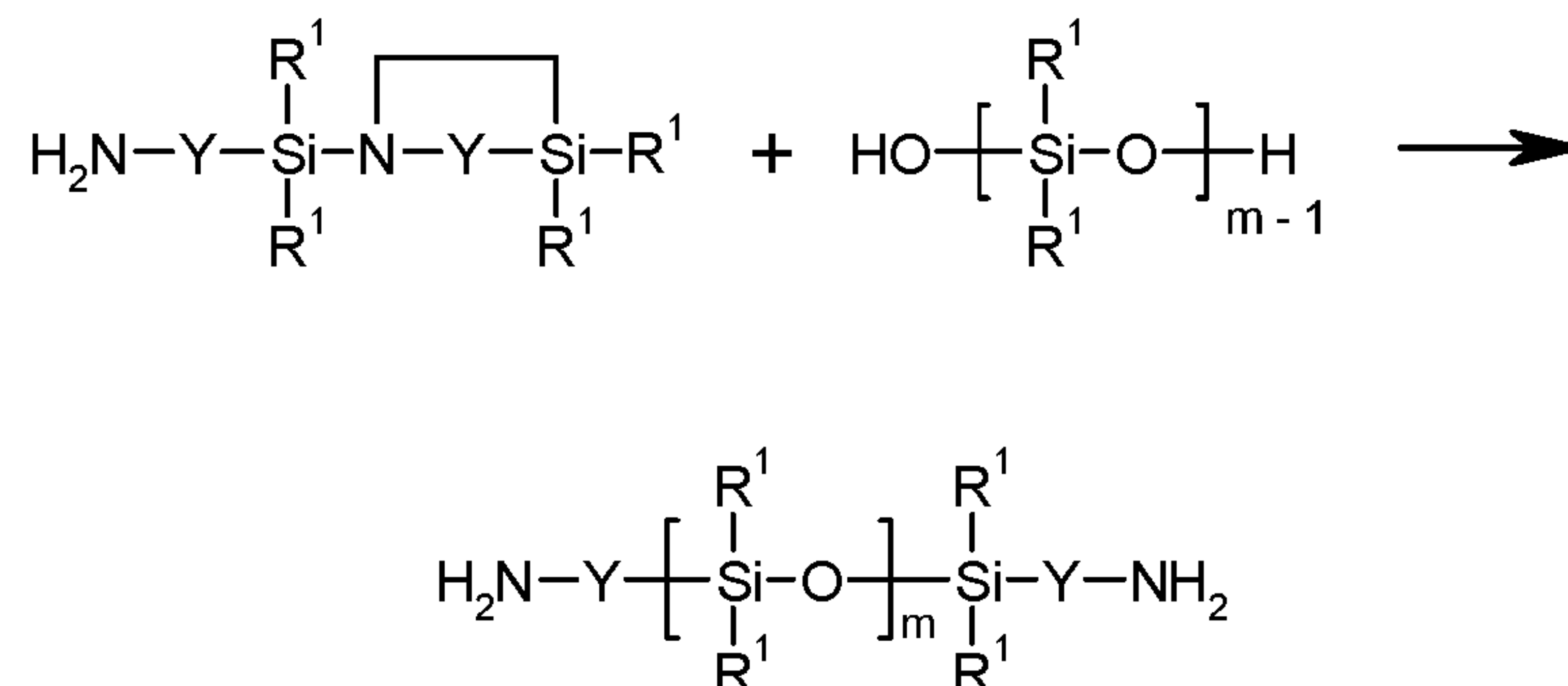


VII

where R¹ and Y are the same as described for Formula I and where the subscript x is equal to an integer of 1 to 150; (b) sufficient cyclic siloxane to obtain a polydiorganosiloxane diamine having an average molecular weight greater than the average molecular weight of the amine functional end blocker; and (c) a catalyst selected from cesium hydroxide, cesium silanolate, rubidium silanolate, cesium polysiloxanolate,

rubidium polysiloxanolate, and mixtures thereof. The reaction is continued until substantially all of the amine functional end blocker is consumed. This method is further described in U.S. Patent No. 6,355,759 B1 (Sherman et al.). This procedure can be used to prepare any molecular weight of the polydiorganosiloxane diamine.

Yet another method of preparing the polydiorganosiloxane diamine of Formula III is described in U.S. Patent No. 6,531,620 B2 (Brader et al.). In this method, a cyclic silazane is reacted with a siloxane material having hydroxy end groups as shown in the following reaction.



The groups R^1 and Y are the same as described for Formula I. The subscript m is an integer greater than 1.

In Reaction Scheme B, an oxalate of Formula IV is reacted with the polydiorganosiloxane diamine of Formula III under an inert atmosphere. The two R^2 groups in the oxalate of Formula IV can be the same or different. In some methods, the two R^2 groups are different and have different reactivity with the polydiorganosiloxane diamine of Formula III in Reaction Scheme B.

The oxalates of Formula IV in Reaction Scheme B can be prepared, for example, by reaction of an alcohol of formula $\text{R}^2\text{-OH}$ with oxalyl dichloride. Commercially available oxalates of Formula IV (*e.g.*, from Sigma-Aldrich, Milwaukee, WI and from VWR International, Bristol, CT) include, but are not limited to, dimethyl oxalate, diethyl oxalate, di-n-butyl oxalate, di-tert-butyl oxalate, bis(phenyl) oxalate, bis(pentafluorophenyl) oxalate, 1-(2,6-difluorophenyl)-2-(2,3,4,5,6-pentachlorophenyl) oxalate, and bis(2,4,6-trichlorophenyl) oxalate.

A molar excess of the oxalate is used in Reaction Scheme B. That is, the molar ratio of oxalate to polydiorganosiloxane diamine is greater than the stoichiometric molar ratio, which is $(p + 1): p$. The molar ratio is often greater than 2:1, greater than 3:1, greater than 4:1, or greater than 6:1. The condensation reaction typically occurs under an inert atmosphere and at room temperature upon mixing of the components.

The condensation reaction used to produce the precursor of Formula II (*i.e.*, Reaction Scheme B) can occur in the presence or absence of a solvent. In some methods, no solvent or only a small amount of solvent is included in the reaction mixture. In other methods, a solvent may be included such as, for example, toluene, tetrahydrofuran, dichloromethane, or aliphatic hydrocarbons (*e.g.*, alkanes such as hexane).

Removal of excess oxalate from the precursor of Formula II prior to reaction with the diamine in Reaction Scheme A tends to favor formation of an optically clear polydiorganosiloxane polyoxamide. The excess oxalate can typically be removed from the precursor using a stripping process. For example, the reacted mixture (*i.e.*, the product or products of the condensation reaction according to Reaction Scheme B) can be heated to a temperature up to 150 °C, up to 175 °C, up to 200 °C, up to 225 °C, or up to 250 °C to volatilize the excess oxalate. A vacuum can be pulled to lower the temperature that is needed for removal of the excess oxalate. The precursor compounds of Formula II tend to undergo minimal or no apparent degradation at temperatures in the range of 200 °C to 250 °C or higher. Any other known methods of removing the excess oxalate can be used.

The by-product of the condensation reaction shown in Reaction Scheme B is an alcohol (*i.e.*, R²-OH is an alcohol). Group R² is often limited to an alkyl having 1 to 4 carbon atoms, a haloalkyl having 1 to 4 carbon atoms, or an aryl such as phenyl that form an alcohol that can be readily removed (*e.g.*, vaporized) by heating at temperatures no greater than about 250 °C. Such an alcohol can be removed when the reacted mixture is heated to a temperature sufficient to remove the excess oxalate of Formula IV.

Either pressure sensitive adhesives or heat activated adhesives can be formulated by combining the polydiorganosiloxane polyoxamides with a silicate tackifying resin. As used herein, the term “pressure sensitive adhesive” refers to an adhesive that possesses the following properties: (1) aggressive and permanent tack; (2) adherence to a substrate with no more than finger pressure; (3) sufficient ability to hold onto an adherend; and (4) sufficient cohesive strength to be removed cleanly from the adherend. As used herein, the term “heat activated adhesive” refers to an adhesive composition that is essentially non-tacky at room temperature but that becomes tacky above room temperature above an activation temperature such as above about 30 °C. Heat activated adhesives typically have the properties of a pressure sensitive adhesive above the activation temperature.

Tackifying resins such as silicate tackifying resins are added to the polydiorganosiloxane polyoxamide copolymer to provide or enhance the adhesive properties of the copolymer. The silicate tackifying resin can influence the physical properties of the resulting adhesive composition. For example, as silicate tackifying resin content is increased, the glassy to rubbery transition of the adhesive composition occurs at increasingly higher temperatures. In some exemplary adhesive compositions, a plurality of silicate tackifying resins can be used to achieve desired performance.

Suitable silicate tackifying resins include those resins composed of the following structural units M (*i.e.*, monovalent R'₃SiO_{1/2} units), D (*i.e.*, divalent R'₂SiO_{2/2} units), T (*i.e.*, trivalent R'SiO_{3/2} units), and Q (*i.e.*, quaternary SiO_{4/2} units), and combinations thereof. Typical exemplary silicate resins include MQ silicate tackifying resins, MQD silicate tackifying resins, and MQT silicate tackifying resins. These silicate tackifying resins usually have a number average molecular weight in the range of 100 to 50,000 or in the range of 500 to 15,000 and generally have methyl R' groups.

MQ silicate tackifying resins are copolymeric resins having $R'_3SiO_{1/2}$ units ("M" units) and $SiO_{4/2}$ units ("Q" units), where the M units are bonded to the Q units, each of which is bonded to at least one other Q unit. Some of the $SiO_{4/2}$ units ("Q" units) are bonded to hydroxyl radicals resulting in $HOSiO_{3/2}$ units (" T^{OH} " units), thereby accounting for the silicon-bonded hydroxyl content of the silicate tackifying resin, and some are bonded only to other $SiO_{4/2}$ units.

Such resins are described in, for example, *Encyclopedia of Polymer Science and Engineering*, vol. 15, John Wiley & Sons, New York, (1989), pp. 265-270, and U.S. Pat. Nos. 2,676,182 (Daudt et al.), 3,627,851 (Brady), 3,772,247 (Flannigan), and 5,248,739 (Schmidt et al.). Other examples are disclosed in U.S. Pat. No. 5,082,706 (Tangney). The above-described resins are generally prepared in solvent.

Dried or solventless, M silicone tackifying resins can be prepared, as described in U.S. Pat. Nos. 5,319,040 (Wengrovius et al.), 5,302,685 (Tsumura et al.), and 4,935,484 (Wolfgruber et al.).

Certain MQ silicate tackifying resins can be prepared by the silica hydrosol capping process described in U.S. Pat. No. 2,676,182 (Daudt et al.) as modified according to U.S. Pat. No. 3,627,851 (Brady), and U.S. Pat. No. 3,772,247 (Flannigan). These modified processes often include limiting the concentration of the sodium silicate solution, and/or the silicon-to-sodium ratio in the sodium silicate, and/or the time before capping the neutralized sodium silicate solution to generally lower values than those disclosed by Daudt et al. The neutralized silica hydrosol is often stabilized with an alcohol, such as 2-propanol, and capped with $R_3SiO_{1/2}$ siloxane units as soon as possible after being neutralized. The level of silicon bonded hydroxyl groups (*i.e.*, silanol) on the MQ resin may be reduced to no greater than 1.5 weight percent, no greater than 1.2 weight percent, no greater than 1.0 weight percent, or no greater than 0.8 weight percent based on the weight of the silicate tackifying resin. This may be accomplished, for example, by reacting hexamethyldisilazane with the silicate tackifying resin. Such a reaction may be catalyzed, for example, with trifluoroacetic acid. Alternatively, trimethylchlorosilane or trimethylsilylacetamide may be reacted with the silicate tackifying resin, a catalyst not being necessary in this case.

MQD silicone tackifying resins are terpolymers having $R'_3SiO_{1/2}$ units ("M" units), $SiO_{4/2}$ units ("Q" units), and $R'_2SiO_{2/2}$ units ("D" units) such as are taught in U.S. Pat. No. 2,736,721 (Dexter). In MQD silicone tackifying resins, some of the methyl R' groups of the $R'_2SiO_{2/2}$ units ("D" units) can be replaced with vinyl ($CH_2=CH-$) groups (" D^{Vi} " units).

MQT silicate tackifying resins are terpolymers having $R'_3SiO_{1/2}$ units, $SiO_{4/2}$ units and $R'SiO_{3/2}$ units ("T" units) such as are taught in U.S. Pat. No. 5,110,890 (Butler) and Japanese Kokai HE 2-36234.

Suitable silicate tackifying resins are commercially available from sources such as Dow Corning, Midland, MI, General Electric Silicones Waterford, NY and Rhodia Silicones, Rock Hill, SC. Examples of particularly useful MQ silicate tackifying resins include those available under the trade designations SR-545 and SR-1000, both of which are commercially available from GE Silicones, Waterford, NY. Such resins are generally supplied in organic solvent and may be employed in the formulations of the

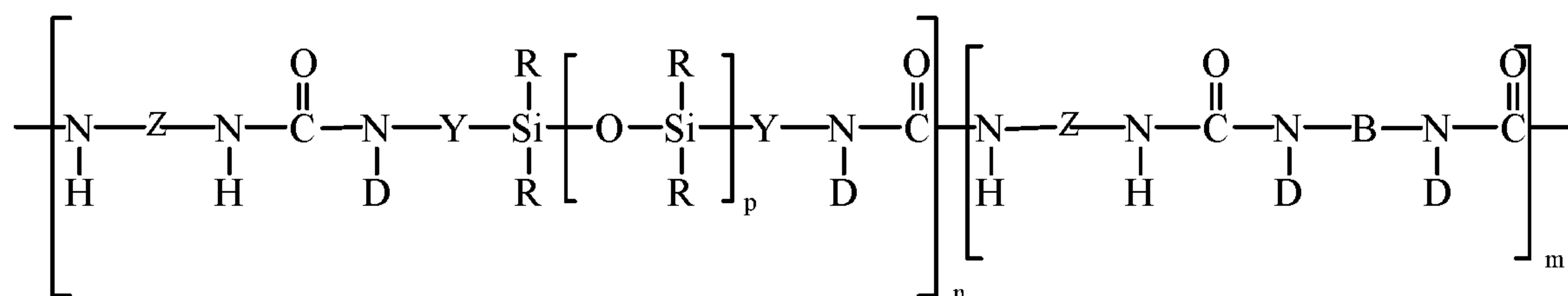
adhesives of the present disclosure as received. Blends of two or more silicate resins can be included in the adhesive compositions.

The adhesive compositions typically contain 20 to 80 weight percent polydiorganosiloxane polyoxamide and about 0.1 weight percent to about 20 weight percent silicate tackifying resin based on the combined weight of polydiorganosiloxane polyoxamide and silicate tackifying resin. For example, the adhesive compositions can contain 30 to 70 weight percent polydiorganosiloxane polyoxamide and about 1 to about 15 weight percent silicate tackifying resin, 35 to 65 weight percent polydiorganosiloxane polyoxamide and about 5 to about 10 weight percent silicate tackifying resin, or 40 to 60 weight percent polydiorganosiloxane polyoxamide and about 6 to about 8 weight percent silicate tackifying resin.

The adhesive composition can be solvent-free or can contain a solvent. Suitable solvents include, but are not limited to, toluene, tetrahydrofuran, dichloromethane, aliphatic hydrocarbons (*e.g.*, alkanes such as hexane), or mixtures thereof.

The adhesive compositions can further include other additives to provide desired properties. For example, dyes and pigments can be added as colorant; electrically and/or thermally conductive compounds can be added to make the adhesive electrically and/or thermally conductive or antistatic; antioxidants and antimicrobial agents can be added; and ultraviolet light stabilizers and absorbers, such as hindered amine light stabilizers (HALS), can be added to stabilize the adhesive against ultraviolet degradation and to block certain ultraviolet wavelengths from passing through the article. Other additives include, but are not limited to, adhesion promoters, fillers (*e.g.*, fumed silica, carbon fibers, carbon black, glass beads, glass and ceramic bubbles, glass fibers, mineral fibers, clay particles, organic fibers such as nylon, metal particles, or unexpanded polymeric microspheres), tack enhancers, blowing agents, hydrocarbon plasticizers, and flame-retardants.

Another example of a useful class of silicone polymers is silicone polyurea block copolymers. Silicone polyurea block copolymers include the reaction product of a polydiorganosiloxane diamine (also referred to as silicone diamine), a diisocyanate, and optionally an organic polyamine. Suitable silicone polyurea block copolymers are represented by the repeating unit shown and described in International Publication No. WO2016106040 (Sherman et al.):



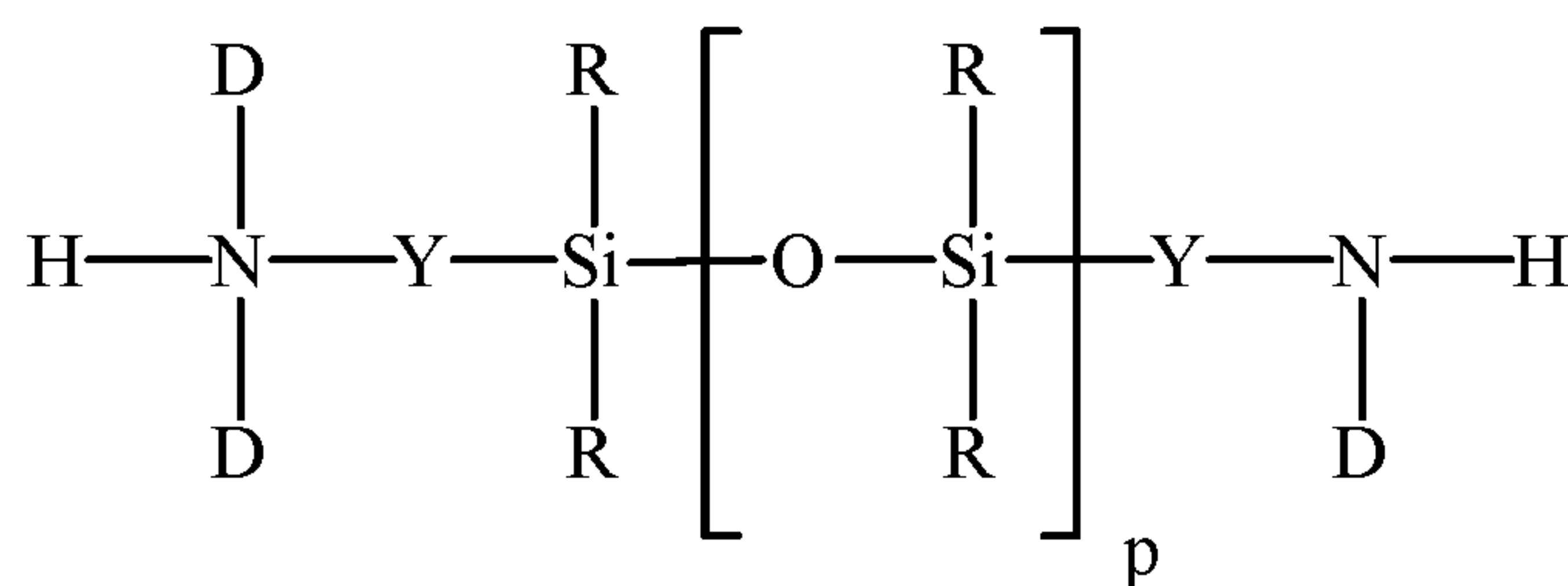
VIII

wherein each R is a moiety that, independently, is an alkyl moiety, preferably having about 1 to 12 carbon atoms, and may be substituted with, for example, trifluoroalkyl or vinyl groups, a vinyl radical or higher alkenyl radical preferably represented by the formula $\text{R}^2 (\text{CH}_2)_b -$ or $-(\text{CH}_2)_c \text{CH}=\text{CH}_2$ wherein R^2 is $-(\text{CH}_2)_b -$ or $-(\text{CH}_2)_c \text{CH}----$ and a is 1, 2 or 3; b is 0, 3 or 6; and c is 3, 4 or 5, a cycloalkyl moiety having

from about 6 to 12 carbon atoms and may be substituted with alkyl, fluoroalkyl, and vinyl groups, or an aryl moiety preferably having from about 6 to 20 carbon atoms and may be substituted with, for example, alkyl, cycloalkyl, fluoroalkyl and vinyl groups or R is a perfluoroalkyl group as described in U.S. Pat. No. 5,028,679 (Terae et al.), and incorporated herein, or a fluorine-containing group, as described in U.S. Pat. No. 5,236,997 (Fujiki) and incorporated herein, or a perfluoroether-containing group, as described in U.S. Pat. Nos. 4,900,474 (Terae et al.) and 5,118,775 (Inomata et al.) and incorporated herein; preferably at least 50% of the R moieties are methyl radicals with the balance being monovalent alkyl or substituted alkyl radicals having from 1 to 12 carbon atoms, alkenylene radicals, phenyl radicals, or substituted phenyl radicals; each Z is a polyvalent radical that is an arylene radical or an aralkylene radical preferably having from about 6 to 20 carbon atoms, an alkylene or cycloalkylene radical preferably having from about 6 to 20 carbon atoms, preferably Z is 2,6-tolylene, 4,4'-methylenediphenylene, 3,3'-dimethoxy-4,4'-biphenylene, tetramethyl-m-xylylene, 4,4'-methylenedicyclohexylene, 3,5,5-trimethyl-3-methylenecyclohexylene, 1,6-hexamethylene, 1,4-cyclohexylene, 2,2,4-trimethylhexylene and mixtures thereof; each Y is a polyvalent radical that independently is an alkylene radical of 1 to 10 carbon atoms, an aralkylene radical or an arylene radical preferably having 6 to 20 carbon atoms; each D is selected from the group consisting of hydrogen, an alkyl radical of 1 to 10 carbon atoms, phenyl, and a radical that completes a ring structure including B or Y to form a heterocycle; where B is a polyvalent radical selected from the group consisting of alkylene, aralkylene, cycloalkylene, phenylene, polyalkylene oxide, including for example, polyethylene oxide, polypropylene oxide, polytetramethylene oxide, and copolymers and mixtures thereof; m is a number that is 0 to about 1000; n is a number that is at least 1; and p is a number that is at least 10, preferably about 15 to about 2000, more preferably 30 to 1500.

Useful silicone polyurea block copolymers are disclosed in, *e.g.*, U.S. Pat. Nos. 5,512,650, 5,214,119, and 5,461,134, WO 96/35458, WO 98/17726, WO 96/34028, WO 96/34030 and WO 97/40103, each incorporated herein.

Examples of useful silicone diamines used in the preparation of silicone polyurea block copolymers include polydiorganosiloxane diamines represented by the formula shown and described in US Patent No. 8,334,037 (Sheridan et al.):



IX

wherein each of R, Y, D, and p are defined as above. Preferably the number average molecular weight of the polydiorganosiloxane diamines is greater than about 700.

Useful polydiorganosiloxane diamines include any polydiorganosiloxane diamines that fall within Formula IX above and include those polydiorganosiloxane diamines having molecular weights in the range of about 700 to 150,000, preferably from about 10,000 to about 60,000, more preferably from about 25,000 to about 50,000. Suitable polydiorganosiloxane diamines and methods of manufacturing
5 polydiorganosiloxane diamines are disclosed in, *e.g.*, U.S. Pat. Nos. 3,890,269, 4,661,577, 5,026,890, and 5,276,122, International Patent Publication Nos. WO 95/03354 and WO 96/35458, each of which is incorporated herein by reference.

Examples of useful polydiorganosiloxane diamines include polydimethylsiloxane diamine, polydiphenylsiloxane diamine, polytrifluoropropylmethylsiloxane diamine, polyphenylmethylsiloxane
10 diamine, polydiethylsiloxane diamine, polydivinylsiloxane diamine, polyvinylmethylsiloxane diamine, poly(5-hexenyl)methylsiloxane diamine, and mixtures and copolymers thereof.

Suitable polydiorganosiloxane diamines are commercially available from, for example, Shin Etsu Silicones of America, Inc., Torrance, Calif., and Huls America, Inc. Preferably the polydiorganosiloxane diamines are substantially pure and prepared as disclosed in U.S. Pat. No. 5,214,119 and incorporated
15 herein. Polydiorganosiloxane diamines having such high purity are prepared from the reaction of cyclic organosilanes and bis(aminoalkyl)disiloxanes utilizing an anhydrous amino alkyl functional silanolate catalyst such as tetramethylammonium-3-aminopropyldimethyl silanolate, preferably in an amount less than 0.15% by weight based on the weight of the total amount of cyclic organosiloxane with the reaction run in two stages. Particularly preferred polydiorganosiloxane diamines are prepared using cesium and
20 rubidium catalysts and are disclosed in U.S. Pat. No. 5,512,650 and incorporated herein.

The polydiorganosiloxane diamine component provides a means of adjusting the modulus of the resultant silicone polyurea block copolymer. In general, high molecular weight polydiorganosiloxane diamines provide copolymers of lower modulus whereas low molecular polydiorganosiloxane polyamines provide copolymers of higher modulus.

Examples of useful polyamines include polyoxyalkylene diamines including, *e.g.*,
25 polyoxyalkylene diamines commercially available under the trade designation D-230, D-400, D-2000, D-4000, ED-2001 and EDR-148 from Hunstman Corporation (Houston, Tex.), polyoxyalkylene triamines including, *e.g.*, polyoxyalkylene triamines commercially available under the trade designations T-403, T-3000 and T-5000 from Hunstman, and polyalkylenes including, *e.g.*, ethylene diamine and polyalkylenes
30 available under the trade designations Dytek A and Dytek EP from DuPont (Wilmington, Del.).

The optional polyamine provides a means of modifying the modulus of the copolymer. The concentration, type and molecular weight of the organic polyamine influence the modulus of the silicone polyurea block copolymer.

The silicone polyurea block copolymer preferably includes polyamine in an amount of no greater
35 than about 3 moles, more preferably from about 0.25 to about 2 moles. Preferably the polyamine has a molecular weight of no greater than about 300 g/mole.

Any polyisocyanate including, *e.g.*, diisocyanates and triisocyanates, capable of reacting with the above-described polyamines can be used in the preparation of the silicone polyurea block copolymer. Examples of suitable diisocyanates include aromatic diisocyanates, such as 2,6-toluene diisocyanate, 2,5-toluene diisocyanate, 2,4-toluene diisocyanate, m-phenylene diisocyanate, p-phenylene diisocyanate, methylene bis(o-chlorophenyl diisocyanate), methylenediphenylene-4,4'-diisocyanate, polycarbodiimide-modified methylenediphenylene diisocyanate, (4,4'-diisocyanato-3,3',5,5'-tetraethyl) diphenylmethane, 4,4'-diisocyanato-3,3'-dimethoxybiphenyl (o-dianisidine diisocyanate), 5-chloro-2,4-toluene diisocyanate, and 1-chloromethyl-2,4-diisocyanato benzene, aromatic-aliphatic diisocyanates, such as m-xylylene diisocyanate and tetramethyl-m-xylylene diisocyanate, aliphatic diisocyanates such as 1,4-diisocyanatobutane, 1,6-diisocyanatohexane, 1,12-diisocyanatododecane and 2-methyl-1,5-diisocyanatopentane, and cycloaliphatic diisocyanates such as methylenedicyclohexylene-4,4'-diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate) and cyclohexylene-1,4-diisocyanate.

Any triisocyanate that can react with a polyamine, and in particular with the polydiorganosiloxane diamine is suitable. Examples of such triisocyanates include, *e.g.*, polyfunctional isocyanates, such as those produced from biurets, isocyanurates, and adducts. Examples of commercially available polyisocyanates include portions of the series of polyisocyanates available under the trade designations DESMODUR and MONDUR from Bayer and PAPI from Dow Plastics.

The polyisocyanate is preferably present in a stoichiometric amount based on the amount of polydiorganosiloxane diamine and optional polyamine.

The silicone polyurea block copolymer can be prepared by solvent-based processes, solventless processes or a combination thereof. Useful solvent-based processes are described in, *e.g.*, Tyagi et al., "Segmented Organosiloxane Copolymers: 2. Thermal and Mechanical Properties of Siloxane-Urea Copolymers," Polymer, vol. 25, December, 1984, and U.S. Pat. No. 5,214,119 (Leir et al.), and incorporated herein by reference. Useful methods of manufacturing silicone polyurea block copolymers are also described in, *e.g.*, U.S. Pat. Nos. 5,512,650, 5,214,119, and 5,461,134, WO 96/35458, WO 98/17726, WO 96/34028, and WO 97/40103, and incorporated herein.

Silicone polyurea block copolymer-based pressure sensitive adhesive compositions can also be prepared by solvent-based processes, solventless processes or a combination thereof.

In solvent-based processes, the MQ silicone resin can be introduced before, during or after the polyamines and polyisocyanates have been introduced into the reaction mixture. The reaction of the polyamines and the polyisocyanate is carried out in a solvent or a mixture of solvents. The solvents are preferably nonreactive with the polyamines and polyisocyanates. The starting materials and final products preferably remain completely miscible in the solvents during and after the completion of the polymerization. These reactions can be conducted at room temperature or up to the boiling point of the reaction solvent. The reaction is preferably carried out at ambient temperature up to 50° C.

In substantially solventless processes, the polyamines and the polyisocyanate and the MQ silicone resin are mixed in a reactor and the reactants are allowed to react to form the silicone polyurea block copolymer, which, with the MQ resin, forms the pressure sensitive adhesive composition.

One useful method that includes a combination of a solvent-based process and a solventless process includes preparing the silicone polyurea block copolymer using a solventless process and then mixing silicone polyurea block copolymer with the MQ resin solution in a solvent. Preferably the silicone polyurea block copolymer-based pressure sensitive adhesive composition prepared according to the above-described combination method to produce a blend of silicone polyurea block copolymer and MQ resin.

Adhesive articles and methods of making adhesive articles

An adhesive article is provided that includes a substrate and an adhesive layer adjacent to at least one surface of the substrate. Some embodiments of the adhesive composition include at least one of a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%. The substrates can include a single layer of material or can be a combination of two or more materials.

The substrates can have any useful form including, but not limited to, films, sheets, membranes, filters, nonwoven or woven fibers, hollow or solid beads, bottles, plates, tubes, rods, pipes, or wafers.

The substrates can be porous or non-porous, rigid or flexible, transparent or opaque, clear or colored, and reflective or non-reflective. The substrates can have a flat or relatively flat surface or can have a texture such as wells, indentations, channels, bumps, or the like. The substrates can have a single layer or multiple layers of material. Suitable substrate materials include, for example, polymeric materials, glasses, ceramics, sapphire, metals, metal oxides, hydrated metal oxides, or combinations thereof.

Suitable polymeric substrate materials include, but are not limited to, polyolefins (*e.g.*, polyethylene such as biaxially oriented polyethylene or high density polyethylene and polypropylene such as biaxially oriented polypropylene), polystyrenes, polyacrylates, polymethacrylates, polyacrylonitriles, polyvinyl acetates, polyvinyl alcohols, polyvinyl chlorides, polyoxymethylenes, polyesters such as polyethylene terephthalate (PET), polytetrafluoroethylene, ethylene-vinyl acetate copolymers, polycarbonates, polyamides, rayon, polyimides, polyurethanes, phenolics, polyamines, amino-epoxy resins, polyesters, silicones, cellulose based polymers, polysaccharides, nylon, neoprene rubber, or combinations thereof. Some polymeric materials are foams, woven fibers, non-woven fibers, or films.

Suitable glass and ceramic substrate materials can include, for example, silicon, aluminum, lead, boron, phosphorous, zirconium, magnesium, calcium, arsenic, gallium, titanium, copper, or combinations thereof. Glasses typically include various types of silicate containing materials.

Some substrates are release liners. The adhesive layer can be applied to a release liner and then transferred to another substrate such as a backing film or foam substrate. Suitable release liners typically

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contain a polymer such as polyester or polyolefin or a coated paper. Some adhesive articles transfer tape that contains an adhesive layer positioned between two release liners. Exemplary release liners include, but are not limited to, polyethylene terephthalate coated with a fluorosilicone such as that disclosed in U.S. Pat. No. 5,082,706 (Tangney) and commercially available from Loparex, Inc., Bedford Park, IL.

5 The liner can have a microstructure on its surface that is imparted to the adhesive to form a microstructure on the surface of the adhesive layer. The liner can be removed to provide an adhesive layer having a microstructured surface.

In some embodiments, the adhesive article is a single sided adhesive tape in which the adhesive layer is on a single major surface of a substrate such as a foam or film. In other embodiments, the
10 adhesive article is a double-sided adhesive tape in which the adhesive layer is on two major surfaces of a substrate such as a foam or film. The two adhesive layers of the double-sided adhesive tape can be the same or different. For example, one adhesive can be a pressure sensitive adhesive and the other a heat activated adhesive where at least one of the adhesives is based on the polydiorganosiloxane polyoxamide or silicone polyurea block copolymer. Each exposed adhesive layer can be applied to another substrate.

15 The adhesive articles can contain additional layers such as primers, barrier coatings, metal and/or reflective layers, tie layers, and combinations thereof. The additional layers can be positioned between the substrate and the adhesive layer, adjacent the substrate opposite the adhesive layer, or adjacent to the adhesive layer opposite the substrate.

A method of making an adhesive article typically includes providing a substrate and applying an
20 adhesive composition to at least one surface of the substrate. The adhesive composition includes at least one of The adhesive composition can be applied to the substrate by a wide range of processes such as, for example, solution coating, solution spraying, hot melt coating, extrusion, coextrusion, lamination, and pattern coating. The adhesive composition is often applied as an adhesive layer to a surface of substrate with a coating weight of 0.02 grams/154.8 cm² to 2.4 grams/154.8 cm².

25 The adhesive articles of the disclosure may be exposed to post processing steps such as curing, crosslinking, die cutting, heating to cause expansion of the article, *e.g.*, foam-in-place, and the like.

The foregoing describes the disclosure in terms of embodiments foreseen by the inventor for which an enabling description was available, notwithstanding that insubstantial modifications of the disclosure, not presently foreseen, may nonetheless represent equivalents thereto.

EXAMPLES

30 These examples are merely for illustrative purposes only and are not meant to be limiting on the scope of the appended claims. All parts, percentages, ratios, etc. in the examples and the rest of the specification are by weight, unless noted otherwise.

Test Methods90° Peel Adhesion Strength Test

5 The peel adhesion strength and removability were evaluated by the following method. Test strips were applied to adherends by rolling down with a 15 lb. roller. Adhered samples were aged at 72° F (22°C), 50% relative humidity for 7 days before testing. The strips were peeled from the panel using an INSTRON universal testing machine with a crosshead speed of 12 in/min (30.5 cm/min). The peel force was measured and the panels were observed to see if visible adhesive residue remained on the panel or if
10 any damage had occurred. The peel data in the Tables represent an average of three tests.

Static Shear Test Method

Static shear was determined according to the method of ASTM D3654-82 entitled, "Holding Power of Pressure-Sensitive Tapes," with the following modifications. The release liner(s), where present, was removed from the test sample. Test samples having the dimensions 0.75 in x 0.75 in (1.91
15 cm x 1.91 cm) were adhered to the test substrate through the adhesive composition at 72°F (22°C) and 50 % relative humidity by passing a 15 lb. (6.8 kg) hand held roller over the length of the sample two times at a rate of 12 in/min (30.48 cm/min). A metal vapor coated polyester film having the dimensions 0.75 in x 4 in (1.91 cm x 10.16 cm) was bonded to one side of the adhesive test sample for the purpose of attaching the load.

20 The test sample was allowed to dwell on the test substrate for 1 hour at 22°C and 50 % relative humidity; thereafter a 2.2 lb. (1 kg) weight was applied to the metal vapor coated polyester film. The time to failure was recorded in minutes and the average value, calculated pursuant to procedures A and C of section 10.1 of the standard, for all of the test samples was reported. Four samples were tested and the average time to failure of the four samples and the failure mode of each sample was recorded. A value
25 was reported with a greater than symbol (i.e., >) when at least one of the three samples had not failed at the time the test was terminated.

Test Adherends

30 Drywall panels (obtained from Materials Company, Metzger Building, St. Paul, MN) were single coat primed with Sherwin Williams Prep-Rite Interior Latex Primer, then single top-coated with Sherwin Williams DURATION Interior Acrylic Latex Ben Bone Paint "SW Ben Bone" (Sherwin-Williams Company, Cleveland, OH) or BEHR PREMIUM PLUS ULTRA Primer and Paint 2 in 1 Flat Egyptian Nile "Behr FEN" (obtained from Behr Process Corporation of Santa Ana, CA).

35 Panels of sheet glass 2 in x2 in (5.08 cm x 5.08 cm) were used when glass was used as the test adherend for shear testing.

Examples 1-5Polydisiloxane polyoxamide block copolymer based adhesive

The polydisiloxane polyoxamide elastomer (PDMS Elastomer I) used in the pressure-sensitive adhesive compositions in Tables 1 and 2 was like that of Example 12 of US Patent No. 8,765,881. Example 12 refers to an amine equivalent weight of 10,174 g/mol, or a molecular weight of about 20,000 g/mol. The polydisiloxane polyoxamide elastomer (PDMS Elastomer II) was like that of Example 12 of US Patent No. 8,765,881 except the diamine had a molecular weight of about 15,000 g/mol (or an amine equivalent weight of about 7500 g/mol) The MQ resin tackifier resin used in the pressure-sensitive adhesive compositions was SR545 (61% solids in toluene) (available from GE Silicones, Waterford, NY).

The pressure sensitive adhesive compositions were prepared by adding all indicated components to glass jars in the indicated proportions at 30 weight % solids in ethyl acetate. The jars were sealed and the contents thoroughly mixed by placing the jars on a roller at about 2-6 rpm for at least 24 hours prior to coating.

Preparation of Transfer Adhesive Films

Pressure sensitive adhesive compositions were knife-coated onto a paper liner web having a silicone release surface. The paper liner web speed was 2.75 meter/min. After coating, the web was passed through an oven 11 meter long (residence time 4 minutes total) having three temperature zones. The temperature in zone 1 (2.75 meter) was 57° C; temperature in zone 2 (2.75 meter) was 80° C; temperature in zone 3 (about 5.5 meter) was 93° C. The caliper of the dried adhesive was approximately 2.5-3.0 mils thick. The transfer adhesive films were then stored at ambient conditions.

Multi-Layer Composite Tape Preparation

The transfer adhesives were then laminated to film-foam-film composites and the desired size and geometry was die cut. In specific, the test adhesive composition was adhered to the first side of a composite film-foam-film construction like that found on COMMAND strip products (31 mil 6 lb. foam with 1.8 mil polyethylene film on both sides of the foam). This side of the film-foam-film construction was primed with 3M Adhesion Promoter 4298UV (3M Company, St. Paul, MN) prior to adhesive lamination. The second side of the composite foam had a second non-peelable adhesive adhered along the entire width and length of the test sample. A 3M DUAL LOCK mechanical fastener backing or a 2 mil PET film was adhered to the second side for peel adhesion testing; a metalized PET film was adhered to the second side for shear testing. Samples of the adhesive coated film-foam-film composites were die cut into 1 in wide x 6 in long strips (2.54 cm by 15.24 cm) for peel testing from drywall or 0.75 in x 0.75 in (1.91 cm x 1.91 cm) for shear testing.

90° Peel Adhesion data and Static Shear data for Examples 1-5 are summarized in Tables 1 and 2. All 90° Peel Adhesion testing for Examples 1-5 was performed on "SW Ben Bone".

Table 1

Example	PDMS Elastomer I:MQ resin ratio	90° Peel Adhesion (oz/in) after 1 hour	90° Peel Adhesion (oz/in) after 1 week	90° Peel Adhesion (oz/in) after 2 weeks	90° Peel Adhesion (oz/in) after 4 weeks	90° Peel Adhesion (oz/in) after 12 weeks
1	98:2	0.29	-	10.30	-	-
2	90:10	-	20.34	-	23.18	20.63
3	83:17	8.35	-	12.26	-	-
4	80:20	-	23.44	-	-	-
5	90 ^a :10	-	20.80	-	24.35	22.18

^aPDMS Elastomer II was used instead of PDMS Elastomer I

5

Table 2

Example	PDMS Elastomer I: MQ resin ratio	Static Shear (minutes) glass	Static Shear (minutes) “SW Ben Bone”	Static Shear (minutes) “Behr FEN”
1	98:2	22.6	0	0
2	90:10	-	-	-
3	83:17	>20536	>20547	>20542
4	80:20	>14136	>50390	>50402
5	90 ^a :10	-	-	-

^aPDMS Elastomer II was used instead of PDMS Elastomer I

Examples 6-11

The silicone polyurea block copolymer based pressure-sensitive adhesive compositions used for Examples 6-11 were prepared according to the method described for Example 28 in US Patent No. 6569521, except that the compositions were prepared to have the weight % MQ resin amounts as set forth in Table 3. Multi-layer composite tape were prepared as described above for Examples 1-5.

90° Peel Adhesion data and Static Shear data for Examples 6-11 are summarized in Tables 3 and 4. All 90° Peel Adhesion testing for Examples 6-11 was performed on “SW Ben Bone”.

Table 3

Example	Weight% MQ Resin	90° Peel Adhesion (oz/in) after 1 hour	90° Peel Adhesion (oz/in) after 1 week	90° Peel Adhesion (oz/in) after 2 weeks
6	2	0	0	0
7	8	3.79	7.24	8.434
8	14	7.12	14.76	16.09
9	20	19.71	32.42	23.53
10	26	24.30	23.19	23.63
11	32	23.56	21.50	24.87

Table 4

Example	% MQ Resin	Static Shear (minutes) "SW Ben Bone"
6	2	0
7	8	15635
8	14	>28716
9	20	>28716
10	26	>28716
11	32	>28716

5

The recitation of all numerical ranges by endpoint is meant to include all numbers subsumed within the range (*i.e.*, the range 1 to 10 includes, for example, 1, 1.5, 3.33, and 10).

10

The terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

15

Moreover, the terms top, bottom, over, under and the like in the description and the claims are used for descriptive purposes and not necessarily for describing relative positions. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other orientations than described or illustrated herein.

All references mentioned herein are hereby incorporated by reference in their entirety.

20

It is understood that connector systems may have many different properties that make them particularly suitable for certain applications or for connecting certain types of objects together. Thus, in

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accordance with the present invention, any such connector system can be used, but the chosen connector system can be advantageously picked based upon its properties that make it particularly suitable for a specific application or for connecting certain types of objects together.

WE CLAIM:

1. An adhesive composition comprising:
 - (a) a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or
 - (b) a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%.
2. The adhesive composition of claim 1, wherein the adhesive composition is a pressure sensitive adhesive.
3. The adhesive composition of claim 1, wherein the adhesive composition is a heat activated adhesive.
4. The adhesive composition of claim 1, wherein each R^1 is methyl and R^3 is hydrogen.
5. The adhesive composition of claim 1, wherein the copolymer has a first repeat unit where p is equal to 1 and a second repeat unit where p is at least 2.
6. The adhesive composition of claim 1, wherein G is an alkylene, heteroalkylene, arylene, aralkylene, polydiorganosiloxane, or a combination thereof.
7. The adhesive composition of claim 1, wherein Y is an alkylene.
8. The adhesive composition of claim 1, wherein n is an integer of 40 to 500.
9. The adhesive composition of claim 1, wherein the silicate tackifying resin is an MQ silicate tackifying resin.
10. The adhesive composition of claim 1, wherein the tackifier is present in an amount of between about 5 weight percent and about 15 weight percent based on the weight of the adhesive composition.

11. An article comprising:
 a substrate; and
 an adhesive layer adjacent to at least one surface of the substrate, the adhesive layer comprising at least one of

- 5 (a) a polydiorganosiloxane polyoxamide copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 20 wt%; or
 (b) a silicone polyurea block copolymer and a silicate tackifying resin in an amount of between about 0.1 wt% and about 30 wt%.

10 12. The article of claim 11, wherein the adhesive layer is a heat activated adhesive.

13. The article of claim 11, wherein the adhesive layer is a pressure sensitive adhesive.

15 14. The article of claim 11, wherein each R¹ is methyl and R³ is hydrogen.

15 15. The article of claim 11, wherein the silicate tackifying resin comprises a MQ silicate tackifying resin.

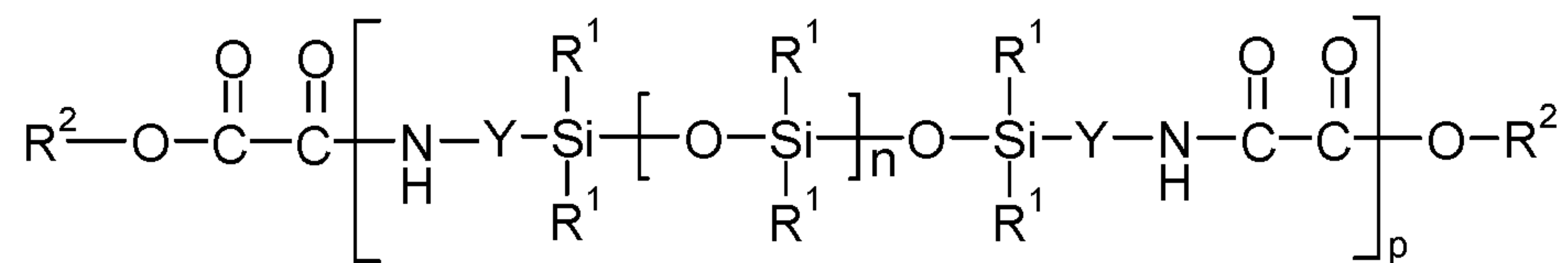
20 16. The article of claim 11, having a peel adhesion between about 0.5 oz/in and about 120 oz/in and shear of between at least about 1500 minutes.

17. A method of preparing an adhesive article, the method comprising:
 providing an adhesive composition of any of claims 1-16; and
 applying the adhesive composition to a surface of a substrate.

25 18. The method of claim 17, further comprising removing a release liner to provide an adhesive layer having a microstructured surface.

19. The method of claim 17, wherein the polydiorganosiloxane polyoxamide copolymer is the reaction product of

i) a precursor of Formula II



II

wherein each R² is independently an alkyl, haloalkyl, aryl, or aryl substituted with an alkyl, alkoxy, halo, or alkoxycarbonyl; and

ii) a diamine of formula R³HN-G-NHR³

wherein

G is a divalent residue unit equal to the diamine minus the two -NHR³ groups; and

R³ is hydrogen or alkyl or R³ taken together with G and with the nitrogen to which they are both attached forms a heterocyclic group.

20. The method of claim 19, wherein the diamine is of formula H₂N-G-NH₂ and G comprises an alkylene, heteroalkylene, arylene, aralkylene, polydiorganosiloxane, or a combination thereof.