TISSUE PRODUCTS TREATED WITH A SOFTENING COMPOSITION CONTAINING A LAYERED POLYSILOXANE MICELLE

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ABSTRACT

A tissue product having a softening composition applied to at least one side is generally disclosed. The softening composition includes a polysiloxane micelle having a core polysiloxane and an outer layer polysiloxane. The core polysiloxane is more hydrophobic than the outer layer polysiloxane. In one embodiment, the core polysiloxane is an amino-functional polysiloxane, and the outer layer polysiloxane is a polyether polysiloxane. The softening composition can also contain other optional ingredients, such as surfactants and beneficial agents.
TISSUE PRODUCTS TREATED WITH A SOFTENING COMPOSITION CONTAINING A LAYERED POLYSILOXANE MICELLE

BACKGROUND OF THE INVENTION

[0001] Consumers use paper-wiping products, such as facial tissues and bath tissues, for a wide variety of applications. Facial tissues are not only used for nose care but, in addition to other uses, may also be used as a general wiping product. Consequently, there are many different types of tissue products currently commercially available.

[0002] In some applications, tissue products are treated with softening agents in order to increase the softness of the tissue. Adding softening agents to a tissue may impart improved softness to the tissue while maintaining the tissue’s strength and reducing the amount of lint produced by the tissue during use. For example, tissue products treated with amino-functional polysiloxanes have a silky-soft handfeel. In addition to polysiloxanes, long chain alkyl chemicals are also used as softeners. These chemicals provide tissue products with a lotiony, greasy-soft handfeel.

[0003] In some applications, tissue products may be treated with other beneficial agents as well. For example, in addition to softening agents such as polysiloxane lotions, other desirable agents may be added to a tissue in order to provide a benefit to the user. For example, vitamins, plant extracts, medications, antimicrobial compounds, and the like may also be added to the web in order to transfer the desired agent to the consumer upon use.

[0004] Some additives, however, such as softening agents, may have a tendency to impart hydrophobicity to the treated tissue web, reducing the wettability characteristics of the web. Although hydrophobicity may be desirable in some applications, in other applications, increased hydrophobicity may adversely affect the product. For instance, increased hydrophobicity in a bath tissue may prevent the bath tissue from being wetted in a sufficient amount of time and prevent disintegration and dispersing when disposed in a commode or toilet. Hence, in some applications, it is difficult to find a proper balance between softness and absorbency, both of which are desirable attributes for tissues, particularly bath tissues.

[0005] Thus, a need currently exists for a softening composition that, when uniformly treated on the surface of a tissue product can provide the product with a lotiony-soft handfeel without completely degrading the wettability characteristics of the product.

SUMMARY OF THE INVENTION

[0006] In general, one embodiment of the present invention is directed to a tissue product comprising at least one tissue web containing pulp fibers. The tissue product has a first side and a second side. A softening composition is applied to at least one side of the tissue product. The softening composition includes a polysiloxane micelle having a core polysiloxane and an outer layer polysiloxane. The core polysiloxane is more hydrophobic than the outer layer polysiloxane. The softening composition can further include at least one beneficial agent.

[0007] In one embodiment, the softening composition can be applied to both sides of the tissue product. For instance, the softening composition can be applied to each side of the tissue product so as to cover from about 40% to about 95% of the surface area of each side of the product. The polysiloxane micelle can be applied to the tissue product at a total add-on level of from about 0.25% to about 8% by weight, such as from about 0.5% to about 5% by weight.

[0008] In one embodiment, the core polysiloxane can comprise an amino-functional polysiloxane, such as a polysiloxane having the following structure:

\[
G_1 - \begin{array}{c}
\begin{array}{ccc}
R_1 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R_2 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R_3 & S_i & O_i
\end{array}
\end{array} - R_4 - \begin{array}{c}
\begin{array}{ccc}
R_5 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R_6 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R_7 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R_8 & S_i & O_i
\end{array}
\end{array} - G_2
\end{array}
\]

wherein,

- \( m \) is 10 to 100,000;
- \( n \) is 1 to 5,000;
- \( G_1 \) is \( R_9 \) or \( R_{10} - [X - R_1]_{m} - Y - R_{12} \);
- \( G_2 \) is independently \( R_9 \), a hydroxy radical, an alkoxyl radical, or \( R_{10} - [X - R_1]_{m} - Y - R_{12} \);
- \( R_1 \) through \( R_5 \) are independently selected from the group consisting of \( C_1 \) to \( C_{20} \) substituted or unsubstituted, aliphatic or aromatic alkyl radicals;
- \( R_{11} \) and \( R_{12} \) are independently a substituted or unsubstituted \( C_2 \) to \( C_6 \) alkenyl diradical;
- \( X \) and \( Y \) are independently a \( NR_3 \) diradical;
- \( R_9 \) and \( R_{10} \) are independently a hydrogen or a substituted or unsubstituted \( C_1 \) to \( C_{20} \) alkyl radical; and

[0009] \( S \) is 0 or 1.

[0009] In one particular embodiment, the outer layer polysiloxane can comprise a polyether polysiloxane, such as a polysiloxane having the following structure:

\[
R^2 - \begin{array}{c}
\begin{array}{ccc}
S_i & O_i & S_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
S_i & O_i & S_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
S_i & O_i & S_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
S_i & O_i & S_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R^0 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R^1 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R^2 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R^3 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R^4 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R^5 & S_i & O_i
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{ccc}
R^6 & S_i & O_i
\end{array}
\end{array}
\]

wherein, \( \gamma \) and \( \delta \) are integers \( \geq 0 \), \( \gamma \) is an integer \( \geq 0 \), the mole ratio of \( X \) to \( (x+y+z) \) is from about 0.05 percent to about 95 percent, the ratio of \( y \) to \( x+y+z \) is from about 0 percent to about 25%; the \( R^9 \) and \( R^9 \) moieties are independently selected from the organofunctional group consisting of \( C_1 \) or higher alkyl groups, ethers, polyethers, polyesters, amines, imines, amides, and alkyl and alkyl analogues of such groups; the \( R^{10} \) moiety is an amino functional moiety; \( R^{11} \) is a polyether functional group having the generic formula: \( R^{12} - (R^{13} - O)_{m} - (R^{14}O)_{n} - R^{15} \), wherein \( R^{12} \), \( R^{13} \), and \( R^{14} \) are independently \( C_1 \) alkyl groups, linear or branched; \( R^{15} \) is \( H \) or a \( C_{1-30} \) alkyl group; and, ‘‘a’’ and ‘‘b’’ are integers of from about 1 to about 100.

[0020] In another embodiment, the present invention is directed to a method of making a tissue product. The method includes forming a tissue web containing pulp fibers and applying a softening composition to at least one side of the tissue product. The softening composition comprising a polysiloxane micelle having a core polysiloxane and an outer layer polysiloxane. The core polysiloxane is more hydrophobic than said outer layer polysiloxane.

[0021] Other features and aspects of the present invention are discussed in greater detail below.
BRIEF DESCRIPTION OF THE DRAWINGS

[0022] A full and enabling disclosure of the present invention, including the best mode thereof to one skilled in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying figures, in which:

[0023] FIG. 1 is a representation of an exemplary polysiloxane micelle;
[0024] FIG. 2 is a representation of an exemplary surfactant stabilized polysiloxane micelle;
[0025] FIG. 3 is a schematic diagram of an uncreped through-air dried process for making tissue webs; and
[0026] FIG. 4 is a schematic diagram of one embodiment for applying a softening composition to both sides of a tissue web.

[0027] Repeat use of reference characters in the present specification and drawings is intended to represent the same or analogous features of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0028] Reference now will be made to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not as a limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations may be made in the invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment may be used in another, embodiment to yield a still further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents. It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary constructions.

[0029] In general, one embodiment of the present invention is directed to a softening composition for a tissue product in order to provide the product with a non-greasy, lotiony-soft handfeel. Also, the softening composition of the present invention has been formulated such that the composition may be applied to a tissue product without substantially interfering with the wettability characteristics of the product.

[0030] More particularly, the softening composition is applied to the tissue in an emulsion containing a layered polysiloxane micelle. The layered polysiloxane micelle includes a core of a first polysiloxane surrounded by at least one outer layer of a second, different polysiloxane. For example, the polysiloxane of the core of the micelle can be more hydrophobic than the polysiloxane of the outer layer(s). Referring to FIG. 1, an exemplary polysiloxane micelle 100 having a core 105 and an outer layer 110. Although only one outer layer 110 is shown, additional polysiloxane outer layers can be included in the micelle. It is also noted that the polysiloxane micelle 100 is actually a 3-dimensional micelle, though it is depicted in only 2-dimensions.

[0031] Of particular advantage, utilizing a polysiloxane micelle having two different polysiloxanes forming the core and the outer layer allows certain properties and characteristics of both polysiloxanes to be maximized, while minimizing or avoiding other disadvantageous properties of the polysiloxanes.

[0032] Polysiloxanes encompass a very broad class of compounds. They are characterized in having a backbone structure:

\[
\begin{array}{c}
R' & \text{Si-O} & R'' \\
\end{array}
\]

wherein, \( R' \) and \( R'' \) can be a broad range of organo and non-organo groups including mixtures of such groups and where \( n \) is an integer greater than 2. These polysiloxanes may be linear, branched or cyclic. They include a wide variety of polysiloxane copolymers containing various compositions of functional groups, hence, \( R' \) and \( R'' \) actually may represent many different types of groups within the same polymer molecule. The organo or non-organo groups may be capable of reacting with cellulose to covalently, ionically or hydrogen bond the polysiloxane to the cellulose. These functional groups may also be capable of reacting with themselves to form crosslinked matrixes with the cellulose. For instance, when \( R' \) and \( R'' \) are alkyl groups, such as \( C_1-C_{10} \) linear or branched alkyl groups, the polysiloxane component is referred to as a polydialkylsiloxane component.

[0033] Functionalized polysiloxanes and their aqueous emulsions are well known commercially available materials. The functional groups on the polysiloxanes can affect the hydrophobicity characteristics of the polysiloxane. In order to produce the polysiloxane micelle of the softening composition, the polysiloxanes of the core have more hydrophobic functional groups than the functional groups of the outer layer(s) polysiloxane(s). Thus, the more hydrophilic outer layer polysiloxane can help stabilize a more hydrophobic polysiloxane in an aqueous emulsion. For instance, a relatively hydrophobic polysiloxane that is likely to phase separate under normal conditions in water can be stabilized by surrounding it with an outer layer of a more hydrophilic polysiloxane. In this case, the more hydrophilic polysiloxane acts much like a surfactant agent.

[0034] One class of functionalized polysiloxanes is amino-functional polysiloxanes, which generally have the following structure:

\[
\begin{array}{c}
R^1 & \text{Si-O} & R^7 \\
R^2 & \text{Si-O} & R^8 \\
R^3 & \text{Si-O} & R^9 \\
R^4 & \text{Si-O} & R^{10} \\
\end{array}
\]

wherein, \( x \) and \( y \) are integers \( >0 \). The mole ratio of \( x \) to \( (x+y) \) can be from about 0.005 percent to about 25 percent. The \( R\text{-R'} \) moieties can be independently any organo-functional group including \( C_1 \) or higher alkyl groups, ethers, polyethers, polyesters, amines, imines, amides, or other functional groups including the alkyl and alkenyl analogues of such groups. The \( R^{10} \) moiety is an amino functional moiety including but not limited to primary amine, secondary amine, tertiary amines, quaternary amines, unsubstituted
amides and mixtures thereof. An exemplary R' moiety contains one amine group per constituent or two or more amine groups per constituent, separated by a linear or branched alkyl chain of C₆ or greater. When R' and R'' are alkyl groups such as C₆-C₉ alkyl groups the polysiloxanes are herein referred to as amino-functional polysiloxanes, more specifically amino functional polydimethylsiloxanes, Exemplary materials include DC 2-8220 and DC2-8182 commercially available from Dow Corning, Inc., Midland, Mich. and Y-14344 available from Crompton, Corp., Greenwich, Conn.

In one embodiment, the amino-functional polysiloxane may have the following structure:

wherein,

- m is 10 to 100,000;
- n is 1 to 5,000;
- G₁ is Rₖ or R₁₀—[X—R₁₄]ₕ—Y—R₁₂;
- G₂ are independently R₉, a hydroxyl radical, an alkoxyl radical, or R₁₀—[X—R₁₄]ₕ—Y—R₁₂;
- R₅ through R₉ are independently selected from the group consisting of C₁ to C₉ substituted or unsubstituted, aliphatic or aromatic alkyl radicals;
- R₁₀ and R₁₂ are independently a substituted or an unsubstituted C₂ to C₉ alkenyl diradical;
- X and Y are independently a NR diradical;
- R₁₂ and R₁₃ are independently a hydrogen or a substituted or unsubstituted C₁ to C₂₀ alkyl radical; and
- S is 0 or 1.

Representative species within the foregoing general structure include the following:
Commercially available amino-functional polysiloxanes that may be made according to the above structures are marketed by Kelmar Industries, Inc. under the trade-names AF-21, AF-23, AF-26 and HAF-1130.

According to one embodiment of the present invention, the amino-functional polysiloxanes can be utilized to form the polysiloxane core of the micelle. This amino-functional polysiloxane core can be surrounded by an outer layer of another class of functionalized polysiloxanes having a more hydrophilic functional group(s), such as polyether polysiloxanes, which are generally more hydrophilic than the amino-functional polysiloxanes.

Such polyether polysiloxanes generally have the following structure:

\[
\begin{align*}
R^1 & \begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\end{array} \\
R^6 & \begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\end{array} \\
R^7 & \begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\end{array} \\
R^8 & \begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\end{array} \\
R^9 & \begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\end{array} \\
R^{10} & \begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\end{array} \\
\end{align*}
\]

wherein, x and z are integers &gt;0, y is an integer &gt;= 0. The mole ratio of x to (x+y+z) can be from about 0.05 percent to about 95 percent. The ratio of y to (x+y+z) can be from about 0 percent to about 25 percent. The R^8-R^6 moiety can be independently any organofunctional group including C1 or higher alkyl groups, ethers, polyethers, polyesters, amines, imines, amides, or other functional groups including the alkyl and alkenyl analogues of such groups. The R^15 moiety is an amino functional moiety including but not limited to primary amine, secondary amine, tertiary amine, quaternary amines, unsubstituted amides and mixtures thereof. An exemplary R^15 moiety contains one amine group per constituent or two or more amine groups per substituent, separated by a linear or branched alkyl chain of C1 or greater. R^11 is a polyether functional group having the generic formula: R^12-[(R^{13}-O)]_{x}-(R^{14}-O)]_{y}-(R^{15}-O)]_{z}, wherein R^{12}, R^{13}, and R^{14} are independently C1-C4 alkyl groups, linear or branched; R^{15} can be H or a C1-C6 alkyl group; and, "a" and "b" are integers of from about 1 to about 100, more specifically from about 5 to about 30.

When R^7-R^8 are alkyl groups such as C1-C4 alkyl groups, and y and z are both &gt;0 the polysiloxanes are usually referred to as amino functional polyetherpolydialkylsiloxane copolymers. Such definition also applies to cases where y=0 but R^11 contains amine functional polyether groups.

Exemplary amino functional polyetherpolysiloxanes and amino functional polyetherpolydialkylsiloxanes are the Wetsoft® CTW family manufactured and sold by Wacker, Inc., Adrian, Mich. For example, the polyetherpolysiloxanes in the Wetsoft® CTW is believed to have the following structure:

[0053] Other exemplary polysiloxanes can be found in U.S. Pat. No. 6,432,270 by Liu, et.al, and incorporated by reference herein.
In one embodiment, the polysiloxane micelle can be formed from a relatively small amount of the outer layer polysiloxane, when compared to the amount of the core polysiloxane. For example, the core polysiloxane can be greater than 50% by weight of the total amount of polysiloxane in the polysiloxane micelle, such as greater than about 60%. In some embodiments, the core polysiloxane can be greater than 70% by weight of the total amount of polysiloxane in the polysiloxane micelle, such as greater than about 80%. Conversely, the outer layer polysiloxane can be from about 5% to about 50% by weight of the polysiloxane micelle, such as from about 10% to about 40% by weight. For instance, in one embodiment, the outer layer polysiloxane can be from about 10% to about 30% by weight of the polysiloxane micelle, such as from about 15% to about 25% by weight.

Even though amount of outer layer polysiloxane in the polysiloxane micelle is relatively small, the properties of the outer layer can overshadow those of the core polysiloxane, especially while still in an emulsion form. Thus, a less expensive polysiloxane can be used for the core, while still benefiting from the properties of the outer layer polysiloxane.

The polysiloxane micelle can be present in the softening composition in an amount from about 2% to about 50% by weight, such as from about 5% to about 30% by weight, and such as from about 20% to about 50% by weight. In other embodiments, the polysiloxane micelle can be present in a greater weight present of the softening composition, such as greater than about 30% by weight and greater than about 40% by weight.

In one particular embodiment, the polysiloxane micelle can be utilized in combination with a surfactant. For example, referring to FIG. 2, a polysiloxane micelle 100 is shown have a core 105 and an outer layer 110. Surfactants 115 are shown interacting with the polysiloxane of the outer layer 110. The surfactant 115 is used to form a layer between the outer layer 110 and the water of the emulsion, stabilizing the polysiloxane of the outer layer 110 in the aqueous emulsion.

Examples of non-ionic surfactants include, but are not limited to polyoxyethylene alkylamines, trialkylamine oxides, triethanolamine fatty acid esters and partial fatty acid esters, polyoxyethylene alkyl ethers such as those obtained by ethoxylation of long chain alcohols, polyoxyethylene alkylphenyl ethers, alkylphenyl ethers, polyoxyethylene polyalcohol ethers, polyoxyethylene glycol fatty acid esters and alkyl ethers, polyoxyethylene glycol fatty acid esters and alkyl ethers, and polyoxyethylene glycol polyhydric alcohol fatty acid esters and alkyl ethers, glycerin fatty acid esters, polyglycerin fatty acid esters, polyoxyethylene polyhydric alcohol fatty acid partial esters and alkyl ethers, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene glycerin fatty acid esters, polyoxyethylene glycerin fatty acid esters and alkyl ethers, polyglycerin fatty acid esters, ethoxylated/proxylated vegetable oils and the like including mixtures of said surfactants.

Examples of ionic surfactants include primary, secondary and tertiary amine salts of the corresponding alkyl amines, alkytrimethyl ammonium salts, dialkyldimethyl benzonium salts, dialkyldimethyl ammonium salts, trialkylmethyl ammonium salts, tetra alkyl ammonium salts, polyethylenopolyamine fatty acid amide salts, fatty acid salts, alkylbenzenesulfonates, dialkylsulfosuccinates, alkylsulfonates, N-acyl-N-methyltaurate, alkylsulfates, sulfonated fats and oils, polyoxyethylene alkylether sulfonates, polyoxyethylene styrenated phenyl ether sulfonates, alkylyphosphates, polyoxyethylene alkyl phenyl ether phosphates, N,N-dimethyl-N-alkyl-N-carboxymethylammonium betaines, N,N-dialkylaminoalkylene carboxylates, N,N,N-trialkyl-N-sulfooalkeneammonium betaines, N,N-dialkyl-N, N-bispolyoxyethyleneammonium sulfate ester betaines, and the like including mixtures of such surfactants.

In general, any suitable tissue product may be treated in accordance with the present invention. The tissue product may be a single ply product or a multi-ply product. The plys of the tissue product may generally be formed in any of a variety of papermaking processes known in the art. In the present invention may utilize adhesive creping, wet creping, double creping, embossing, wet-pressing, air pressing, through-air drying, creped through-air drying, uncreped through-air drying, as well as other steps known in the art.

Tissue products that may be treated in accordance with the present invention include not only bath tissue and facial tissue, but may also include paper towels and industrial wipers. The tissue products may have a basis weight up to about 120 gsm, such as from about 60 gsm to about 80 gsm. Bath tissues and facial tissues, for instance, may have a basis weight of from about 10 gsm to about 45 gsm, such as from about 30 gsm to about 40 gsm.

In one particular embodiment, the softening composition of the present invention is applied to a single ply uncreped through-air dried web. Referring to FIG. 3, shown is a schematic flow diagram of a throughdrying process for making uncreped throughdried tissue sheets. Shown is the headbox 1 which deposits an aqueous suspension of papermaking fibers onto an inner forming fabric 3 as it traverses the forming roll 4. Outer forming fabric 5 serves to contain the web while it passes over the forming roll and sheds some of the water. The wet web 6 is then transferred from the inner forming fabric to a wet end transfer fabric 8 with the aid of a vacuum transfer shoe 9. This transfer is preferably carried out with the transfer fabric traveling at a slower speed than the forming fabric (rush transfer) to impart stretch into the final tissue sheet.

The wet web is then transferred to the throughdrying fabric 11 with the assistance of a vacuum transfer roll 12. The throughdrying fabric carries the web over the throughdrying dryer 13, which blows hot air through the web to dry it while
preserving bulk. There can be more than one throughdryer in series (not shown), depending on the speed and the dryer capacity.

The dried tissue sheet 15 is then transferred to a first dry end transfer fabric 16 with the aid of vacuum transfer roll 17. The tissue sheet shortly after transfer is sandwiched between the first dry end transfer fabric and the transfer belt 18 to positively control the sheet path. The air permeability of the transfer belt is lower than that of the first dry end transfer fabric, causing the sheet to naturally adhere to the transfer belt. At the point of separation, the sheet follows the transfer belt due to vacuum action. Suitable low air permeability fabrics for use as transfer belts include, without limitation, COTPA Mononap NP 50 dryer felt (air permeability of about 50 cubic feet per minute per square foot) and Asten 960C (impermeable to air). The transfer belt passes over two winding drums 21 and 22 before returning to pick up the dried tissue sheet again. The sheet is transferred to the parent roll 25 at a point between the two winding drums. The parent roll is wound onto a reel spool 26, which is driven by a center drive motor.

Particularly suitable methods of producing uncreped throughdried tissue sheets for purposes of this invention are described in U.S. Pat. No. 6,017,417 issued Jan. 25, 2000 to Wendt et al. and U.S. Pat. No. 5,944,273 issued Aug. 31, 1999 to Lin et al., both of which are herein incorporated by reference.

The softening composition as described above may be applied to a single side of a tissue product or may be applied to opposite sides. In order to maximize an increase in softness, the softening composition may be applied to both sides of the tissue product. When added to the tissue product, the total solids add-on is generally less than about 5% by weight, such as less than about 4% by weight, or less than about 3% by weight. For example, in one embodiment, the total solids add-on may be from about 0.5% by weight to about 2.5% by weight. When applied to the tissue product, the softening composition may cover from about 20% to about 100% of the surface area of both sides of the product, such as from about 40% to about 95% of the surface area of each side.

As mentioned above, the softening composition of the present invention has been found to not only improve the handle of tissue products, but may also be applied so as to minimize any increase in wettability. For instance, softening compositions containing the above proportion of ingredients at the above add-on amounts may be applied to a bath tissue that still retains a wet-out time of less than about 8 seconds, such as less than about 7 seconds. For example, in one embodiment, the wet-out time of a tissue product treated in accordance with the present invention may be less than about 6 seconds, and even less than about 5 seconds. For purposes of comparison, an untreated tissue product may have a wet-out time of from about 3 seconds to about 4 seconds.

The softening composition may be applied to the tissue product using any suitable method or technique without limitation. For instance, the softening composition may be sprayed onto the tissue product or printed onto the tissue product. When sprayed or printed onto a tissue sheet, the softening composition may be combined with water, preservatives, anti-foamers, and surfactants to form an emulsion. Water, for instance, may be combined with a softening composition in order to reduce the viscosity in order to print or spray the composition onto a tissue web.

In one particular embodiment, the softening composition is contained in an emulsion and applied to a tissue web using an offset rotogravure printer as particularly illustrated in FIG. 4. When the softening composition is contained in an emulsion and applied to a tissue product by printing or spraying, the softening composition may comprise from about 10% to 60% by weight of the emulsion, such as from about 20% to about 50% by weight of the emulsion. In one particular embodiment, for instance, the softening composition may comprise from about 25% to about 45% by weight of the emulsion.

Referring to FIG. 4, shown is the parent roll 25 being unwound and passed through two calender nips between calender rolls 30a and 31a and 30b and 31b. The calendered web is then passed to the rotogravure coating station comprising a first closed doctor chamber 33 containing the emulsion of the softening composition to be applied to a first side of the web, a first engraved steel gravure roll 34, a first rubber backing roll 35, a second rubber backing roll 36, a second engraved steel gravure roll 37 and a second closed doctor chamber 38 containing the emulsion of the softening composition to be applied to the second side of the web. If both sides of the web are to be treated, the two emulsions can be the same or different. The calendered web passes through a fixed-gap nip between the two rubber backing rolls where the emulsion of the softening composition is applied to the web. The treated web is then passed to the rewinder where the web is wound onto rolls 40 and slit into rolls of bath tissue.

EXAMPLES

An amino-functional polysiloxane (AF-23, Kelmar Industries, Inc.) was combined with a polyether polysiloxane (Wetsoft® CTW, Wacker, Inc., Adrian, Mich.) to form an aqueous emulsion. Other ingredients in the emulsion include Pulpasil KCD50EN is a defoamer available from Wacker Chemical, Kelmar Division (Duncan, S.C.); SM-205P is a biocide preservative available from Wacker Chemical, Kelmar Division (Duncan, S.C.); and TDA-9C is a ethylated alcohol surfactant available from Wacker Chemical, Kelmar Division (Duncan, S.C.).

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Ingredient</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF-23</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>CTW</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Pulpasil KCD50EN</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>SM-205P</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>TDA-9C</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>68.73</td>
<td></td>
</tr>
</tbody>
</table>

For comparison, two softening compositions were also made, each having only one polysiloxane present:

<table>
<thead>
<tr>
<th>TABLE 2</th>
<th>Ingredient</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTW</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Pulpasil KCD50EN</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2-continued

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Control A</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM-205P</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>TDA-9C</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>67.73</td>
<td></td>
</tr>
</tbody>
</table>

TABLE 3

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Control B</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF-23</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>Pulpol KCD50EN</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>SM-205P</td>
<td>0.77</td>
<td></td>
</tr>
<tr>
<td>TDA-9C</td>
<td>22.5</td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>68.73</td>
<td></td>
</tr>
</tbody>
</table>

It was found that the two polysiloxanes used in the formulation of Table 1 formed a micelle with the polyether polysiloxane (Wetsoft® CTW, Wacker, Inc., Adrian, Mich.) as an outer layer of the amino-functional polysiloxane (AF-23, Kelmar Industries, Inc.) core. Also, the present inventors have found that surrounding the amino-functional polysiloxane (AF-23, Kelmar Industries, Inc.) with an outer layer of the more hydrophilic polyether polysiloxane (Wetsoft® CTW, Wacker, Inc., Adrian, Mich.), the processing characteristics of the amino-functional polysiloxane (AF-23, Kelmar Industries, Inc.) have been substantially improved. For instance, when used alone, the amino-functional polysiloxane (AF-23, Kelmar Industries, Inc.) has been known to readily phase separate in the emulsion. However, when used in combination with the polyether polysiloxane (Wetsoft® CTW, Wacker, Inc., Adrian, Mich.), the emulsion was much more stable to heat and shear forces.

Each of the emulsions described above, was applied to the bath tissue according to the process described in FIG. 4, with an add-on level of about 0.466 lb/1000 ft². Panel tests revealed that tissue applied with the Control B emulsion, was less soft than tissue applied with the Control A emulsion; both tissue samples had similar stiffness results.

The tissue including the polysiloxane micelle emulsion of Table 1 showed improvement over the Control A tissue. Panel tests showed that the polysiloxane micelle emulsion gave the tissue more softness, significantly less stiffness, significantly less greasy tissue feel and residue, significantly less coating felt on the tissue, significantly more waxy tissue feel and residue, and significantly less odor intensity and objectionable odor, as compared to Control A. Bench testing results measuring Overall Softness showed that the tissue with polysiloxane micelle emulsion applied is softer than the tissue with Control A applied.

Panel tests which compared the polysiloxane micelle emulsion, of Table 1, to Control B, revealed that the polysiloxane micelle emulsion gave the tissue significantly more softness and significantly less stiffness, as well as less odor intensity and objectionable odor over the Control B tissue. Bench testing results measuring Overall Softness, showed that the tissue with polysiloxane micelle emulsion applied is softer than the tissue with Control B applied.

The tissue including the polysiloxane micelle emulsion of Table 1 also showed improvement over the Control A tissue in the following areas: less greasy tissue feel, less greasy residue, less coating felt on the tissue, more waxy tissue residue, and significantly less odor intensity and objectionable odor. The tissue including the polysiloxane micelle emulsion of Table 1 also showed less odor intensity and objectionable odor over the Control B tissue.

These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention, which is more particularly set forth in the appended claims. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims.

What is claimed:

1. A tissue product comprising:
   a softening composition applied to at least one side of the tissue product, the softening composition comprising a polysiloxane micelle, said polysiloxane micelle comprising a core polysiloxane and an outer layer polysiloxane, wherein said core polysiloxane is more hydrophobic than said outer layer polysiloxane.
   2. A tissue product as in claim 1, wherein said core polysiloxane comprises an amino-functional polysiloxane having the following structure:

\[
\text{R}_1 \text{Si-O-Si-O-Si-O}_n \text{Si-O-Si-O}_m \text{Si-Si-G}_2
\]

wherein, m is 10 to 100,000; n is 1 to 5,000; G is R or R \_10-[X-R_11]-Y-R_12; G \_2 is independently R or a hydroxyl radical, an alkoxy radical, or R \_10-[X-R_1]-Y-R_12; R \_3 through R \_9 are independently selected from the group consisting of C_1 to C_8 substituted or unsubstituted, aliphatic or aromatic alkyl radicals; R \_10 and R \_11 are independently a substituted or unsubstituted C_1 to C_20 alkyl radical; X and Y are independently a NR \_3, or a hydrogen or a substituted or unsubstituted C_1 to C_20 alkyl radical; and S is 0 or 1.

3. A tissue product as defined in claim 1, wherein the softening composition has been applied to both sides of the tissue product, and wherein the polysiloxane micelle is applied to the tissue product at a total add-on level of from about 0.25% to about 8% by weight.

4. A tissue product as defined in claim 3, wherein the polysiloxane micelle is applied to the tissue product at a total add-on level of from about 0.5% to about 5% by weight.

5. A tissue product as defined in claim 3, wherein the softening composition is applied to each side of the tissue product so as to cover from about 40% to about 95% of the surface area of each side of the product.
6. A tissue product as defined in claim 1, wherein said core polysiloxane comprises an amino-functional polysiloxane selected from the group consisting of

[Chemical structure diagram]

and
7. A tissue product as in claim 1, wherein said outer layer polysiloxane comprises a polyether polysiloxane.

8. A tissue product as in claim 7, wherein said core polysiloxane comprises an amino-functional polysiloxane.

9. A tissue product as in claim 7, wherein said outer layer polysiloxane has the following structure:

$$\begin{align*}
R_1 & R_7 & R_9 & R_0 & R_4 & R^{--0}_1 & R^{--0}_n & R^{--0}_m & R^{--0}_s & R_3 & R_8 & R_{10} & R_{11} & X, y, Z \\
\end{align*}$$

wherein, $X$ and $Z$ are integers $>0$, $y$ is an integer $\geq 0$; the mole ratio of $x$ to $(x+y+z)$ is from about 0.05 percent to about 95 percent; the ratio of $y$ to $(x+y+z)$ is from about 0 percent to about 25%; the $R^2-R^6$ moieties are independently selected from the organofunctional group consisting of $C_1$ or higher alkyl groups, ethers, polyethers, polyesters, amines, imines, amides, and alkyl and alkynyl analogues of such groups; the $R^{10}$ moiety is an amino functional moiety; $R^{11}$ is a polyether functional group having the generic formula: $R^{12}-(R^{13}-O)_a-(R^{14}O)_b-R^{15}$, wherein $R^{12}$, $R^{13}$, and $R^{14}$ are independently selected from the group consisting of $C_1$ to $C_9$ substituted or unsubstituted, aliphatic or aromatic alkyl radicals; $R^{15}$ is H or a $C_1$ to $C_{30}$ alkyl group; and, "a" and "b" are integers of from about 1 to about 100.

10. A tissue product as in claim 7, wherein said outer layer polysiloxane has the following structure:

$$\begin{align*}
\text{(CH}_3\text{)}_3\text{SiO} & \text{O}_x & \text{Si(CH}_3)_3 \\
\text{(CH}_3\text{)}_3 & \text{O}_y & \text{Si(CH}_3)_3 \\
\text{H}_2 & \text{C} & \text{OH} & \text{OH} \\
\text{H}_2 & \text{C} & \text{OH} & \text{OH} \\
\end{align*}$$

wherein $x$ is an integer from 40 to 150; $y$ is an integer from 1 to 5; $z$ is an integer from 1 to 5; $n$ is an integer from 10 to 30; and $m$ is an integer from 10 to 30.

11. A tissue product as in claim 1, wherein said softening composition further comprises at least one beneficial agent.

12. A tissue product comprising:

- at least one tissue web containing pulp fibers, the tissue product having a first side and a second side;
- a softening composition applied to at least one side of the tissue product, the softening composition comprising a polysiloxane micelle and a surfactant, said polysiloxane micelle comprising a core polysiloxane and an outer layer polysiloxane, wherein said core polysiloxane comprises an amino-functional polysiloxane having the following structure:

$$\begin{align*}
R_1 & R_3 & R_5 & R_7 & R_9 & R_11 & R_5 \\
R_2 & R_4 & R_6 & R_8 & R_10 & R_12 & R_7 \\
\end{align*}$$

wherein, $m$ is 10 to 100,000; $n$ is 1 to 5,000; $G_1$ is $R_5$ or $R_10-\{X-R_1\}_{12}^{--Y}-R_{12}$; $G_2$ is independently $R_5$, a hydroxyl radical, an alkoxyl radical, or $R_2-\{X-R_1\}_{12}^{--Y}-R_{12}$; $R_1$ through $R_8$ are independently selected from the group consisting of $C_1$ to $C_9$ substituted or unsubstituted, aliphatic or aromatic alkyl radicals; $R_{10}$ and $R_{11}$ are independently a substituted or unsubstituted $C_2$ to $C_9$ alkylene diradical; $X$ and $Y$ are independently a NR$_3$ or diradical; $R_{12}$ and $R_{13}$ are independently a hydrogen or a substituted or unsubstituted $C_1$ to $C_{30}$ alkyl radical; and $S$ is 0 or 1; and wherein said outer layer polysiloxane has the following structure:

$$\begin{align*}
R_1 & R_7 & R_9 & R_0 & R_4 & R^{--0}_1 & R^{--0}_n & R^{--0}_m & R^{--0}_s & R_3 & R_8 & R_{10} & R_{11} & X, y, Z \\
\end{align*}$$

wherein, $x$ and $z$ are integers $>0$, $y$ is an integer $\geq 0$; the mole ratio of $x$ to $(x+y+z)$ is from about 0.05 percent to about 95 percent; the ratio of $y$ to $(x+y+z)$ is from about 0 percent to about 25%; the $R^2-R^6$ moieties are independently selected from the organofunctional group consisting of $C_1$ or higher alkyl groups, ethers, polyethers, polyesters, amines, imines, amides, and alkyl and alkynyl analogues of such groups; the $R^{10}$ moiety is an amino functional moiety; $R^{11}$ is a polyether functional group having the generic formula: $R^{12}-(R^{13}-O)_a-(R^{14}O)_b-R^{15}$ wherein $R^{12}$, $R^{13}$, and $R^{14}$ are independently selected from the group consisting of $C_1$ to $C_9$ substituted or unsubstituted, aliphatic or aromatic alkyl radicals; $R^{15}$ is H or a $C_1$ to $C_{10}$ alkyl group; and, "a" and "b" are integers of from about 1 to about 100.
13. A tissue product as in claim 12, wherein said outer layer polysiloxane has the following structure:

wherein x is an integer from 40 to 150; y is an integer from 1 to 5; z is an integer from 1 to 5; n is an integer from 10 to 30; and m is an integer from 10 to 30.

14. A tissue product as in claim 12, wherein said core polysiloxane comprises an amino-functional polysiloxane selected from the group consisting of
15. A method of making a tissue product comprising forming a tissue web containing pulp fibers, the tissue product having a first side and a second side; applying a softening composition to at least one side of the tissue product, the softening composition comprising a polysiloxane micelle, said polysiloxane micelle comprising a core polysiloxane and an outer layer polysiloxane, wherein said core polysiloxane is more hydrophobic than said outer layer polysiloxane.

16. A method as in claim 15, wherein said core polysiloxane comprises an amino-functional polysiloxane having the following structure:

\[
G_1 \xrightarrow{\text{Si-O-Si-O-Si}} G_2
\]

wherein,
- \(m\) is 10 to 100,000;
- \(n\) is 1 to 5,000;
- \(G_1\) is \(R_9\) or \(R_{10} - [X - R_{11}] - Y - R_{12}\);
- \(G_2\) are independently \(R_{13}\), a hydroxyl radical, an alkoxyl radical, or \(R_{14} - [X - R_{15}] - Y - R_{16}\);
- \(R_2\) through \(R_8\) are independently selected from the group consisting of \(C_1\) to \(C_6\) substituted or unsubstituted, aliphatic or aromatic alkyl radicals;
- \(R_{10}\) and \(R_{11}\) are independently a substituted or unsubstituted \(C_2\) to \(C_6\) alkylene diradical;
- \(X\) and \(Y\) are independently a \(NR_{13}\) diradical;
- \(R_{12}\) and \(R_{13}\) are independently a hydrogen or a substituted or unsubstituted \(C_1\) to \(C_{20}\) alkyl radical; and
- \(S\) is 0 or 1.

17. A method as in claim 15, wherein the softening composition has been applied to both sides of the tissue product, the softening composition being applied to the tissue product such that the total solids add-on is from about 0.5% to about 5% by weight.

18. A method as in claim 15, wherein the softening composition is applied to each side of the tissue product so as to cover from about 40% to about 95% of the surface area of each side of the product.

19. A method as in claim 15, wherein said core polysiloxane comprises an amino-functional polysiloxane selected from the group consisting of
20. A method as in claim 15, wherein said outer layer polysiloxane comprises a polyether polysiloxane.

21. A method as in claim 20, wherein said core polysiloxane comprises a amino-functional polysiloxane.

22. A method as in claim 15, wherein said outer layer polysiloxane has the following structure:

\[
\begin{array}{c}
\text{R}^1 \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si-O} \quad \text{Si} \\
\text{R}^2 \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{Si} \\
\text{R}^3 \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{Si} \\
\text{R}^4 \quad \text{Si} \quad \text{Si} \quad \text{Si} \quad \text{Si} \\
\end{array}
\]

wherein, \( x \) and \( z \) are integers \( >0 \), \( y \) is an integer \( \geq 0 \); the mole ratio of \( x \) to (\( x+y+z \)) is from about 0.05 percent to about 95 percent; the ratio of \( y \) to (\( x+y+z \)) is from about 0 percent to about 25 percent; the \( R^a-R^f \) moieties are independently selected from the organofunctional group consisting of \( C_1 \) or higher alkyl groups, ethers, polyethers, polyesters, amines, imines, amides, and alkyl and alkenyl analogues of such groups; the \( R^{10} \) moiety is an amino functional moiety; \( R^{11} \) is a polyether functional group having the generic formula: \( R^{12}-(R^{13}-O)_a-(R^{14}O)_b-R^{15} \), wherein \( R^{12}, R^{13}, \) and \( R^{14} \) are independently \( C_{1-4} \) alkyl groups, linear or branched; \( R^{15} \) is \( H \) or a \( C_{1-3} \) alkyl group; and, \( \text{“a” and “b” are integers of from about 1 to about 100.} \)

23. A method as in claim 15, wherein said outer layer polysiloxane has the following structure:

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{HO} \quad \text{CH} \quad \text{OH} \\
\text{H}_2\text{C} \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CH}_2 \quad \text{CH}_2 \\
\end{array}
\]

wherein \( x \) is an integer from 40 to 150; \( y \) is an integer from 1 to 5; \( z \) is an integer from 1 to 5; \( n \) is an integer from 10 to 30; and \( m \) is an integer from 10 to 30.

24. A method as in claim 15, wherein the softening composition further comprises at least one beneficial agent.

25. A method as in claim 15, wherein the softening composition further comprises a surfactant.

* * * * *