The invention describes the use of organic compounds that have multiple unsaturations as a substrate for the cross-linking reaction with hydrosilane terminated polydimethylsiloxanes. This reaction results in organic solvent compatible silicone crosslinked unsaturated hydrocarbon based polymers that have excellent lubricity and are clear gels. These compounds have many applications in cosmetic and personal care product formulations.
Silicone Crosslinked Unsaturated Hydrocarbon based Polymers

FIELD OF THE INVENTION

The present invention relates to the use of organic compounds that have multiple olefinic unsaturations as a substrate for a crosslinking reaction with hydrosilane terminated polydimethylsiloxanes. The resulting siloxane crosslinked hydrocarbons exhibit superior characteristics to siloxane crosslinked polydimethylsiloxanes, especially including improved organic solubility, consistent gelation characteristics and stability, as well as other favorable characteristics, including enhanced lubricity.

RELATED APPLICATIONS

This application claims the benefit of United States provisional application serial number 61/516,100, filed March 29, 2011, entitled "Silicone crosslinked unsaturated hydrocarbon based polymers", which is incorporated by reference in its entirety herein.

BACKGROUND

Silicone elastomers are well known materials in the cosmetics and personal care products industries. These materials are typically prepared by reacting a polydimethylsiloxane that has several pendant (and often terminal) hydrosilane (-O-Si(R)₂-H) (where R is most desirably methyl) functional groups with vinyl terminated polydimethylsiloxanes to produce a crosslinked three dimensional elastomeric gel structure. As is well known in the industry, the hydrosilane groups readily react with unsaturated groups such as vinyl and allyl groups and other alkenes. Thus, the reaction of a multi-functional hydrosilane polydimethylsiloxane with a dialkene (or multi-alkene) compound will result in a crosslinked polymer. Reactions of this type are detailed in US Patent No. 6,936,686 which is incorporated in its entirety by reference herein. The properties of the final elastomer polymer will depend upon the number of hydrosilane and vinyl functional groups contained in each of the starting materials and the molecular weights of each starting polymer. As would be expected, the reaction greatly increases the overall molecular weight of the silicone polymer by forming cross-linking structures between the starting polymers. The crosslinks also impart elasticity, greatly improve the film forming properties, greatly improve the substantivity and greatly reduce the solubility of the final elastomer in many
common solvents. In order to increase the organic solvent compatibility, an alpha olefin
(with from 4 to 24 carbons) is often added to the vinyl terminated polydimethylsiloxane
reaction component. The alpha olefin can then react with the hydrosilane groups during the
elastomeric crosslinking reaction to form pendant alkyl groups. Other olefin containing
compounds (such as an ethoxylated allyl alcohol) can be chosen, and added to the vinyl
terminated polydimethylsiloxane reaction component. These materials will impart a degree
of hydrophilicity making the final silicone elastomer gel more compatible with water and, in
some instances, even a water-in-oil (w/o) emulsifier.

For the purpose of making elastomers, the usual practice is to react a bis-divinyl
polydimethylsiloxane with a polydimethylsiloxane having multiple pendant
methylhydrosilane groups. Thus, the bis-divinyl polydimethylsiloxane becomes the bridging
or crosslinking group between the polydimethylsiloxanes that have the hydrosilane groups.
Typically, this crosslinking reaction is very fast after addition of the catalyst and, as described
in US Patent No. 6,936,686, visible gelation occurs within about 5 to about 40 minutes after
addition of the catalyst. This gelation is a critical point in the production of the polymer (as
described in US Patent No. 6,936,686) after which mixing is stopped to allow the reaction to
proceed without disrupting the structure of the gelled matrix.

Further, as is well known in the industry, an organic substrate having multiple
unsaturations (such as a polybutadiene or an unsaturated vegetable oil such as soybean or
olive oil) can be reacted with multi functional hydrosilane polydimethylsiloxanes to produce
an elastomeric gel. This is a well known reaction, but it can be difficult to control
reproducibly and, due to compatibility issues between the unsaturated component and the
multi functional hydrosilane polydimethylsiloxane, it may not make a clear gel.

In order to better control the reaction, produce clear elastomeric gels, follow the
teachings of US Patent 6,936,686 and to make elastomeric gels that combine an organic
molecule with silicone, the present inventors attempted to react a vegetable oil (i.e., soybean
oil and tung oil) with a bis-dihydrosilane polydimethylsiloxane. In this scheme, the bis-
dihydropolydimethylsiloxanes become the crosslinking groups between the vegetable oil
molecules, producing an elastomeric gel. The reactants were combined in a solvent medium
selected from the group consisting of low viscosity silicone oils, cyclomethicones,
hydrocarbon oils and low viscosity cosmetic esters or mixtures thereof. A zero valent
platinum divinyl complex was added as a catalyst and the mixture was heated to about 20°C to about 50°C with stirring. Surprisingly, gelation did not occur - even when the reaction mixture was stored for one week at 50°C. However, when a similar reaction scheme was run in which the bis-hydrosilane polydimethylsiloxane was replaced by polydimethylsiloxane that had multiple pendant hydrosilane groups, gelation occurred within about 4 hours to about 12 hours at 50°C. This showed that the reaction was chemically viable. However, this technique produced an elastomeric network based upon the bonding of several polydimethylsiloxanes to several triglycerides rather than the desired silicone crosslinked triglyceride oil.

The reasons for wanting to maintain a high polydimethylsiloxane to unsaturated component ratio is to be able to control the reaction and to produce a final elastomer that has a "silicone" feel and slip yet is composed of a non-silicone backbone that is crosslinked by silicone molecules.

The next approach, then, was to select another organic molecule that had multiple double bonds and a controllable molecular weight. We chose polybutadiene. The reaction of polybutadiene with bis-dihydropolydimethylsiloxane produced an elastomer gel, but surprisingly, gelling does not occur as quickly as it does during the crosslinking reaction described in US Patent 6,936,686.

OBJECTS OF THE INVENTION

It is an object of this invention to react di-functional hydrosilane terminated polysiloxanes with hydrocarbons that have multiple unsaturations in a cosmetically acceptable ester or solvent to form silicone crosslinked elastomers that have a hydrocarbon backbone.

It is an object of this invention to produce the silicone crosslinked hydrocarbon elastomers having a hydrocarbon backbone, as described in the first objective, in accordance with the teachings of US Patent No. 6,936,686.

It is an object of this invention to produce the silicone crosslinked hydrocarbon elastomers, as described in the first objective, at such a concentration in a cosmetically
acceptable solvent such that an essentially complete reaction of the crosslinking di-functional hydrosilane terminated polydimethylsiloxane occurs to form a solid gel that is then triturated and extended into additional cosmetically acceptable solvent.

It is a further object of this invention to react di-functional hydrosilane terminated polysiloxanes with a hydrocarbon that has multiple unsaturations along with an ethoxylated alkene alcohol in a cosmetically acceptable ester or solvent to form a silicone crosslinked hydrocarbon elastomer that has a hydrocarbon backbone and increased hydrophilicity.

It is yet another object of this invention to react di-functional hydrosilane terminated polysiloxanes with polyurethane molecules having multiple unsaturations and additional functional groups, such as, but not limited to, ethoxy groups, glyceryl groups, amines, siloxanes and/or aromatic groups, in a cosmetically acceptable ester or solvent to form silicone crosslinked hydrocarbon elastomers that have a polyurethane/hydrocarbon as the backbone of the polymer.

It is an object of the invention to react di-functional hydrosilane terminated polydimethylsiloxanes with polyesters having multiple unsaturations (with or without the addition of a hydrocarbon that has multiple unsaturations) in a cosmetically acceptable solvent to form silicone crosslinked elastomers that have a polyester backbone.

It is an object of the invention to react di-functional hydrosilane terminated polydimethylsiloxanes with polyurethanes having multiple unsaturations (with or without the addition of a hydrocarbon that has multiple unsaturations) in a cosmetically acceptable solvent to form silicone crosslinked elastomers that have a polyurethane backbone.

It is an object of the invention to react di-functional hydrosilane terminated polydimethylsiloxanes with polyurethanes that contain alkyl, glyceryl, dimethylsiloxy, ethoxy and/or amino functional groups, in addition to having multiple unsaturations (with or without the addition of a hydrocarbon that has multiple unsaturations) in a cosmetically acceptable solvent to form silicone crosslinked elastomers that have a polyurethane backbone as well as the additional functional groups.
Any one or more of these and/or other objects of the invention may be readily gleaned from the invention which is described hereinbelow.

**BRIEF DESCRIPTION OF THE INVENTION**

The present invention is directed to the production of clear, solvent swollen, elastomeric gels based upon α,ω-terminal dihydrosilane containing polydimethylsiloxanes reacted with non-silicone organic compounds containing multiple unsaturations (e.g. polybutadiene, unsaturated polyurethanes and unsaturated polyesters, among others) as otherwise described here. The present invention is directed to the polymeric compositions which are produced, personal care compositions to which polymeric compositions according to the present invention are added and related methods.

Compositions according to the present invention exhibit characteristics of increased solubility, consistent gelation characteristics, gel clarity and enhanced stability, as well as other favorable characteristics, including increased organic solvent compatibility/solvency as otherwise described herein. Compositions according to the present invention may be modified to provide hydrophobic as well as hydrophilic materials and amines based upon additional chemical components which may be added to the present compositions.

**DETAILED DESCRIPTION OF THE INVENTION**

In describing the present invention, the following terms shall be used.

The term "patient or subject" is used to describe a mammal, including a human to which compositions according to the present invention may be applied.

The term "effective" is used, in context, to describe an amount or concentration of a compound, composition or component, as otherwise described herein which is included or used to provide an intended effect or trait, such as emulsification (emulsifiers), emolliency, wettability, skin adherence, storage stability, and/or solubility to a formulation of a personal care product or are used to produce a compound or composition according to the present invention.
The term "personal care product" or "personal care composition" is used to describe a chemical composition used for the purpose of cleansing, conditioning, grooming, beautifying, or otherwise enhancing the appearance of the human body, especially keratinous tissue, including skin, nails and hair. Personal care products include skin care products, cosmetic products, antiperspirants, deodorants, toiletries, perfumes, soaps, bath oils, feminine care products, hair-care products, oral hygiene products, depilatories, including shampoos, conditioners, hair straightening products and other hair care products, color cosmetics such as lipsticks, creams, make-ups, skin creams, lotions (preferably comprised of water-in-oil or oil-in-water emulsions), shave creams and gels, after-shave lotions and shave-conditioning compositions and sunscreen products, among numerous others.

Personal care products according to the present invention comprise an admixture of a silicone crosslinked hydrocarbon elastomer as otherwise described herein alone or optionally in combination with an oil and water (to produce an emulsion which may be further added to other components to produce a personal care composition) in the weight percentages as otherwise disclosed herein and at least one or more additional component selected from the group consisting of an aqueous solvent (e.g. alcohol or other compatible solvent), a non-aqueous solvent, emollients, humectants, oils (polar and non-polar), conditioning agents, surfactants, thickeners/thickening agents, stiffening agents, emulsifiers, including secondary emulsifiers, medicaments, fragrances, preservatives, deodorant components, anti-perspirant compounds, skin protecting agents, pigments, dyes, coloring agents, sunscreens and mixtures thereof, among others.

Preferred personal care products according to the present invention comprise about 0.01% to about 95% by weight of an emulsion which comprises a silicone crosslinked hydrocarbon elastomer as otherwise described herein, an oil and water, with the remainder of the composition comprising at least one additional component selected from the group consisting of an aqueous solvent (e.g. alcohol or other water compatible solvent), a non-aqueous solvent, emollients, humectants, a secondary oils (polar and non-polar), conditioning agents, emulsifiers, including secondary emulsifiers, surfactants, thickeners, stiffening agents, medicaments, fragrances, preservatives, deodorant components, anti-perspirant compounds, skin protecting agents, pigments, sunscreens and mixtures thereof, among others.
The term "silicone crosslinked hydrocarbon elastomer" or "silicone crosslinked hydrocarbon polymer" describes a multi alkene functional compound which may or may not be a polymer (preferably, polybutadiene or a multi-unsaturated polyurethane, more preferably polybutadiene) which is crosslinked (or chain-extended) with a bis-hydrosilane terminated polysiloxane and exhibits favorable characteristics of gelation, solubility and stability. The polyorganosiloxane polymer (bis-hydrosilane silicone polymer) which is crosslinking (or chain-extending) the hydrocarbon according to the present invention may vary significantly in chemical composition but preferably is a polymeric composition comprised of

$$ R^2_1 \text{O-Si} - 0 - R^3_3 $$

units, where $R^2$ and $R^3$ are each independently a Ci-Cio alkyl (preferably Ci-C3 alkyl, more preferably methyl) (as described below), and optionally, in a small number of instances in certain embodiments as otherwise described herein, Si-H groups or hydroxyl groups, and may vary in average molecular weight $M_w$ from about 1,000 to about 1,500,000 or more, preferably about 1,000 to about 100,000, more preferably about 2,500 to about 25,000 or more, depending upon the final viscosity and other characteristics desired.

Silicone crosslinking agents (bis-hydrosilane terminated polyalkylsiloxanes) described herein may comprise as little as 2% and as much as 98% by weight of the final silicone crosslinked hydrocarbon elastomer, the remainder comprising the multifunctional hydrocarbon compound, but in preferred aspects the silicone crosslinking agent comprises about 50% to about 98% of the final silicone crosslinked hydrocarbon elastomer and the multifunctional hydrocarbon compound (e.g. polybutadiene) comprising about 0.1% to about 25%, about 0.25% to about 20%, about 0.5% to about 15%, about 1% to about 10% by weight of the final silicone crosslinked hydrocarbon elastomer. In preferred aspects, the multifunctional hydrocarbon comprises about 0.1% to about 10% by weight of the silicone crosslinking agent used in the preparation of the silicone crosslinked hydrocarbon elastomers of the present invention. As further described in greater detail herein, the silicone crosslinked hydrocarbon elastomers may also comprise allyl alcohol ethoxylate units and/or polyurethane units.

Silicone polymers according to the present invention which are used to produce silicone crosslinked hydrocarbon elastomers preferably comprise one Si-H group at each of
the distil ends of the elastomer (e.g. bis-hydrosilane polydimethylsiloxane) which are capable of crosslinking with multi vinyl functional hydrocarbon as otherwise described herein (e.g. polybutadiene, unsaturated polyurethane, among others).

In preferred aspects, an allyl alcohol ethoxylate may optionally comprise (in the final polymer) an amount of about 0.01% to about 7.5%, about 0.05% to about 5%, about 0.1% to about 1% by weight of the monomers/polymers which ultimately form certain embodiments of the silicone crosslinked hydrocarbon elastomer according to the present invention. The inclusion of allyl alcohol ethoxylate may increase the hydrophilicity of the final silicone crosslinked hydrocarbon elastomers according to the present invention. In certain other aspects, a polyurethane polymer also may be added to the multifunctional unsaturated hydrocarbon crosslinkable agent and reacted with the bis-hydrosilane polyorganosiloxane polymer to provide final hydrophilic silicone crosslinked hydrocarbon elastomers. The polyurethane polymer comprising (when optionally present) about 0.01% to about 15%, about 0.05% to about 10%, about 0.05% to about 5% or more by weight of the final polymeric composition in order to provide a further hydrophilic/skin adhering component, solubilizer or UV absorbing component.

The final silicone crosslinked hydrocarbon polymers (which may optionally include allyl alcohol ethoxylate and/or polyurethane units to increase hydrophilicity or, in the case of polyurethanes, hydrophilic, skin-adherent, solubilizing or UV absorbing qualities of the final polymers) according to the present invention are multifunctional unsaturated hydrocarbon compounds, including polybutadiene which are crosslinked with a bis-hydrosilane terminated polysiloxane compound (the reaction preferably occurring between the olefinic groups on the multiply unsaturated hydrocarbon and the Si-H groups and, in some cases, optional alkenyl groups on the crosslinking silicone polymer. Optionally, the crosslinking bis-hydrosilane polydimethylsiloxane may be reacted with an unsaturated polymeric silicone compound, an alpha olefin and/or an allyl alcohol ethoxylate prior to crosslinking with the multiply unsaturated hydrocarbon compound. For example, polydimethylsiloxanes with several pendant hydrosilane groups may be used to introduce an allyl alcohol ethoxylate (each allyl alcohol monomer preferably containing from 5 to about 100, about 10 to about 50, about 15 to about 45, about 10 to about 65, about 15 to about 25, about 50 to about 100, about 65 to about 85, about 75 ethoxylate/ethylene glycol units) monomer into the final silicone crosslinked hydrocarbon polymer. These groups can also be used to introduce polyurethane
or polyester compounds having the appropriate unsaturated group. Alternatively, the hydrophilic silicone elastomer (hydrophilic through introduction of allyl alcohol ethoxylate groups) and/or polyurethane or polyester may simply be admixed without further crosslinking/polymerization.

In certain preferred aspects of the present invention, the final silicone crosslinked hydrocarbon polymer is prepared from a reaction mixture which comprises a hydrosilane terminated polydimethylsiloxane polymer as described above (which may optionally further comprise an allyl alcohol ethoxylate group as described herein and/or a reactive polyurethane or polyester wherein the hydrosilane terminated polydimethylsiloxane and the allyl alcohol ethoxylate and/or polyurethane or polyester are covalently linked) as a crosslinking agent. This crosslinking agent is then reacted with a multifunctional unsaturated hydrocarbon such as polybutadiene as described herein. The polybutadiene itself may be optionally mixed or combined with an allyl alcohol ethoxylate and/or a polyurethane or polyester prior to reaction with the hydrosilane terminated polydimethylsiloxane crosslinking agent to form the final silicone crosslinked hydrocarbon polymer according to the present invention. Thus, silicone crosslinked hydrocarbon polymers according to the invention comprise the reaction product of a crosslinking silicone polymer as otherwise described herein above that contains hydrosilane groups at the distil ends of the polysiloxane, as well as an optional allyl alcohol ethoxylate component and/or an optional polyurethane or polyester component. Each of the optional allyl alcohol ethoxylate component and the optional polyurethane or polyester component independently comprise about 0.1% to about 75%, about 0.5% to about 50%, about 1% to about 10% by weight of the bis-hydrosilane polydimethylsiloxane crosslinking agent which is reacted with the multifunctional hydrocarbon polymer backbone.

Alternatively, the final silicone crosslinked hydrocarbon elastomers comprise the reaction product of a crosslinking silicone polymer as otherwise described herein (i.e., without allyl alcohol ethoxylate and/or a polyurethane) with a multiply unsaturated hydrocarbon (e.g., polybutadiene) which may optionally include an allyl alcohol ethoxylate and/or a polyurethane as described above (preferably comprising about 0.01% to about 7.5%, about 0.05% to about 5%, about 0.1% to about 1% by weight of the multifunctional hydrocarbon.
For preparation of silicone crosslinked hydrocarbon elastomers which contain a bonded polyurethane to optionally instill at least a portion of hydrophilic, self-adhering, solubilizing and/or UV absorbing character to the final silicone elastomer, the polyurethane compound comprises about 0.01% to about 7.5%, about 0.01% to about 5%, about 0.05% to about 1% of the final hydrocarbon silicone crosslinked hydrocarbon elastomer.

In certain preferred embodiments, the bis-hydrosilane polydimethylsiloxanes (silicone polymer crosslinkers) which are used to prepare silicone crosslinked hydrocarbon elastomers according to the present invention have the following structure:

\[
\begin{array}{c}
\text{R}^1 \\
\text{Si} \\
\text{R}^2 \\
\text{Si} \\
\text{R}^3 \\
\text{R}^a \\
\text{Si} \\
\text{R}^3 \\
\end{array}
\]

Where \( \text{R}^1 \) and \( \text{R}^a \) are each independently H groups;

Each \( \text{R}^2 \) and \( \text{R}^3 \) is independently a Ci-Cio alkyl group (preferably Ci-C3 alkyl, preferably methyl); and

\( n \) is from 5 to 50,000, about 10 to about 25,000, about 100 to about 10,000, about 100 to about 5,000, about 200 to about 5,000, about 500 to about 2500.

Silicone crosslinked hydrocarbon elastomers are generally formed by reacting a polysiloxane polymer which contains two Si-H bonds at distil ends of the molecule (a bis hydrosilane polydialkylsiloxane as otherwise described herein) with a multifunctional hydrocarbon (e.g. polybutadiene), each of which is reactive with a Si-H group. The multifunctional hydrocarbon may vary in size, but generally ranges in size from a molecular weight of several hundred to 25,000 or more, with a preferred molecular weight range of at least about 500 to about 10,000, about 1500-7500, about 2,000-5,000 or about 2500.

The term "crosslinking" is used to describe the reaction of the silicone polymer with the multifunctional hydrocarbon backbone in the present compositions. It is noted that the silicone polymer has only two functional groups, e.g. a Si-H group on each of the distil ends of the silicone polymer, the polymer may also be referred to as a chain extender or chain extending agent. However, it will be understood the term crosslinking may be used to refer
to the silicone polymer or crosslinker used in the present invention and the reaction of the silicone polymer or crosslinker with the (multiply unsaturated) hydrocarbon.

The term "polybutadiene" shall mean, within the context of its use, a polymeric material which is produced from butadiene monomers. Polybutadiene polymers for use in the present invention have a structure according to the chemical formula:

\[
\text{CH}_3\text{--HC=CH--CH}_2\left(\text{CH}_2\text{-HC=CH--CH}_2\right)_j\text{CH}_2\text{-HC=CH--CH}_3
\]

Where \( j \) is from 5 to about 500 or more, about 16 to about 200, about 30 to about 150, about 40 to about 100, about 90 to 110, about 100. Preferred polybutadiene polymers for use as multifunctional hydrocarbon polymer backbone herein comprise about 5% to about 50% by weight of olefinic character (also referred to as "vinyl content") based upon the molecular weight of olein within the polybutadiene molecule), about 5 to about 35% by weight olefin, about 15% to about 25% by weight olefin. Preferred polybutadiene polymers for use in the present invention comprise about 90+% cis olefins (of a mixture of cis and trans olefins within the polybutadiene molecule), about 95+% cis olefins, about 99+% cis olefins, about 99.5+% cis olefins, about 99.9+% cis olefins. It is noted that the polybutadiene component of the present invention contains a number of vinyl groups which may react with Si-H or other groups (as otherwise described herein) within the silicone elastomer crosslinking agents to produce silicone crosslinked hydrocarbon elastomers according to the present invention. In the present invention, it is contemplated that the multifunctional hydrocarbon (polybutadiene), especially including polybutadiene functions as a hydrocarbon backbone in the silicone crosslinked hydrocarbon elastomer polymers according to the present invention.

Preferred polybutadiene polymers for use in the present invention comprise about 0.005% to about 7.5% by weight of the final silicone crosslinked hydrocarbon elastomer, about 0.05% to about 5% by weight, about 0.1% to about 2.5% by weight, about 0.25 to about 4%.

Because of the physicochemical characteristics of polybutadiene and its ability to react with hydrosilane terminated polydimethylsiloxanes, the compatibility of polybutadiene as a hydrocarbon backbone with silicone crosslinking agents/chain extenders as otherwise described herein is exceptional and results in final compositions which can be manufactured
with a high degree of purity, consistency, gelation characteristics, flexibility and compatibility for inclusion in personal care products. It is noted that the inherent high compatibility between the polybutadiene polymer backbone and the silicone crosslinkers/chain extenders (of varying compositions as otherwise described herein) provides an easily and consistently manufactured silicone crosslinked hydrocarbon elastomer which can be varied quite markedly in final characteristics by incorporation of additional components (such as allyl alcohol ethoxylate and polyurethanes) as otherwise described herein.

The term "polyurethane" shall mean, within the context of its use, a polymeric urethane compound comprising at least one and preferably, two or more urethane linkages which are generally formed by reacting at least one compound containing a free alcohol (primary, secondary or tertiary), preferably at least one compound containing at least two alcohol groups ("polyol") and a diisocyanate compound. Thus, the term polyurethane as used herein incorporates dimer urethanes (those compounds which contain two urethane bonds) which are formed from a diisocyanate and a monohydric alcohol of varying structure, which structure may contain, for example, an active group or a protected active group such as a silyl-protected hydroxyl group or amine group wherein the protecting group may be removed subsequent to formation of the polyurethane or an olefinic group (such as for example, a vinyl group, acrylate or methacrylate group) which can participate in a reaction with a silane group from the silicone polymer crosslinker to produce a silicone crosslinked hydrocarbon elastomer/polyurethane composition.

In addition, polyurethanes according to the present invention preferably are formed by reacting at least one polyol (a compound which is either hydrocarbon or siloxane based and which contains at least two free hydroxy groups with a diisocyanate to produce a polyurethane, with the polyol optionally and preferably containing at least one functional group which does not participate in the polymerization reaction to form the polyurethane composition, but which, subsequent to the polymerization reaction, can be used to crosslink the polyurethane composition to a silicone elastomer in preferred compositions according to the present invention. In preferred aspects of the invention, polyurethane compounds which are reacted with a silicone elastomer to produce hydrophilic silicone elastomers preferably have sufficient hydrophilic character (for example, by containing sufficient hydroxyl groups
and/or ethoxylated-polyethylene oxide or PEG groups) to instill hydrophilic character to the final hydrophilic silicone elastomers according to the present invention.

Preferred urethane polymers according to the present invention have the general structure V:

\[
\begin{array}{c}
\text{H} \\
\text{R}^5 \quad \text{O} \quad \text{C} \quad \text{N} \quad \text{H} \quad \text{R'} \quad \text{N} \quad \text{C} \\
\text{O} \quad \text{R}^{5a} \\
\end{array}
\]

\text{V}

Where \( R^5 \) is an optionally substituted hydrocarbon or optionally substituted siloxane group, preferably, an optionally substituted (with hydroxyl groups and/or PEG groups comprising from 1 to 100 or 2 to 25 ethylene oxide units) \( \text{C}_1\text{-C}_{50} \) hydrocarbon group containing at least one olefinic group or a polyethylene oxide group comprising between 1 and 500, 2 and 100, 5 and 25, 5 and 20, 5 and 15 ethylene oxide groups which may be optionally endcapped with or contain a polymerizable group such as an alkenyl or (meth)acrylate group, or a siloxane group according to the structure:

\[
\begin{array}{c}
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{Si} \\
\text{Si} \\
\end{array}
\]

\( R^{5a} \) is an optionally substituted hydrocarbon (which may contain hydroxyl and/or PEG groups as otherwise described here) or a siloxane group, preferably, an optionally substituted \( \text{C}_1\text{-C}_{50} \) hydrocarbon group, optionally containing at least one olefinic group, or a siloxane group according to the structure:
Wherein Y is absent, O or a
\[ W - (O - Z) \quad Q -(CH_2)_q - T \] group;
X is absent or a
\[ T - (CH_2)_q - Q -(Z - O)_r \] group;
X' is absent or a
\[ W' - (O - Z)_r \quad Q - (CH_2)_q - T \] group;
Y' is absent or a
\[ T - (CH_2)_q - Q -(Z - O)_r \] group;

W is absent when r is an integer of 1 or more and W is absent or 0 when r is 0;
Q is absent or O;
q is an integer from 0 to 10, preferably 1 to 6, preferably 1 to 3;
r is an integer from 0 to 100, 0 to 40, preferably 1 to 20 or 1 to 10, with the proviso that q or r is at least 1;
T is absent or O;
W is absent when r is 0 and is a Z group when r is 1 or more;
W^2 is H;
Z is independently an ethylene group, a propylene group or a mixture of ethylene and propylene groups;
R^{2b} and R^{3b} are each independently a C_1-C_{10} alkyl group (preferably both are a C_1-C_3 alkyl group, preferably both are methyl groups), preferably R^{2b} and R^{3b} are both C_1-C_{10} alkyl groups, preferably C_1-C_3 alkyl groups, preferably both are the same C_1-C_3 alkyl group, preferably both are methyl groups;
R^{2c} and R^{3c} are independently selected from an optionally substituted C_1-C_6 alkyl group (substitution with OH or a C_1-C_3 alkyl group which itself may be optionally substituted with a hydroxyl group) and optionally, an Si-H group, an alkenyl group and/or a hydroxyl group in small percentages of the total number of R^{2c} and R^{3c} substituents within the polymer. In certain embodiments, R^{2b}, R^{3b}, R^{2c} and R^{3c} optionally may comprise a small percentage (i.e., less than about 2%, 1.5%, 1.0%, 0.75%, 0.5%, 0.25%, 0.1%, 0.05% or 0.002%) of Si-H groups, alkenyl groups and/or hydroxyl groups of the total number of R^{2b}, R^{3b}, R^{2c} and R^{3c} groups which are found in the silicone group;
R' is an optionally substituted C_2 through C_{36} (preferably, C_6 through C_{22}, most preferably an isophorone group) linear, cyclic or branch-chained saturated or unsaturated hydrocarbon group (which may be monomeric or dimeric, an aromatic group, including a phenyl or benzyl
group or substituted phenyl or benzyl group, an alkylphenyl, alkylbenzyl or substituted alkylphenyl or alkylbenzyl group);
i is an integer from 0 to 50, preferably 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 (preferably 0 or 1);
k is an integer from 0 to 100, 1 to 100, about 5 to 50, about 10 to 45, preferably about 20 to 40; and
m is from 1 to 100,000, about 1 to 25,000, about 5 to 25,000, about 50 to 20,000, about 50 to 20,000, about 100 to 20,000, about 100 to 10,000, about 200 to 5,000, about 250 to 2,500,
about 500 to about 2,000, 1 to about 1,000, 1 to about 750, 2 to about 650, about 50 to
15,000, about 10 to 10,000, about 200 to 5,000, about 250 to about 2,500, about 5 to about
150, about 3 to 100, about 5 to 250. Preferably, the polyurethane according to the present
invention is obtained by reacting a polyol (which may be hydrocarbon based or siloxane
based and contains at least two hydroxyl groups) with a diisocyanate compound to produce a
polyurethane composition accordingly.

In certain preferred aspects of the present invention in the polyurethane formula V
described above, R^5 is a O-R^6 group and R^{5a} is a R^{6a}-OH group where R^6 and R^{6a} are each
independently an optionally substituted hydrocarbon or an optionally substituted siloxane
group as set forth for R^5 and R^{5a}, respectively and generally described above.

One or more polyols and/or diisocyanates may be used to produce polyurethane
polymers according to the present invention, with preferred polyols having, in addition to
having at least two free hydroxy groups to participate in polymerization reactions to form
polyurethanes, at least one reactive alkene (unsaturated hydrocarbon) group must be available
for reaction with the hydroxilane terminated polydimethylsiloxane crosslinking agents of the
present invention, and with the diisocyanate preferably being isophorone diisocyanate.
Further preferred polyols contain multiple hydroxyl groups or alternatively, polyethylene
oxide groups wherein the PEG groups contain from 2 to 100 ethylene oxide groups,
preferably 3 to 50, 5 to 25 or 5 to 10.

Alternative polyurethanes according to the present invention also are prepared from a
diisocyanate, preferably isophorone diisocyanate, glycerin and glycerin esters, propylene
glycol and its esters, dipropylene glycol and its esters, alkyl amines, ethoxylated alkyl
amines, propoxylated alkyl amines, silicone ethoxylates and silicone propoxylates, among
others.
The term "polyol" refers to a hydrocarbon or siloxane based compound having at least two free hydroxyl groups which can participate in a reaction with diisocyanate to provide a polyurethane composition. In preferred aspects of the invention, a polyol according to the present invention, in addition to the two free hydroxyl groups which react with diisocyanate compounds, also contains an additional "reactive functional group" which, subsequent to the formation of the polyurethane compound, may participate in a crosslinking reaction with a reactive functional group on a silicone polymer admixed with the polyurethane, to produce silicone crosslinked hydrocarbon/polyurethane elastomer compositions.

The term "monohydric alcohol" refers to a compound containing a single hydroxyl group which may react with a diisocyanate compound to produce dimer urethane compounds according to the present invention. Monohydric alcohols advantageously contain at least one reactive functional group which, after formation of the dimer urethane, can react with a reactive group on a silicone polymer admixed with the dimer urethane to produce a silicone crosslinked hydrocarbon/polyurethane elastomer compositions.

The polyol(s) used to polymerize with diisocyanate may vary widely in character from hydrophilic (polar) to hydrophobic (non-polar), but are preferably hydrophilic in nature. Although a large number of polyols can be used to produce polyurethane compositions according to the present invention, preferred polyols include triglycerides which contain fatty acids having free hydroxyl groups and/or olefinic groups such as castor oil triglycerides or other triglycerides, glycerol, substituted glycerols or polyglycerols such as $C_{10}-C_{24}$ di-fatty polyglycerol (preferably, polyglycerol-2-diisostearate), di-fatty alkanolmonoglycerol, such as glycerol diricinoleate, polyethylene glycol alkylamines, especially polyethyleneglycol fatty amines, such as PEG-15 cocamine, or di-PEG-15 soyamine or related dipolyethylene glycol fatty amines, including di-PEG soyamine, polyethyleneglycol (PEG), substituted polyethyleneglycol, polydialkylsiloxane such as polydimethylsiloxane (e.g. dimethicone), or a di-polyethyleneglycol dimethicone, or related polysiloxane and bis-hydroxy terminated polybutadienes. Polyols are polymerized with a diisocyanate compound, preferably isophorone diisocyanate.

In an alternative embodiment, multiply unsaturated polyols, such as hydroxyl-terminated polybutadiene may be reacted with a diisocyanate to form a multiply unsaturated
hydrocarbon/polyurethane that can then be crosslinked with \( \alpha,\omega \)-hydrosilanepolydimethyl siloxane to form a silicone crosslinked polyurethane elastomer. Further, the hydroxyl terminated polybutadiene may be reacted with an acid, acid anhydride or acid halide to form a diester that can then be crosslinked with \( \alpha,\omega \)-hydrosilanepolydimethyl siloxane to form a silicone crosslinked hydrocarbon/ester elastomer. Alternatively, the hydroxyl terminated polybutadiene may be reacted with ethylene oxide, propylene oxide and the like to form a polyether that can then be crosslinked with \( \alpha,\omega \)-hydrosilanepolydimethyl siloxane to form a silicone crosslinked hydrocarbon/polyether elastomer.

The term "polyester" is used throughout the specification to describe a polymer which may be incorporated into compositions herein, in addition to a polyurethane as otherwise described herein or as an alternative to a polyurethane. Polyesters may be formed by reacting monomeric compounds which are diols (of a wide variety including silicone containing diols) with diacids (varying widely, but often an organic acid having between 2 and 20 carbon atoms) or alternatively one or more monomers which contain a hydroxyl group and an acid, such that an ester group may be formed by the reaction of a hydroxyl group with an acid, thus forming a polyester. Polyesters which may be used according to the present invention may vary widely depending upon the physicochemical characteristics which are to be included into compositions according to the present invention. Polyesters may be incorporated into compositions according to the present invention at a free hydroxyl group or free carboxyl acid group which may be used to start a polymerization reaction to produce a polyester sidechain. Alternative approaches are also provided and include, for example, reacting an allyl alcohol moiety with one or more of the functional groups on the crosslinked silicone polymer and then forming a polyester off of the free alcohol group from the reacted allyl alcohol.

The term "diisocyanate" is used throughout the specification to describe a linear, cyclic or branch-chained hydrocarbon having two free isocyanate groups. The term "diisocyanate" also includes halogen substituted linear, cyclic or branch-chained hydrocarbons having two free isocyanate groups. Exemplary diisocyanates include, for example, isophoronediisocyanate, m-phenylene-diisocyanate, p-phenylenediisocyanate, 4,4-butyl-m-phenylene-diisocyanate, 4-methoxy-m-phenylenediisocyanate, 4-phenoxy-m-phenylenediisocyanate, 4-chloro-m-phenyldiisocyanate, toluene diisocyanate, m-xylylene diisocyanate, p-xylylene diisocyanate, 1,4-napthalene diisocyanate, cumene-1,4-diisocyanate,
durene diisocyanate, 1,5-napthylene diisocyanate, 1,8-napthylene diisocyanate, 1,5-tetrahydronaphthylene diisocyanate, 2,6-napthylene diisocyanate, 1,5-tetrahydronaphthylene diisocyanate; \( \rho \),diphenylene diisocyanate; 2,4-diphenylhexane-1,6-diisocyanate; methylene diisocyanate; ethylene diisocyanate; trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, nonamethylene diisocyanate, decamethylene diisocyanate, 3-chloro-trimethylene diisocyanate and 2,3-dimethyltetramethylene diisocyanate, among numerous others. Isophorone diisocyanate is the preferred diisocyanate used in the present invention.

The term "unsubstituted" when used in context is used to describe a hydrocarbon moiety such as an alkyl group or alkene or other group which contains only hydrogen atoms bonded to carbons within the moiety. It can include aryl (aromatic groups such as phenyl) groups, as well. The term "substituted" is used in context to describe a hydrocarbon moiety which is substituted, i.e., it contains, within the context of its use, a pendant hydroxyl group (in preferred aspects numerous alcohol groups, an ether group (such as within a glycol or polyglycol/PEG), glycerol or polyglycerol or other group), a keto group, an amine (which may itself be substituted with alkyl groups, including fatty \((\text{C}_8\text{-C}_{30})\) alkyl groups or alkanol groups, for example), an alkyl or alkene group attached to a carbon atom of the moiety. The number of carbon atoms within a substituent group may vary from 0 to 30 or more, 0 to 24 or more, 0 to 18, 0 to 12, 0 to 10, 1 to 8, and 1 to 6 and may contain 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30 or more carbon atoms, depending upon the context of the use of the compound to which the substituent is attached. The term "optionally" means that a particular component, substituent or the like may or may not be present, depending upon the context within which the component, substituent or the like is used.

The term "oil" is used throughout the specification to describe any of various lubricious, hydrophobic and combustible substances obtained from animal, vegetable and mineral matter. These are used in combination with silicone crosslinked hydrocarbon elastomers to provide emollient characteristics (with from 1\% by weight to 99\% by weight of a combination of hydrocarbon elastomer and oil). Alternatively, the hydrocarbon elastomers may be used to form emulsions of the present invention by combining an effective amount of an oil and water with the silicone crosslinked hydrocarbon elastomers according to the present invention to provide oil-in-water or water-in-oil emulsions which may be used alone.
or in lotions or creams in certain aspects of the invention. The amount of hydrocarbon elastomer in emulsions will range from about 0.1% to about 50%, about 0.25% to about 25%, about 0.5% to about 20%, about 1% to about 15%, about 2% to about 10%, about 0.75% to about 5% by weight; the amount of oil will range from about 0.1% to about 50%, about 0.25% to about 25%, about 0.5% to about 20%, about 1% to about 15%, about 2% to about 10%, about 0.75% to about 5% by weight and the amount of water will range from about 0.25% to about 95%, about 0.5% to about 85%, about 0.75% to about 80%, about 1% to about 75%, about 2% to about 70%, about 5% to about 65%, about 1% to about 15%, about 2% to about 10%, about 0.75% to about 5% by weight; about 45% to about 99% by weight of the emulsion produced.

Emollient oils for use in the present invention may include petroleum-based oil derivatives such as purified petrolatum and mineral oil. Petroleum-derived oils include aliphatic or wax-based oils, aromatic or asphalt-based oils and mixed base oils and may include relatively polar and non-polar oils. Non-polar oils are generally oils such as petrolatum or mineral oil or its derivatives which are hydrocarbons and are more hydrophobic and lipophilic compared to synthetic oils, such as esters, which may be referred to as polar oils. It is understood that within the class of oils, the use of the terms "non-polar" and "polar" are relative within this very hydrophobic and lipophilic class, and all of the oils tend to be much more hydrophobic and lipophilic than the water phase which is used to produce the water-in-oil emulsion of the present invention. Preferred hydrophobic oils for use in the present invention include mineral oil and petrolatum. Preferred less hydrophobic (i.e., more polar) oils for use in the present invention include a number of maleates, neopentanoates, neopentanoyle, citrates and fumarates, and any other cosmetically acceptable ester emollient.

In addition to the above-described oils, certain essential oils derived from plants such as volatile liquids derived from flowers, stems and leaves and other parts of the plant which may include terpenoids and other natural products including triglycerides may also be considered oils for purposes of the present invention.

Petrolatum (mineral fat, petroleum jelly or mineral jelly) and mineral oil products for use in the present invention may be obtained from a variety of suppliers. These products may range widely in viscosity and other physical and chemical characteristics such as molecular
weight and purity. Preferred petrolatum and mineral oil for use in the present invention are those which exhibit significant utility in cosmetic and pharmaceutical products. Cosmetic grade oils are preferred oils for use in the present invention.

Additional oils for use in the present invention may include, for example, mono-, di- and tri- glycerides which may be natural or synthetic (derived from esterification of glycerol and at least one organic acid, saturated or unsaturated, such as for example, such as butyric, caproic, palmitic, stearic, oleic, linoleic or linolenic acids, among numerous others, preferably a fatty organic acid, comprising between 8 and 26 carbon atoms). Glyceride esters for use in the present invention include vegetable oils derived chiefly from seeds or nuts and include drying oils, for example, linseed, iticica and tung, among others; semi-drying oils, for example, soybean, sunflower, safflower and cottonseed oil; non-drying oils, for example castor and coconut oil; and other oils, such as those used in soap, for example palm oil. Hydrogenated vegetable oils also may be used in the present invention. Animal oils are also contemplated for use as glyceride esters and include, for example, fats such as tallow, lard and stearin and liquid fats, such as fish oils, fish-liver oils and other animal oils, including sperm oil, among numerous others. In addition, a number of other oils may be used, including C_{12} to C_{30} (or higher) fatty esters (other than the glyceride esters, which are described above) or any other acceptable oil.

The term "cosmetic ester" is used to describe any ester which is cosmetically compatible, i.e., may be safely incorporated into cosmetic products. In preferred aspects of the invention, a cosmetic ester has between 12 and 26 carbon atoms, about 14 and 20 carbon atoms within the ester compound, even more preferably about 16 and 19 carbon atoms within the ester compound, with a preferred cosmetic ester having at least one of the two chains, i.e., either the ether portion of the ester or the acyl portion of the ester being an optionally substituted (with alkyl or hydroxyl), preferably an unsubstituted branched-chain alkyl group. Preferred alkyl chains which correspond to the ether portion of the cosmetic ester include, for example, C_{3}-C_{18} branched-chain alkyl groups (including alkyl groups having sany number of carbon atoms within that range), such as, for example, isopropyl, isobutyl, tert-butyl, isopentyl, neo-pentyl, branched-chain hexyl, branched-chain heptyl, branched-chain octyl, branched-chain nonyl, branched-chain decyl, branched-chain undecyl, branched-chain dodecyl, branched-chain tridecyl, branched-chain tetradecyl, branched-chain pentadecyl, branched-chain hexadecyl, branched-chain heptadecyl and branched-chain octadecyl groups.
linked to varying acyl groups ranging in size from \( C_2 - C_{22} \) acyl groups (including acyl groups having any number of carbon atoms within that range), accordingly. It is noted here that alternatively, the acyl group may be a branched-chain acyl group and the ether group may be an unbranched, straight chain, alkyl group. Both ether and acyl groups may comprise branched-chain alkyl groups as well.


Silicone crosslinked hydrocarbon elastomers according to the present invention are prepared by well known methods in the art to produce elastomers with the following idealized structure:
Where $n$ and $j$ are as otherwise described herein.

Reaction Scheme

\[
\text{CH}_3\text{-CH} = \text{CH}-\text{CH}_2 \left( \text{CH}_2-\text{CH} = \text{CH}-\text{CH}_2 \right)_j \text{CH}_2-\text{CH} = \text{CH}-\text{CH}_3
\]
Where \( j \) is an integer from 5 to about 500; and

\( k, 1 \) and \( m \) are each independently an integer from 5 to about 50,000.

As shown in the reaction scheme above, to prepare compositions according to the present invention, a multifunctional hydrocarbon, preferably polybutadiene, is reacted with a hydrosilane terminated silicone polymer (e.g. bis-hydrosilane polydimethylsiloxane) in solvent (such as isododecane, cyclodecamethylsiloxane, mixtures of isododecane and cyclodecamethylsiloxane, among others) in the presence of catalyst at elevated temperature. In preferred methods, the polybutadiene component is first added to the solvent and thereafter, the silicone crosslinking polymer is then added to the polybutadiene/solvent mixture all at once or slowly. The components are then heated to approximately 50°C whereupon polymerization catalyst is added. The reaction mixture is allowed to react for a period of between approximately 8-24 hours, usually about 12-16 hours resulting in a gelled product which may be stored, packaged and/or formulated into final product. The above reaction scheme may be modified to provide a silicone crosslinked hydrocarbon elastomer which comprises allyl alcohol ethoxylate groups and/or polyurethane or polyester compounds in order to instill hydrophilicity, adhesion characteristics, solubilizing and/or UV absorbing characteristics to final formulations.
Polyurethanes which also may be used in the present invention may be prepared using a general scheme involving the reaction of at least about two moles of a monohydric alcohol or at least about one mole of (purchased commercially or prepared using well known methods in the art) polyol with at least one mole of a diisocyanate in the presence of heat and either an amine or tin catalyst such as stannous octanoate. Each isocyanate moiety thereby may be converted to a urethane moiety while maintaining the presence of "free and unreacted" unsaturated reactive functional groups which may be later used to further react with the bis-hydrosilane terminated polydimethylsiloxane crosslinking agents in admixture. Heat is maintained until "no FTIR detectable isocyanate groups are seen." The reaction mass is cooled, washed, neutralized dried and distilled if necessary. The product should be essentially odorless, and is usually a yellow to amber liquid and contains a substantial absence of isocyanate or residual catalyst.

In certain embodiments according to the present invention which includes an unsaturated polyurethane component, the polyurethane and bis-dihydriopolydimethylsiloxane polymer may be reacted together to produce a polyurethane modified silicone elastomer component according to the present invention. The silicone polymer and polyurethane are reacted without solvent or preferably in the presence of solvent according to the nature of the reactive functional group on the silicone elastomer and the polyurethane and the type of reaction which produces a crosslinked product, where applicable. Preferably, the solvent is isododecane or a cosmetic ester as per US patent number 6,936,686. The reactions may be conducted at temperatures at (ambient) or below room temperature, but preferably the reactions occur at elevated temperatures alone or in the presence of a catalyst or acid scavenger (such as triethyl amine, etc.). The resulting silicone crosslinked hydrocarbon elastomer/polyurethane polymer (especially the final viscosity) may vary according to the reaction conditions chosen to effect the crosslinking reaction. Alternatively, allyl alcohol ethoxylate may be added to the reaction between the silicone elastomer and polyurethane to produce polyurethane and alcohol ethoxylate modified silicone elastomers for further reaction or alternatively, the allyl alcohol ethoxylate may be used to substitute for the polyurethane to provide hydrophilic silicone elastomers comprising alcohol ethoxylate groups. Once prepared, the modified silicone crosslinkers which contain distil hydrosilane groups, may be reacted with the multifunctional hydrolinkers containing polybutadiene, squalene) to provide silicone crosslinked hydrocarbon elastomers according to the present invention exhibiting varying characteristics.
The silicone crosslinked hydrocarbon elastomer compositions prepared above may be added to a number of additional components to produce favorable characteristics in personal care products, including skin care products, cosmetic products, antiperspirants, deodorants, perfumes, toiletries, soaps, bath oils, feminine care products, hair-care products, oral hygiene products, depilatories, including shampoos, conditioners, hair straightening products and other haircare products, color cosmetics such as lipsticks, creams, make-ups, skin creams, lotions and sunscreen products, among numerous others.

Compounds/compositions of the present invention may be used as thickening agents and emulsifiers having a number of additional characteristics including emollient and adherence characteristics for the skin and epithelial tissue such as hair, ungual tissue (nails), skin and related mucous membranes, especially given the combined attributes of emolliency (from the silicone elastomer) and skin adherence, viscosity enhancement and favorable skin interaction (generally) and wettability, enhanced solubility, UV absorbing characteristics, etc. and other attributes (which can be formulated into the polymer depending upon the inclusion of which allyl alcohol ethoxylate and/or polyurethane is chosen). By addition of an effective amount of the present compositions, emulsion formulations which may be included in personal care products, including cosmetic and toiletry products will acquire a soothing and favorable interaction which promotes skin adherence, moisturization, wettability and favorable viscosity attributes of the final personal care formulation. In addition, because the size of the silicone elastomer and polyurethane can be varied substantially, numerous characteristics may be "dialed in" to the final hydrophilic silicone elastomers in addition to the basic emulsifier characteristics and incorporated into personal care products ranging from lotions and creams to thickened formulations to be used in stick deodorants and related products can be readily formulated.

Effective amounts of the present compositions may also serve a dual function, for example, as emulsifiers exhibiting gloss-producing characteristics for lipsticks and lip balm formulations in the personal care, cosmetic and toiletry industries as a substitute(s) for castor oil normally used in such formulations, especially where the polyurethane is made from castor oil. The compounds of the present invention exhibit outstanding solubility characteristics for producing water-in-oil or oil-in-water emulsions and may form the basis
for numerous and varied personal care compositions, depending upon the components of the final silicone crosslinked hydrocarbon elastomer composition.

Silicone crosslinked hydrocarbon elastomers according to the present invention exhibit one or more of a number of unexpected characteristics including providing compositions containing polyurethanes which do not exhibit a typical "sticky tactile" sensation when deposited on the skin of a subject (such as an animal, including a human) and provide a smooth, non-tacky feel which is especially advantageous for bodycare lotions and other personal care compositions used on the skin and hair of a subject. In addition, the compositions of the present invention provide "substantivity" to personal care products and can be used to accommodate functional ingredients, especially including hydrophilic functional ingredients such as polar hydrophilic materials. In certain hydrophilic silicone crosslinked hydrocarbon elastomers (which comprise allyl alcohol ethoxylate and/or hydrophilic polyurethane components) because of the hydrophilic nature of the compositions, it is easier to formulate water-in-oil emulsions, including water-in-oil in water emulsions, which results in an emulsion or final personal care composition which accommodates (on a relative scale compared to typical silicone elastomers) large amounts of water, thus reducing the cost of components and the final cost of the formulated personal care composition.

In addition, silicone crosslinked hydrocarbon elastomer compositions according to the present invention may be used advantageously as couplers (in emulsions or in compositions which are not emulsions)- for example, to couple a hydrophilic or hydrophobic component such as water and an aliphatic component (such as an oil, fatty waxes and esters) into a single formulation.

In general, silicone crosslinked hydrocarbon elastomer compositions according to the present invention are included in personal care products/formulations in effective amounts, i.e., amounts which produce an intended effect. The amount of composition generally ranges from about 0.01% to about 50% by weight or more of personal care formulations according to the present invention. Alternatively, compositions according to the present invention may be included in final personal care compositions in amounts ranging from about 0.05% to about 45% by weight, about 0.1% to about 40% by weight, about 0.25% to about 30% by weight, about 0.25% to about 20% by weight, about 0.5% to about 15% by weight, about
0.75% to about 10% by weight, about 1% to about 7.5% by weight, about 1% to about 5% by weight and about 1% to about 3% by weight of the final personal care composition.

In preferred embodiments of emulsion-based formulations (wherein the formulation comprises an oil, water and the present composition as an emulsifier, compositions according to the present invention are included in amounts ranging from about 0.1% to about 25% by weight, in addition to the oil and water and optionally, other components. Emulsions according to the present invention may be used in any number of personal care products, but find particularly useful applicability in formulations which are based upon lotions and/or skin creams.

The compositions according to the present invention may be used in numerous additional compositions. In the case of shampoos and conditioners, compositions according to the present invention are included in amounts ranging from about 0.1% to about 15% by weight of the formulation, in certain cases to instill conditioning attributes in addition to surfactant-like qualities. One can use amounts up to about 20% to 25% in shampoos and conditioners. For example, in haircare products, such as shampoos, rinses, conditioners, hair straighteners, hair colorants and permanent wave formulations, the compositions according to the present invention preferably comprise about 0.1% to about 20% by weight, more preferably about 0.25% to about 5% by weight of the final end-use hair-care composition. Other components which may be included in hair-care formulations include, for example, a solvent or diluent such as water and/or alcohol, other surfactants, emulsifiers, thickeners, coloring agents, dyes, preservatives, additional conditioning agents and humectants, among numerous others.

In the case of shave creams and gels, after-shave lotions and shave-conditioning compositions (for example, pre-electric shave formulations), the compositions according to the present invention are included in amounts ranging from about 0.25% to about 15% or more by weight, more preferably about 0.5% to about 10% by weight. Other components which may be included in these end-use compositions include, for example, water, and at least one or more of emollients, humectants and emulsifiers, thickeners and optionally, other conditioning agents, medicaments, fragrances and preservatives.
In the case of skin lotions and creams, the present compositions are included in amounts ranging from about 0.25% to about 45% by weight, more preferably, about 0.5 to about 25% by weight. Additional components which may be employed in these compositions include, for example, water, emollients and emulsifiers, surfactants, oils, and optionally, other conditioning agents, thickeners, medicaments, fragrances and preservatives.

In the case of sunscreens and skin-protective compositions, the present compositions are included in amounts ranging from about 0.25% to about 45% or more by weight, preferably about 0.5% to about 25% by weight of the final formulations. These compositions form the basis of lotions or skin creams which may be used to deliver pigments and/or sunscreen components in compositions according to the present invention. Additional components which may be employed in these compositions may include, for example, a UV absorbing composition such as para-amo
to benzoic acid (PABA) or a related UV absorber or a pigment such as TiO₂ and optional components including, for example, one or more of an oil, water, suspending agents, other conditioning agents and emollients, among others.

In the case of bar and liquid soaps, compositions according to the present invention are included for their surfactant and emollient-like qualities in amounts ranging from about 0.25% to about 20% by weight or more, preferably about 0.5% to about 10% by weight. Additional components which may be included in bar and liquid soaps include water and surfactants and optionally, bactericides, fragrances and colorants, among others.

Other personal care products, not specifically mentioned, generally comprise about 0.1% to about 50% by weight of a composition according to the present invention and other components of personal care products as otherwise set forth in detail herein.

The present invention also relates to a method of preparing a silicone crosslinked hydrocarbon elastomer according to the present invention by reacting a silicone elastomer crosslinking composition with a multifunctional hydrocarbon as otherwise described herein. Prior to crosslinking the multifunctional hydrocarbon composition, the silicone elastomer may be reacted with from about ss0.25% to about 20%, about 1% to about 15%, about 1% to about 10% by weight of the reaction mixture of an allyl alcohol ethoxylate monomer and/or a polyurethane as otherwise described herein either stepwise, or in a single step reaction, preferably in a single pot. As indicated, the optional allyl alcohol ethoxylate monomer and/or
polyurethane may be reacted with the polyorganosiloxane prior to crosslinking the multifunctional hydrocarbon composition. The reactions are optimally prepared in a single pot, although separation and purification of intermediates prior to further reaction may prove to be advantageous in certain instances. The silicone elastomer is reacted with multifunctional hydrocarbon as described above to provide silicone crosslinked hydrocarbon elastomers pursuant to the present invention, which may be stored, packaged and/or formulated into personal care compositions according to the present invention.

Typically, in preparing the present compositions, visible gelation occurs within about 8 to about 36 hours (usually within 12 hours to 24 hours) during which time, the reaction mixture may or may not be stirred. Once gelation occurs, the reaction mixture is left to stand without mixing for an additional period of time from about 4 to about 24 hours or more. After which reaction period the swollen gel is processed by milling to produce a smooth, clear paste.

An alternative method to prepare the silicone crosslinked hydrocarbon gel is to begin with a concentration of reactants that is in the range of 20% to 30% (or higher - up to about 80%), dissolved in a suitable solvent, heating the mixture to 40°C to 50°C, or higher, with mixing. Once uniform and at the desired temperature, the catalyst is added to the mixture and mixed in well. The batch is then allowed to stand at temperature for 8 to about 36 hours (usually within 12 hours to 24 hours) during which time, gelation occurs resulting in a glassy, friable material. This material is then crushed or pulverized using a Hockmeyer mixer equipped with a disperser blade (other pulverizing equipment may be used). At this time additional solvent is added to reduce the total solids level to a desired amount in the 3% to 15%, more desirably 5% to 12%, and more desirably in the 7% to 10% range. The resulting mixture is refined using a homogenizing mixer such as a Silverson or a colloid mill into a soft paste like material.

The following examples are intended to be illustrative of the invention concepts, and are meant to provide formulas and manufacturing methods to show some of the variations and applications that are possible.
EXAMPLES

The following examples are intended to be illustrative of the invention concepts, and are meant to provide formulas and manufacturing methods intended to show some of the variations and applications that are possible. They are not to be considered as limiting.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Example 1 % w/w</th>
<th>Example 2 % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isododecane</td>
<td>77.92</td>
<td>xxxx</td>
</tr>
<tr>
<td>Cyclodecamethylsiloxane</td>
<td>xxxx</td>
<td>77.95</td>
</tr>
<tr>
<td>Polybutadiene (28% vinyl content)</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Bis-hydrosilane polydimethylsiloxane</td>
<td>21.66</td>
<td>21.66</td>
</tr>
<tr>
<td>Catalyst (Tetramethyldivinyl disiloxane)</td>
<td>0.10</td>
<td>0.07</td>
</tr>
<tr>
<td>Platinum complex</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The silicone crosslinked hydrocarbon elastomers shown in these two examples are made per US Patent No. 6,936,686, from a α,ω-terminal dihydrosilane polydimethylsiloxane reacted with polybutadiene. The components are combined with the exception of the catalyst and mixed until uniform. The catalyst was added, mixing was continued and the mixture was heated to 50°C. When gelation did not occur within the anticipated time frame as taught by US Patent No. 6,936,686, the formula was transferred to a glass container for storage in a 50°C or room temperature oven. When inspected the following morning, the product was beginning to gel. Thus, overnight storage (approx. 14 to 16 hours) at 50°C or room temperature was required for gelation to become apparent. The crosslinking reaction was allowed to continue for an additional 24 hours and the product was then milled per the procedures of US Patent 6,936,686.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Example 3 % w/w</th>
<th>Example 4 % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethypolysiloxane (5cps)</td>
<td>77.95</td>
<td>xxxx</td>
</tr>
<tr>
<td>Isononyl Isononanoate</td>
<td>xxxx</td>
<td>77.95</td>
</tr>
<tr>
<td>Polybutadiene (28% vinyl content)</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Bis-hydrosilane polydimethylsiloxane</td>
<td>21.66</td>
<td>21.66</td>
</tr>
<tr>
<td>Catalyst (Tetramethyldivinyl disiloxane)</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Platinum complex</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Examples 3 and 4 show the use of alternate solvents that are useful in formulating personal care products. These examples gelled with overnight storage at 50°C and were able to be processed into a smooth, clear pastelike product with milling, as per US Patent 6,936,686.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Example 5</th>
<th>Example 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isododecane</td>
<td>77.95</td>
<td>79.43</td>
</tr>
<tr>
<td>Squalene</td>
<td>0.32</td>
<td>xxxx</td>
</tr>
<tr>
<td>Polybutadiene (28% vinyl content)</td>
<td>xxxx</td>
<td>0.50</td>
</tr>
<tr>
<td>Bis-hydrosilane polydimethylsiloxane</td>
<td>21.66</td>
<td>20.00</td>
</tr>
<tr>
<td>Catalyst (Tetramethyldivinyl disiloxane)</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Platinum complex</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Example 5 shows the use of an alternative multiple alkene molecule and Example 6 shows the use of higher levels of the multiple unsaturated compound. While this reaction may be possible, increasing the amount of alkene material results in an elastomer that lacks the slip and luxurious feel of a higher silicone content elastomer and is therefore not desirable.

Example 5 shows the need for a multiply unsaturated hydrocarbon containing more than six olefinic bonds and higher temperatures may be required for gelation to be consistent with a commercial product.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Example 7</th>
<th>Example 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isododecane</td>
<td>77.95</td>
<td>77.95</td>
</tr>
<tr>
<td>Polybutadiene (80% vinyl content)</td>
<td>0.32</td>
<td>xxxx</td>
</tr>
<tr>
<td>Polybutadiene (85% vinyl content)</td>
<td>xxxx</td>
<td>0.32</td>
</tr>
<tr>
<td>Bis-hydrosilane polydimethylsiloxane</td>
<td>21.66</td>
<td>21.66</td>
</tr>
<tr>
<td>Catalyst (Tetramethyldivinyl disiloxane)</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>Platinum complex</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Examples 7 & 8 produced extremely hard polymers that are not commercially acceptable elastomers. This points out the importance of determining the correct number of double bonds available to crosslink with the hydrosilane terminated silicone polymer. Too few and gelation does not occur, too many and an unusable, intractable polymer results.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Example 9</th>
<th>Example 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isododecane</td>
<td>xxxx</td>
<td>77.60</td>
</tr>
<tr>
<td>1,9-dihydroxypolybutadiene</td>
<td>80.925</td>
<td>xxxx</td>
</tr>
<tr>
<td>{M_w 2100 (65% vinyl content)}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In Example 9, a 1,9-dihydroxy polybutadiene (65% w/w vinyl content) was reacted with an isocyanate functional silane (3-isocyanatopropyltriethoxysilane) to produce triethoxysilyl urethane end caps on the terminal hydroxy group of the polybutadiene and on the C-9 secondary alcohol. This material was then crosslinked (Example 10) with the bis-hydrosilane polydimethylsiloxane to form an elastomer. Gelation took 5 days at room temperature after initial heating and mixing for 1 hour at 40°C.

These reactions demonstrate that other materials, not just unsaturated hydrocarbons, can be successfully crosslinked with bis-hydrosilane polydimethylsiloxane. The point is that a hydroxy terminated polybutadiene can be first reacted to form a desired product such as: a diester, a diurethane, a polyurethane, a polyester or a polyether. The level of unsaturation can be easily controlled in, for example, a polyurethane, by adjusting the amount of hydroxy terminated polybutadiene relative to another diol such as: ethylene glycol, propylene glycol, 1,3-propane diol, 1,4-butylene glycol, 1,6-hexylene glycol, bis-PEG-ldimethicone and the like and then forming the polyurethane by reaction with a diisocyanate. Similar diol mixtures can be used to make diesters, diurethanes, polyesters and polyethers. Thus, we can now control many properties of silicone crosslinked hydrocarbon based elastomers, such as, clarity, tackiness, compatibility with solvents and cosmetic raw materials, hydrophilicity, molecular weight and degree of crosslinking.

The following are presented as examples of silicone crosslinked hydrocarbon gels that contain an amino-functional polyurethane.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Example 11</th>
<th>Example 12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isododecane</td>
<td>% w/w</td>
<td>% w/w</td>
</tr>
<tr>
<td>Isododecane</td>
<td>71.6</td>
<td>xxxx</td>
</tr>
<tr>
<td>Isononyl Isononanoate</td>
<td>xxxx</td>
<td>71.6</td>
</tr>
<tr>
<td>Polybutadiene (28% vinyl content)</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Bis-hydrosilane polydimethylsiloxane</td>
<td>21.2</td>
<td>21.2</td>
</tr>
<tr>
<td>Example 13</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Catalyst (Tetramethyldivinyl disiloxane)</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Platinum complex</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

The Example 13 is a commercial product (Polyderm PPI SI-LSA). It is a polyurethane manufactured by Alzo International, Inc. that conforms to the following molar formula:
The product from Example 13 is steam stripped to react any residual diisocyanate to amine; the product is then washed to remove catalyst and amine. It is necessary to remove these compounds because they will interfere with the hydrosilane crosslinking. This product is typical of the material added in Examples 11 and 12. Examples 11 and 12 produce silicone crosslinked hydrocarbon/polyurethane elastomers that have a matte finish on skin, a very soft elegant feel, and the ability to form water-in-oil emulsions. In addition, because of the inclusion of the amino functional polyurethane, the elastomer can ionically react with and complex anionic compounds such as dyes and sunscreens. Thus, these materials become much less water soluble and become trapped within the silicone crosslinked hydrocarbon polymer and yet retain their functionality.

Further Examples-Incorporation of Polyesters

The following are presented as examples of silicone crosslinked hydrocarbon gels that contain an amino-functional polyester.

The Example 16 is a product manufactured by Alzo International, Inc. that conforms to the following molar formula:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Example 16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis PEG-1 dimethicone</td>
<td>from 1.5 to 1.9</td>
</tr>
<tr>
<td>PEG-2 Soyamine</td>
<td>from 0.5 to 0.1</td>
</tr>
<tr>
<td>Dibasic acid (i.e. adipic acid)</td>
<td>from 1.0 to 2.0</td>
</tr>
<tr>
<td>Methanesulfonic acid</td>
<td>0.15</td>
</tr>
</tbody>
</table>
The product from Example 16 is first neutralized with sodium bicarbonate or sodium carbonate, and then washed to remove catalyst. It is important to remove these compounds because they will interfere with the hydrosilane crosslinking reaction. These product mole ratios are typical of the materials added in Examples 14 and 15. Examples 14 and 15 produce silicone crosslinked hydrocarbon/polyester amino functional elastomers (by incorporating the product of example 16 into the compounds/composition) that have a soft elegant feel, and the ability to form water-in-oil emulsions. In addition, because of the inclusion of the amino functional polyurethane, the elastomer can ionically react with and complex anionic compounds such as dyes and sunscreens. Thus, these materials become much less water soluble and become trapped within the silicone crosslinked hydrocarbon polymer and yet retain their functionality.
What is claimed:

1. A silicone crosslinked hydrocarbon elastomer comprising the reaction product of bis-dihydrosilane polydialkylsiloxane and a hydrocarbon containing multiple unsaturations.

2. The hydrocarbon elastomer according to claim 1 wherein said hydrocarbon is polybutadiene.

3. The hydrocarbon elastomer according to claim 1 or 2 wherein said hydrocarbon is a compound according to the chemical structure:

   \[
   \text{CH}_3\text{=HC}\text{=CH}\text{=CH}_2\left(\text{CH}_2\text{=HC}\text{=CH}\text{=CH}_2\right)\text{jCH}_2\text{=HC}\text{=CH}\text{=CH}_3
   \]

   Where j is an integer from 5 to 500.

4. The hydrocarbon elastomer according to claim 3 wherein j is 16 to 200.

5. The hydrocarbon elastomer according to claim 3 wherein j is 30 to 110.

6. The hydrocarbon elastomer according to any of claims 2-5 wherein said polybutadiene comprises at least about 90% by weight cis olefins.

7. The hydrocarbon elastomer according to any of claims 1-5 wherein said bis-dihydrosilane polydialkylsiloxane is a compound according the chemical structure:

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

   where \( R^1 \) and \( R^a \) are each \( H \); 
   each \( R^2 \) and \( R^3 \) is independently a \( C_i-C_{10} \) alkyl group; and 
   \( n \) is from 5 to 50,000.
8. The hydrocarbon elastomer according to claim 7 wherein n is an integer from about 200 to about 5000.

9. The hydrocarbon elastomer according to claim 7 wherein n is an integer from about 500 to about 2500.

10. The hydrocarbon elastomer according to any of claims 7-9 wherein R² and R³ are each independently a C₁-C₃ alkyl group.

11. The hydrocarbon elastomer according to any of claims 7-10 wherein R² and R³ are each a methyl group.

12. The hydrocarbon elastomer according to any of claims 1-11 further comprising about 0.01% to about 7.5% by weight of allyl alcohol ethoxylate units.

13. The hydrocarbon elastomer according to claim 12 wherein each of said allyl alcohol ethoxylate units comprises about 5 to about 100 ethylene glycol units.

14. The hydrocarbon elastomer according to any of claims 1-13 further comprising about 0.01% to about 7.5% by weight of a polyurethane.

15. The hydrocarbon elastomer according to any of claims 1-13 further comprising about 0.01% to about 7.5% by weight of a polyester.

16. The hydrocarbon elastomer according to any of claims 1-15 in the form of a clear gel elastomer.

17. A silicone crosslinked hydrocarbon elastomer having the idealized chemical structure:
Where j is an integer from 5 to about 500;
k, m and l is each independently an integer from 5 to about 50,000.

18. The hydrocarbon elastomer according to claim 17 in the form of a clear gel elastomer.

19. The hydrocarbon elastomer according to claim 17 or 18 wherein j is from 16 to about 200.

20. The hydrocarbon elastomer according to claim 17 or 18 wherein j is about 30 to about 110.

21. The hydrocarbon elastomer according to any of claims 17 to 20 wherein k is about 100 to about 5,000.

22. The hydrocarbon elastomer according to any of claims 17 to 21 wherein k is about 100 to about 2500.

23. A silicone crosslinked hydrocarbon elastomer according to any of claims 1-22 in combination with an oil and optionally water.
24. The hydrocarbon elastomer according to claim 23 wherein said elastomer is combined with water and optionally, at least one oil in effective amounts to form an emulsion.

25. The hydrocarbon elastomer according to claim 24 wherein said emulsion is a water-in-oil emulsion.

26. The hydrocarbon elastomer according to claim 24 wherein said emulsion is an oil-in-water emulsion.

27. A personal care product composition comprising an effective amount of a silicone crosslinked hydrocarbon elastomer according to any of claims 1-22 in combination with at least one additional component selected from the group consisting of an aqueous solvent, a non-aqueous solvent, emollients, humectants, oils, conditioning agents, surfactants, thickeners/thickening agents, stiffening agents, emulsifiers, secondary emulsifiers, medicaments, fragrances, preservatives, deodorant components, anti-perspirant compounds, skin protecting agents, pigments, dyes, coloring agents, sunscreens and mixtures thereof.

28. The personal care product composition according to claim 27 comprising water as an additional component.

29. The personal care product composition according to claim 27 or 28 which is selected from the group consisting of skin care products, antiperspirants, deodorants, toiletries, perfumes, soaps, bath oils, feminine care products, hair-care products, oral hygiene products, depilatories, color cosmetics, creams, make-ups, skin creams, lotions, shave creams and gels, after-shave lotions and shave-conditioning compositions and sunscreen products.

30. The personal care product composition according to claim 27 which is selected from the group consisting of depilatories, shampoos, conditioners, hair straightening products, lipsticks, creams, make-ups, skin creams and lotions.

31. A method of making a silicone crosslinked hydrocarbon elastomer comprising reacting a silicone polymer crosslinking agent with a multifunctional hydrocarbon in the presence of a catalyst and optionally in the presence of solvent selected from the group
consisting of isododecane, cyclomethicone, dimethicone or a cosmetic ester at a temperature ranging from about ambient temperature to up to about 100°C for a period sufficient to produce a clear elastomeric gel.

32. The method according to claim 31 wherein said unsaturated hydrocarbon component elastomer ranges from about 0.1% to about 25% of the monomers in the reaction mixture and said silicone crosslinking agent comprises about 2% to about 99% by weight of the monomers in the reaction mixture.

33. The silicone crosslinked hydrocarbon elastomer of claim 1 in which the unsaturated component is an unsaturated compound selected from the group consisting of an unsaturated diester, an unsaturated diurethane, an unsaturated polyester, an unsaturated polyurethane, an unsaturated polyethoxylate, and mixtures thereof, optionally including (poly)butadiene compound.

34. The silicone crosslinked hydrocarbon elastomer of claim 33 in which the reaction is run in the presence of a solvent selected from the group consisting of isododecane, cyclomethicone, dimethicone, a cosmetic ester or mixtures thereof at a temperature ranging from about ambient temperature to about 50°C for a period sufficient to produce a clear elastomeric gel.