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(54) **CLEAR SILICONE MICROEMULSIONS FORMED SPONTANEOUSLY**

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(57) **ABSTRACT**

Clear microemulsions are formed spontaneously without mixing, stirring, shearing, or input of mechanical energy for agitating ingredients used in making microemulsions, by simply combining (i) water; (ii) a volatile siloxane; (iii) a long chain or high molecular weight silicone polyether; and, as an optional ingredient, (iv) a cosurfactant such as a monohydroxy alcohol, an organic diol, an organic triol, an organic tetraol, a silicone diol, a silicone triol, a silicone tetraol, and a nonionic organic surfactant. In an alternate embodiment, a non-volatile siloxane is included as an ingredient, and the silicone polyether is a long chain or high molecular weight silicone polyether, or a short chain or low molecular weight silicone polyether.

# CLEAR SILICONE MICROEMULSIONS FORMED SPONTANEOUSLY

## CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not applicable.

## STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

## REFERENCE TO A MICROFICHE APPENDIX

[0003] Not applicable.

## FIELD OF THE INVENTION

[0004] This invention is related to clear silicone microemulsions that form spontaneously without input of significant mechanical energy, and more particularly to the use of certain longer chain, higher molecular weight species of silicone polyether (SPE) as primary surfactant. They can also be used in forming clear silicone microemulsions containing oil phases consisting of mixtures of volatile as well as nonvolatile silicone oils.

## BACKGROUND OF THE INVENTION

[0005] Microemulsions are clear or transparent because they contain particles smaller than the wavelength of visible light, i.e., typically 10-100 nanometer. They can contain oil droplets dispersed in water (O/W), water droplets dispersed in oil (W/O), or they may be bi-continuous in their structure. They are characterized by ultra low interfacial tension between oil and water phases.

[0006] While U.S. Pat. No. 5,705,562 (Jan. 6, 1998) teach the use of short chain or low molecular weight silicone polyethers in preparation of spontaneously formed clear silicone microemulsions, they do not teach preparing clear silicone microemulsions using long chain or high molecular weight silicone polyethers. This is not surprising as prior to this invention, there is nothing in the public domain relative to the preparation of clear silicone microemulsions using long chain or high molecular weight silicone polyethers.

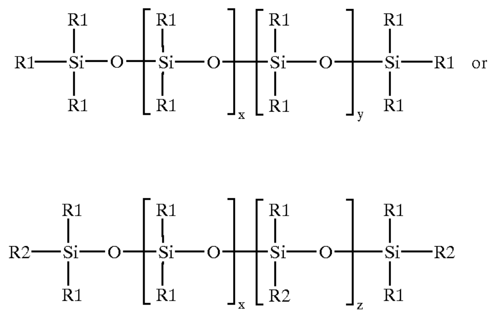
[0007] The '562 patent, unlike the present invention, also fails to teach preparation of clear microemulsions from mixtures of both a volatile silicone oil and a nonvolatile silicone oil. Rather, the clear silicone microemulsions in the '562 patent are limited to oil phases containing only silicone oils which are volatile.

[0008] As a third distinction, according to the '562 patent, the composition should be free of non-essential ingredients such as cosurfactants. According to this invention, however, the composition may contain such non-essential cosurfactants, yet result in formation of clear silicone microemulsions.

## BRIEF SUMMARY OF THE INVENTION

[0009] The invention relates to a method of spontaneously forming a clear microemulsion without mixing, stirring, shearing, or input of mechanical energy for agitating ingredients used in making microemulsions, by simply combining as ingredients (i) water; (ii) a volatile siloxane; (iii) a long chain or high molecular weight silicone polyether; and, as an optional ingredient, (iv) a cosurfactant such as a monohydroxy alcohol, an organic diol, an organic triol, an organic tetraol, a silicone diol, a silicone triol, a silicone tetraol, and a nonionic organic surfactant.

[0010] In this embodiment, the long chain or high molecular weight silicone polyether is a polymer having formula



[0011] where R1 represents an alkyl group containing 1-6 carbon atoms;

[0012] R2 represents the radical $—(CH_2)_aO(C_2H_4O)_b(C_3H_6O)_cR3$; x is 20-1,000; y is 2-500; z is 2-500; a is 3-6; b is 4-20; c is 0-5; and R3 is hydrogen, a methyl radical, or an acyl radical.

[0013] In an alternate embodiment, the invention relates to a method of spontaneously forming a clear microemulsion without mixing, stirring, shearing, or input of mechanical energy for agitating ingredients used in making microemulsions, by simply combining as ingredients (i) water; (ii) a volatile siloxane; (iii) a non-volatile siloxane; (iv) a silicone polyether; and, as an optional ingredient, (v) a cosurfactant such as a monohydroxy alcohol, an organic diol, an organic triol, an organic tetraol, a silicone diol, a silicone triol, a silicone tetraol, and a nonionic organic surfactant.

[0014] A long chain or high molecular weight silicone polyether, or a short chain or low molecular weight silicone polyether can be used in this alternate embodiment.

[0015] Clear microemulsions prepared according to either method are also a feature of the invention.

[0016] These and other features of the invention will become apparent from a consideration of the detailed description.

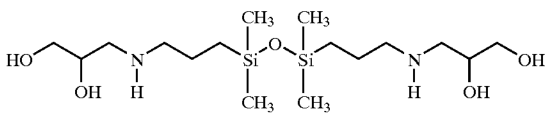
## BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

[0017] Not applicable.

## DETAILED DESCRIPTION OF THE INVENTION

[0018] In a first embodiment of the invention, clear microemulsions are formed by simply combining the components (i) water; (ii) a volatile siloxane; (iii) a long chain or high molecular weight silicone polyether; and, as an optional component, (iv) a cosurfactant such as a monohydroxy alcohol, an organic diol, organic triol, organic tetraol, silicone diol, silicone triol, silicone tetraol, or nonionic organic surfactant.

[0019] Some representative examples of the optional cosurfactant component (iv) include monohydroxy alcohols such as methanol, ethanol, and 2-propanol; organic diols such as ethylene glycol and propylene glycol; organic triols such as glycerol; organic tetraols such as pentaerythritol and 1,2,3,6-hexane tetraol; and a silicone tetraol such as shown below.



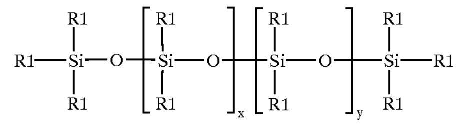
[0020] The nonionic surfactant should be a non-silicon atom containing nonionic emulsifier. Most preferred are alcohol ethoxylates R4-$(OCH_2CH_2)_dOH$, most particularly fatty alcohol ethoxylates. Fatty alcohol ethoxylates typically contain the characteristic group —$(OCH_2CH_2)_dOH$ which is attached to fatty hydrocarbon residue R4 which contains about eight to about twenty carbon atoms, such as lauryl ($C_{12}$), cetyl ($C_{16}$) and stearyl ($C_{18}$). While the value of "d" may range from 1 to about 100, its value is typically in the range of 2 to 40. Some examples of suitable nonionic surfactants are polyoxyethylene (4) lauryl ether, polyoxyethylene (5) lauryl ether, polyoxyethylene (23) lauryl ether, polyoxyethylene (2) cetyl ether, polyoxyethylene (10) cetyl ether, polyoxyethylene (20) cetyl ether, polyoxyethylene (2) stearyl ether, polyoxyethylene (10) stearyl ether, polyoxyethylene (20) stearyl ether, polyoxyethylene (21) stearyl ether, polyoxyethylene (100) stearyl ether, polyoxyethylene (2) oleyl ether, and polyoxyethylene (10) oleyl ether. These and other fatty alcohol ethoxylates are commercially available under names such as ALFONIC®, ARLACEL, BRIJ, GENAPOL®, LUTENSOL, NEODOL®, RENEX, SOFTANOL, SURFONIC®, TERGITOL®, TRYCOL, and VOLPO.

[0021] Compositions according to this embodiment of invention contain 5-90 percent by weight of surfactant, preferably 15-50 percent by weight. The balance of the composition is oil and water, with the proportions of oil and water generally being in the ratios of 5:95 to 95:5, respectively.

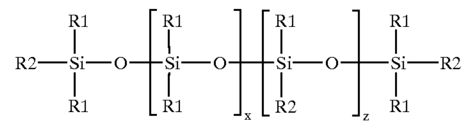
[0022] In a second embodiment of the invention, clear microemulsion are formed by simply combining the components (i) water; (ii) a volatile siloxane; (iii) a nonvolatile siloxane; (iv) a silicone polyether; and as an optional component, (v) a cosurfactant such as a monohydroxy alcohol, an organic diol, an organic triol, an organic tetraol, a silicone diol, silicone triol, silicone tetraol, or a nonionic organic surfactants.

[0023] Compositions according to this embodiment of the invention contain 5-90 percent by weight of surfactant, preferably 15-50 percent by weight. The balance of the composition is oil and water, in proportions of oil and water generally in the ratios of 5:95 to 95:5. The nonvolatile silicone oil in the mixed oil phase constitutes 1-30 percent of the oil component.

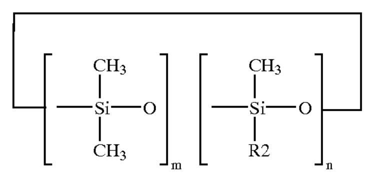
[0024] The long chain or high molecular weight silicone polyether can have a structure represented by:



or



[0025] A cyclic polyether of the type shown below can also be used.



[0026] In these structures, R1 represents an alkyl group containing 1-6 carbon atoms such as methyl, ethyl, propyl, butyl, pentyl, and hexyl; R2 represents the radical —$(CH_2)_aO(C_2H_4O)_b(C_3H_6O)_cR3$; x has a value of 20-1,000; y has a value of 2-500 z has a value of 2-500; m has a value of 3-5; n is one; a has a value of 3-6; b has a value of 4-20; c has a value of 0-5; and R3 is hydrogen, a methyl radical, or an acyl radical such as acetyl. Preferably, R1 is methyl; b is 6-12; c is zero; and R3 is hydrogen.

[0027] Silicone oils suitable for use in making clear silicone microemulsions according to this invention include both volatile and nonvolatile linear and cyclic methyl, higher alkyl, or aryl siloxanes.

[0028] The volatile linear methyl siloxanes have the formula $(CH_3)_3SiO\{(CH_3)_2SiO\}_kSi(CH_3)_3$. The value of k is 0-5. The volatile cyclic methyl siloxanes have the formula $\{(CH_3)_2SiO\}_t$. The value of t is 3-9. Preferably, these volatile polydimethylsiloxanes have a boiling point less than about 250° C. and viscosity of about 0.65 to about 5.0 $mm^2/s$.

[0029] Some representative volatile linear methyl siloxanes are hexamethyldisiloxane (MM) with a boiling point of 100° C., viscosity of 0.65 $mm^2/s$, and formula $Me_3SiOSiMe_3$; octamethyltrisiloxane (MDM) with a boiling point of 152° C., viscosity of 1.04 $mm^2/s$, and formula $Me_3SiOMe_2SiOSiMe_3$; decamethyltetrasiloxane ($MD_2M$) with a boiling point of 194° C., viscosity of 1.53 $mm^2/s$, and formula $Me_3SiO(Me_2SiO)_2SiMe_3$; dodecamethylpentasiloxane ($MD_3M$) with a boiling point of 229° C., viscosity of 2.06 $mm^2/s$, and formula $Me_3SiO(Me_2SiO)_3SiMe_3$; tetradecamethylhexasiloxane ($MD_4M$) with a boiling point of 245° C., viscosity of 2.63 $mm^2/s$, and formula $Me_3SiO(Me_2SiO)_4SiMe_3$; and hexadecamethylheptasiloxane ($MD_5M$) with a boiling point of 270° C., viscosity of 3.24 $mm^2/s$, and formula $Me_3SiO(Me_2SiO)_5SiMe_3$.

[0030] Some representative volatile cyclic methyl siloxanes are hexamethylcyclotrisiloxane ($D_3$) a solid with a boiling point of 134° C. and formula $\{(Me_2)SiO\}_3$; octamethylcyclotetrasiloxane ($D_4$) with a boiling point of 176° C., viscosity of 2.3 $mm^2/s$, and formula $\{(Me_2)SiO\}_4$; decamethylcyclopentasiloxane ($D_5$) with a boiling point of 210° C., viscosity of 3.87 $mm^2/s$, and formula $\{(Me_2)SiO\}_5$; and dodecamethylcyclohexasiloxane ($D_6$) with a boiling point of 245° C., viscosity of 6.62 $mm^2/s$, and formula $\{(Me_2)SiO\}_6$.

[0031] The nonvolatile linear and cyclic higher alkyl and aryl siloxanes are represented respectively by the formulas $R^a_3SiO(R^a_2SiO)_pSiR^a_3$ and $(R^a_2SiO)_r$. $R^a$ can be an alkyl group with 1-20 carbon atoms, or an aryl group such as phenyl. $R^a$ can also be hydrogen, an aralkyl (arylalkyl) group such as benzyl, or an alkaryl (alkylaryl) group such as tolyl. The value of p is 0-80, preferably 5-20. The value of r is 3-9, preferably 4-6. These polysiloxanes generally have a viscosity in the range of about 5-100 $mm^2/s$.

[0032] Nonvolatile polysiloxanes can also be used where p has a value sufficient to provide siloxane polymers with a viscosity in the range of about 100-1,000 $mm^2$/sec. Typically, p can be about 80-375. Illustrative of such polysiloxanes are polydimethylsiloxane, polydiethylsiloxane, polymethylethylsiloxane, polymethylphenylsiloxane, polydiphenylsiloxane, and polymethylhydrogensiloxane.

## EXAMPLES

[0033] The following examples are set forth in order to illustrate the invention in more detail. In these examples, the symbol M is used to indicate the monofunctional polyorganosiloxane structural unit $R_3SiO_{1/2}$, while the symbol D is used to indicate the difunctional polyorganosiloxane structural unit $R_2SiO_{2/2}$.

### Example 1

### Preparation of Single Phase Oil and Water Compositions with Polymeric Silicone Surfactants

[0034] A 60/40, 70/30 and 80/20 mixture of silicone polyether (SPE), and 1,2-hexanediol were each prepared by heating the SPE for 45 seconds in a microwave oven, and then adding 1,2-hexanediol. The mixtures were shaken and spun on the rotary wheel of a Model 7637-01 Roto-Torque device for thirty minutes. The mixtures were all used at room temperature.

[0035] For each sample, a triangular graph was used to determine the desired percentages of each of the three components to be used. Using a Mettler AG204 analytical balance, samples with a total mass of three gram were prepared. For example, 1.65 g of surfactant (60/40) was first weighed into a 13×100 mm Pyrex tube vial, 1.215 g of deionized water was added, and finally 0.135 g of volatile siloxane $D_5$. Other samples prepared included (i) 1.5 g of surfactant (70/30), 1.35 g of deionized water, and 0.15 g of $D_5$ fluid; and (ii) 1.5 g of surfactant (80/20), 1.35 g of deionized water, and 0.15 g of $D_5$ fluid. The sample tube vials were each labeled and spun on the rotary wheel for ten minutes. All formed clear microemulsions.

[0036] Microemulsions were also formed using an SPE, diethylene glycol monohexyl ether, $D_5$ fluid, and deionized water. The best results were obtained using compositions comprising (i) 1.5 g of the 50/50 surfactant, 0.15 g of $D_5$ fluid, and 1.35 g of water; (ii) 0.6 g of 50/50 surfactant, 0.24 g $D_5$ fluid, and 2.16 g of water; and (ii) 1.8 g of 50/50 surfactant, 0.6 g of $D_5$ fluid, and 0.6 g of water.

TABLE 1

| Percent Surfactant | % $H_2O$ | Percent Oil | Appearance |
|---|---|---|---|
| 55% SPE/1,2-hexanediol (60/40) | 40.50 | 4.5% $D_5$ fluid | Clear |
| 50% SPE/1,2-hexanediol (70/30) | 45 | 5% $D_5$ fluid | Clear |
| 50% SPE/1,2-hexanediol (30/20) | 45 | 5% $D_5$ fluid | Clear |
| 50% SPE/$C_6E_2$ (50/50) | 45 | 5% $D_5$ fluid | Clear |
| 20% SPE/$C_6E_2$ (50/50) | 72 | 8% $D_5$ fluid | Clear |
| 60% SPE/$C_6E_2$ (50/50) | 20 | 20% $D_5$ fluid | Clear |

[0037] In this example and in Table 1, SPE represents the long chain or high molecular weight silicone polyether (SPE) with a structure corresponding to $MD_{22}D'(EO_{12})_2M$. $C_6E_2$ represents the nonionic cosurfactant diethylene glycol monohexyl ether. $D_5$ is the volatile siloxane decamethylcyclopentasiloxane.

### Examples 2 to 4

### Preparation of Single Phase Oil and Water Compositions Using Mixtures Containing Low and High Molecular Weight Silicone Oils

[0038] In these examples, microemulsions were prepared using the short chain or low molecular weight SPE surfactant $MD'(EO_7)M$, and the other components shown below in Tables 2-4.

TABLE 2

Example 2—Microemulsions Formed at 39–70° C.

| Component | Actual Weight, gram |
|---|---|
| Surfactant, MD' ($EO_7$)M | 1.0498 |
| Oil, Decamethylcyclopentasiloxane | 0.6276 |
| Oil, Polydimethylsiloxane, 10 cs | 0.1558 |
| Water | 1.1704 |

[0039]

TABLE 3

Example 3—Microemulsions Formed at 41–75° C.

| Component | Actual Weight, gram |
|---|---|
| Surfactant, MD' ($EO_7$)M | 0.9031 |
| Oil, Decamethylcyclopentasiloxane | 0.6293 |
| Oil, Polymethylhydrogensiloxane | 0.2106 |
| Water | 1.2613 |

[0040] The polymethylhydrogensiloxane oil used in Example 3 and shown in Table 3 was a nonvolatile siloxane, and consisted of a trimethylsiloxy endblocked dimethyl methylhydrogen siloxane polymer with a viscosity of about 7 centistoke. It had a structure generally represented by $MD_{8.7}D^H_{3.7}M$.

TABLE 4

Example 4—Microemulsions Formed at 35–45° C.

| Component | Actual Weight, gram |
|---|---|
| Surfactant, MD' ($EO_7$)M | 1.0514 |
| Oil, Decamethylcyclopentasiloxane | 0.7413 |
| Oil, Polydimethylsiloxane, 50 cs | 0.04 |
| Water | 1.1733 |

Example 5

Preparation of Microemulsion with ABA Type SPE

[0041] Six gram of a non-crosslinked and long chain or high molecular weight silicone polyether of the formula $M'D_{50}M'$ wherein M' represents $(CH_3)_2[(CH_2)_{30}(CH_2CH_2O)_7H]SiO$— and D is $(CH_3)_2SiO$=; 2.0 gram of the volatile silicone oil D5, i.e. decamethylcyclopentasiloxane, were loaded into a plastic container and mixed with a dental mixer for 20 seconds. Two gram of deionized water was added and mixed with the dental mixer for 20 seconds, resulting in a clear gel.

Example 6

Preparation of Microemulsion with Rake Type SPE 1

[0042] 5.05 gram of a non-crosslinked and long chain or high molecular weight silicone polyether of the formula $MD_{22}D'_2M$ wherein M represents $(CH_3)_3SiO$—, D is $(CH_3)_2SiO$=, and D' represents $(CH_3)[(CH_2)_{30}(CH_2CH_2O)_7H]SiO$=; and 2.83 gram of volatile silicone oil D5, were loaded into a plastic container and mixed with a dental mixer for 20 seconds. 2.11 gram of deionized water was added and mixed with the dental mixer for 20 seconds, resulting in a clear gel.

Example 7

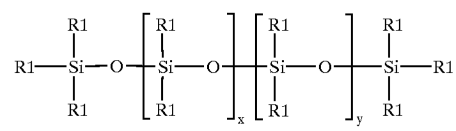
Preparation of Microemulsion with Rake Type SPE 2

[0043] 4.02 gram of a non-crosslinked and long chain or high molecular weight silicone polyether of the formula $MD_{196.6}D'_{63.4}M$ wherein M is $(CH_3)_3SiO$—, D is $(CH_3)_2SiO$=, and D' represents $(CH_3)[(CH_2)_{30}(CH_2CH_2O)_7H]SiO$=, and 2.4 gram of volatile silicone oil D5, were loaded into a plastic container and mixed with a dental mixer for 20 seconds. 3.61 gram of deionized water was added and mixed with the dental mixer for 20 seconds, resulting in a clear gel.

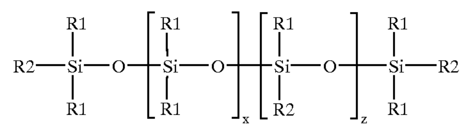
[0044] The microemulsions prepared according to the invention can be used in various over-the-counter (OTC) personal care products. Thus, they can be used in antiperspirants, deodorants, skin creams, skin care lotions, moisturizers, facial treatments such as acne or wrinkle removers, personal and facial cleansers, bath oils, perfumes, colognes, sachets, sunscreens, pre-shave and after-shave lotions, liquid soaps, shaving soaps, shaving lathers, hair shampoos, hair conditioners, hair sprays, mousses, permanents, depilatories, cuticle coats, make-ups, color cosmetics, foundations, blushes, lipsticks, lip balms, eyeliners, mascaras, oil removers, color cosmetic removers, and powders. The microemulsion compositions are also useful as carriers for pharmaceuticals, biocides, herbicides, pesticides, and to incorporate water and water-soluble substances into hydrophobic systems.

[0045] Other variations may be made in compounds, compositions, and methods described herein without departing from the essential features of the invention. The embodiments of the invention specifically illustrated herein are exemplary only and not intended as limitations on their scope except as defined in the appended claims.

1. A method comprising spontaneously forming a clear microemulsion without mixing, stirring, shearing, or input of mechanical energy for agitating ingredients used in making microemulsions, by simply combining as ingredients (i) water; (ii) a volatile siloxane; (iii) a long chain or high molecular weight silicone polyether; and, as an optional ingredient, (iv) a cosurfactant selected from the group consisting of a monohydroxy alcohol, an organic diol, an organic triol, an organic tetraol, a silicone diol, a silicone triol, a silicone tetraol, and a nonionic organic surfactant; the long chain or high molecular weight silicone polyether (iii) having formula



or



where R1 represents an alkyl group containing 1-6 carbon atoms;

R2 represents the radical —$(CH_2)_aO(C_2H_4O)_b(C_3H_6O)_cR3$; x is 20-1,000; y is 2-500; z is 2-500; a is 3-6; b is 4-20; c is 0-5; and R3 is hydrogen, a methyl radical, or an acyl radical.

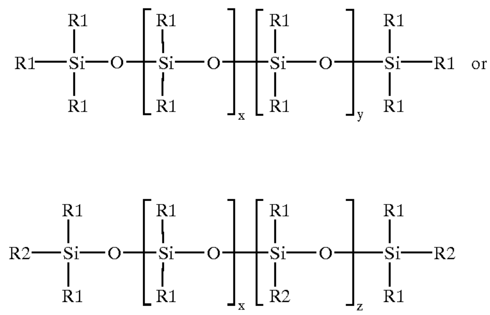
2. A method according to claim 1 in which volatile siloxane (ii) is a volatile linear methyl siloxanes of the formula $(CH_3)_3SiO\{(CH_3)_2SiO\}_kSi(CH_3)_3$ where k is 0-5; or a cyclic methyl siloxane of the formula $\{(CH_3)_2SiO\}_t$ where t is 3-9; the volatile siloxane having a boiling point less than about 250° C., and a viscosity of 0.65-5.0 $mm^2/s$.

3. Clear microemulsions prepared according to the method defined in claim 1.

4. A method comprising spontaneously forming a clear microemulsion without mixing, stirring, shearing, or input of mechanical energy for agitating ingredients used in making microemulsions, by simply combining as ingredients (i) water; (ii) a volatile siloxane; (iii) a non-volatile siloxane; (iv) a long chain or high molecular weight silicone polyether, or a short chain or low molecular weight silicone polyether; and, as an optional ingredient, (v) a cosurfactant selected from the group consisting of a monohydroxy alco-

hol, an organic diol, an organic triol, an organic tetraol, a silicone diol, a silicone triol, a silicone tetraol, and a nonionic organic surfactant.

**5**. A method according to claim 4 in which silicone polyether (iv) is a long chain or high molecular weight silicone polyether having formula



where R1 represents an alkyl group containing 1-6 carbon atoms;

R2 represents the radical $-(CH_2)_aO(C_2H_4O)_b(C_3H_6O)_cR3$; x is 20-1,000; y is 2-500; z is 2-500; a is 3-6; b is 4-20; c is 0-5; and R3 is hydrogen, a methyl radical, or an acyl radical.

**6**. A method according to claim 4 in which volatile siloxane (ii) is a volatile linear methyl siloxanes of the formula $(CH_3)_3SiO\{(CH_3)_2SiO\}_kSi(CH_3)_3$ where k is 0-5 or a cyclic methyl siloxane of the formula $\{(CH_3)_2SiO\}_t$ where t is 3-9; the volatile siloxanes have a boiling point less than about 250° C. and a viscosity of 0.65-5.0 $mm^2/s$.

**7**. A method according to claim 6 in which non-volatile siloxane (iii) is a nonvolatile linear or cyclic higher alkyl or aryl siloxane of the formula $R^a_3SiO(R^a_2SiO)_pSiR^a_3$ or $(R^a_2SiO)_r$ where $R^a$ is an alkyl group with 1-20 carbon atoms or an aryl group, hydrogen, an aralkyl (arylalkyl) group, or an alkaryl (alkylaryl) group; p is 0-375; r is 3-9; and the non-volatile siloxane has a viscosity greater than five $mm^2/s$ to 1,000 $mm^2/sec$.

**8**. Clear microemulsions prepared according to the method defined in claim **4**.

* * * * *