Title: SILICONE NANOEMULSION

Abstract: A detergent formulation comprises a nano-emulsion of a silicone.
This invention relates to cleaning compositions comprising a silicone nano-emulsion and cleaning methods using the emulsion.

Fabric care compositions are well known. These compositions are available in many formats including powders, liquids and tablets.

Most of the liquid formulations are aqueous based for cost reasons and their complimentary nature to the usual water based washing medium. The use of aqueous compositions is typically acceptable in that most of the detergent components used are soluble in water and display a reasonable high degree of stability in such a medium. However, certain fabric care components, due to their chemical nature are not insoluble in water. As such these components need to be suspended in the water in the form of an emulsion.

Examples of insoluble fabric treatment agents include silicones. These find use as fabric softening additives, being able to provide softness and elasticity to the fibres. However, due to the hydrophobic nature of the silicones, simple dissolution in an aqueous medium is not possible. Instead the silicones need to be dispersed in the form of an emulsion.

Whilst emulsions do solve the immediate dispersion problem they are not without their disadvantages. A principal disadvantage is to create and maintain the emulsion a
dispersion agent has to be used. This is unfavourable in terms of cost and potential detrimental interactions with one or more detergent components.

Additionally by the nature of emulsions, e.g. a stabilised / supported particle in a liquid medium it is difficult / impossible to produce an emulsion which is not opaque and as such the aesthetic properties of the emulsion are limited.

It is an object of the present invention to obviate / mitigate the disadvantages above.

According to a first aspect of the invention there is provided a detergent formulation comprising a nano-emulsion of a silicone.

Preferably the nanoemulsion particles have a particle size of less than 1µm; for example less than 0.8µm, more preferably less than 0.6µm, more preferably less than 0.4µm.

In our invention, we have discovered that reducing the size of the droplets of the dispersed phase in the range of the few microns and below, we obtained a clear product not requiring any additive to stabilize the emulsion. Also, the performance of such product was equal or, in some case better, than that of a regular emulsion.
Silicone

The silicone is preferably a fabric-softening silicone. The silicone typically has the general formula:

\[
\begin{array}{c}
\text{R}_1 \\
\text{Si} \\
\text{O} \\
\text{R}_2 \\
\end{array}
\]

\[
\left[ \text{---Si--O---} \right]_x
\]

wherein, each \( R_1 \) and \( R_2 \) in each repeating unit, \(-\left(\text{Si} (R_1) (R_2) \text{O}\right)\)-, are independently selected from branched or unbranched, substituted or unsubstituted C1-C10 alkyl or alkenyl, substituted or unsubstituted phereryl, or units of \(-\left(\text{R}_1\text{R}_2\text{Si-O}\right)-\); \( x \) is a number from 50 to 300,000, preferably from 100 to 100,000, more preferably from 200 to 50,000; wherein, the substituted alkyl, alkenyl or phenyl are typically substituted with halogen, amino, hydroxyl groups, quaternary ammonium groups, polyalkoxy groups, carboxyl groups, or nitro groups; and wherein the polymer is terminated by a hydroxyl group, hydrogen or \(-\text{SiR}_3\)

wherein, \( R_3 \) is hydroxyl, hydrogen, methyl or a functional group.

Suitable silicones include: amino-silicones; quaternary-silicones; high-viscosity silicones; modified polydimethylsiloxane; functionalized polydimethyl siloxane.

The silicone may preferably be a silicone mixture of two or more different types of silicone.
The silicone typically has a viscosity, of from 5,000cP to 5,000,000cP, or from greater than 10,000cP to 1,000,000cP, or from 10,000cP to 600,000cP, more preferably from 50,000cP to 400,000cP, and more preferably from 80,000cP to 200,000cP when measured at a shear rate of 20s less than -1 greater than and at ambient conditions (20°C and 1 atm.). The silicone is typically in a liquid or liquefiable form. Typically, the silicone is a polymeric silicone comprising more than 3, preferably more than 5 or even more than 10 siloxane monomer units.

Further preferred silicones are those of formula (III)

(R1)ₐG₃₋ₐ-Si-(-O-SiG₂)ₙ₋ₐ(OSiGₐ⁻b)ₘ₋ₐ-Si-G₃₋ₐ(R1)ₐ

wherein G is selected from the group consisting of hydrogen, phenyl, OH, and/or Cₙ₋ₘ alkyl; a denotes 0 or an integer from 1 to 3; b denotes 0 or 1; the sum of n + m is a number from 1 to 2,000; R1 is a monovalent radical of formula CpH₂₊L in which p is an integer from 2 to 8 and L is selected from the group consisting of:

- N (R2) CH₂-CH₂-N (R2)₂;
- N(R2)₂;
- N⁺ (R2) A⁻; and
- N⁺ (R2)CH₂-N⁺H₂A⁻

wherein each R2 is chosen from the group consisting of hydrogen, phenyl, benzyl, saturated hydrocarbon radical, and each A⁻ denotes a compatible anion, e.g., a halide ion.
The composition preferably comprises a cationic fabric softener.

**Cationic fabric softener**

Typical levels within the compositions are from 3 to 45%, preferably from 4 to 25%, ideally from 10 to 25%, by weight of the composition.

The preferred, typical, cationic fabric softening actives include the water-dispersible quaternary-ammonium fabric softeners or amine precursors thereof:

Preferred quaternary ammonium compounds herein have the formula (I) or (Ia), and include a mixture thereof;

\[
[R'-(CO)-0-R-N^+(-R''_) (- (RO)_{n^R}) (-R-0- (CO) -R' )]X^- \tag{I}
\]
\[
[R' - (CO)-NH-R-N^+(-R^1) (- (RO)_{n^R}) (-R-NH- (CO) -R' )]X^- \tag{Ia}
\]

wherein:

- R is an alkylene or alkenylene group having 2 to 4 carbon atoms;
- R' is an alkyl or alkenyl group having 8 to 22 carbon atoms;
- n is an integer having a value of 1 to 4;
- R'' is an alkyl group having 1 to 4 carbon atoms; R^1 is an alkyl group having 1 to 4 carbon atoms or hydrogen; and
- X^- is a softener-compatible anion.

Non-limiting examples of softener-compatible anions (X^-) include chloride, formate, nitrate, sulfate or Cl-4 alkyl sulfate, preferably methyl sulfate.
The alkyl or alkenyl $R'$ ideally must contain at least 10 carbon atoms, preferably at least 14 carbon atoms, more preferably at least 16 carbon atoms. The group may be straight or branched.

Unsaturated fatty acid and partially hydrogenated fatty acid derived from vegetable oils are usually convenient and relatively inexpensive sources of long chain alkyl and alkenyl material. The preferred compounds wherein $R'$ represents these mixtures of long chain materials includes, but is not limited to, rape-seed oil, canola oil, peanut oil and sunflower oil. A preferred, non-vegetable sourced, $R'$ group is tallow.

A specific example of quaternary ammonium compounds suitable for use in the invention is di-(tallow carboxyethyl)hydroxyethylmethyl ammoniumX$^-$. The softener compatible anion (X$^-$) is merely present as a counterion of the positively charged quaternary ammonium compound. The nature of the counterion anion is not critical at all to the practice of the present invention. The scope of this invention is not considered limited to any particular anion. By "amine precursors thereof" is meant the secondary or tertiary amines corresponding to the above quaternary ammonium compounds, said amines being substantially protonated in the compositions due to the pH values of the composition.

The composition preferably comprises a cationic fabric co-softener.
Fabric Co-softener

Fabric co-softeners are understood by the skilled person as non-quaternary hydrophilic compounds that are added to boost softening performance. Preferred levels are from 0.1 to 10% by weight or 0.2 to 5% by weight.

Amines

Among the suitable co-softeners are amines of formula (II)

\[ R^3 \overline{R^4} \]
\[ \underline{N} \]
\[ \underline{R^5} \]

at least one, and preferably no more than two, of \( R^3 \), \( R^4 \) and \( R^5 \) are \( \text{C}_{16-22} \) alkyl or alkenyl (preferably alkenyl), preferably \( \text{C}_{17-19} \) ideally \( \text{C}_{18} \); and the remaining group (s), if any, are \( \text{C}_{1-4} \) hydroxyalkyl or hydrogen, preferably \( \text{C}_{1-4} \) hydroxyalkyl, ideally hydroxyethyl.

Further Ingredients

The composition preferably contains up to 75% by weight of sequestrants, limescale preventatives (such as citric acid and pH modifying agents (such as sodium carbonate).
Additional Components

The composition may also optionally contain up to 5% by weight of additional components of at least one of the following; antioxidants and reductive agents, bacteriocides, natural or synthetic extracts, antifoam agents, desiccants, enzymes, bleaches, bleach activators, hydrotropes, opacifiers, foam controllers, preservatives, disinfectants, pearlising agents), optical brighteners, dye transfer inhibitors, colour fading inhibitors, and aesthetic ingredients, for example fragrances and colorants.

Antifoam Agent

The addition of an antifoam agent may be necessary to avoid excess generation of foam during the rinse cycle. Preferably up to 5%wt, ideally less than 3%wt or 2%wt.

Hydrotrope

Hydrotropes aid in the solubility or dispersibility of different surfactants in aqueous solution. This usually has the side effect of lowering the viscosity of the resulting mixture.

Examples of suitable and preferred hydrotropes are the alkali metal salts of a benzene, cumene, toluene and xylene sulfonate, ideally the sodium salt.
According to a second aspect of the invention there is provided a process for the preparation of a detergent formulation comprising a nano-emulsion of a silicone.

Preferably a homogeniser is used in the preparation of the silicon nanoemulsion. Usually the silicone is provided to the homogeniser in the form of a pre-pared micro-emulsion. (We have found that the turbo-mixers which are commonly employed for manufacture of the micro-emulsion cannot be used in the manufacture of the nano-emulsion).

The homogeniser is preferably operated in a cycle time of 10-15 minutes. A number of cycles of the homogeniser may be used in the preparation of the nano-emulsion.

According to a third aspect of the invention there is provided the use of a detergent formulation comprising a nano-emulsion of a silicone to prevent / reduce damage caused by stretching and / or to improve the elasticity of clothing.

In this regard it has been found that with the use of a detergent formulation comprising a nano-emulsion of silicone beneficial properties in regard to reducing / preventing stretching and aiding elasticity of clothing (or other fabric items) are attainable.

Indeed it has been seen that contrary to "normal" washing (conventional laundry treatment in a conventional laundry washing machine using a traditional detergent) wherein generally the force needed to stretch a garment increases over a plurality of washing cycles. As an example the
force needed to stretch a cotton based pair of denim jeans by a certain length typically increases by 20% (from 500N to 600N) after 20 wash cycles.

In contrast with the use of a composition in accordance with the invention it has been found that typically the force required for the same quantum of stretching of the same type of denim jeans decreases over a plurality of washing cycles. This is achieved with acceptable / improved shape recovery of a garment. Moreover the effect is achieved without fibre damage; indeed fibre damage is reduced / prevented with the use of the nano-emulsion of silicone.

Together these factors provide enhanced comfort of wearing for a user and prolonged life / better appearance to a garment over a number of washing cycles.

It is postulated that this effect is achieved because the nano-emulsion of silicone is able to deeply penetrate the fibres of a price of clothing providing a deep nourishing effect.

The invention will now be described with reference to the following non-limiting Examples.

**Example 1:**

**Nano-emulsion Preparation**

The following steps were undertaken: -
1) 12.5g of Silicone Emulsion (Dow Corning Q2-1607 - 36% active) was added to 4987.5g of a liquid detergent base (Woolite) to obtain 5000g of mixture at 0.25% emulsion.

2) The mixture was stirred to obtain a homogeneous dispersion.

3) The dispersion was loaded into the homogenizer tank.

4) 8 homogenizing cycles were run

5) The product was unloaded.

**Testing Protocol**

Performance tests were conducted to evaluate the performance of the laundry additive with new ingredients.

Composition 3 (as shown above) was tested.

**Test: Conditions**

**Products dosages/g**

1. 45g Woolite Liquid.
2. 45g Woolite Liquid (including 0.25% silicone emulsion).
3. 45g Woolite Liquid (including 0.25% silicone nano-emulsion).
Washing Program: Regular 10
Washing Temp.: 30°C
Water Hardness: 12°f - 16°f
Wash Load: 2.0 Kg
Washing Machine: BOSCH WAE 24420 IT
Nr. Replicates: 20

Test Results (r - Value)

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<tr>
<td>Residual Deformation after stretch at 180% length **</td>
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<td>Force to stretch at 180% length **</td>
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<td>Elongation at 25N ****</td>
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<td>Breaking Force ****</td>
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** - the lower the better.
**** - the higher the better.

The results clearly indicate that, in the parameters tested, Composition 3 has equal / superior properties to a normal silicone emulsion.
1. A detergent formulation comprising a nano-emulsion of a silicone.

2. A formulation according to claim 1, wherein the nanoemulsion particles have a particle size of less than 1µm; for example less than 0.8µm, more preferably less than 0.6µm, more preferably less than 0.4µm.

3. A process for the preparation of a detergent formulation comprising a nano-emulsion of a silicone.

4. Use of a composition according to claim 1 to prevent / reduce damage caused by stretching and / or to improve the elasticity of clothing.
A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/37 C11D17/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D B82Y

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>wo 2007/049188 AI (PROCTER &amp; GAMBLE [US]; PANANDIKER RAJAN KESHAV [US]; VETTER KERRY ANDR) 3 May 2007 (2007-05-03) page 2, paragraphs 3,4; claims 1-16; example 1; table 1 page 1, paragraph 1 page 5, paragraph 5 - page 9, paragraph 2</td>
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<td>X</td>
<td>EP 0 646 618 AI (WACKER CHEMI E GMBH [DE]) 5 April 1 1995 (1995-04-05) column 2, lines 9-15; claims 1-3; examples 1-5</td>
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Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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"A" document member of the same patent family

Date of the actual completion of the international search

29 September 2011

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18/10/2011

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