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FLUOROSILICONE LUBRICANTS CONTAINING NITROPHENYL-SUBSTITUTED ORGANOPOLYSILOXANES

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ABSTRACT OF THE DISCLOSURE

Minor amounts of nitrophenyl-substituted siloxanes are added to fluorosilicone lubricants to improve the steel on brass and steel on aluminum antiwear characteristics.

This invention relates to improved fluoroalkylpolysiloxanes which contain minor amounts of nitrophenyl-substituted organopolysiloxanes. In one aspect the invention relates to fluorosilicone fluids exhibiting enhanced antiwear characteristics and superior thermal stability.

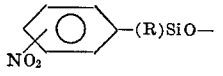
Organopolysiloxane fluids are known lubricants. Dimethylpolysiloxanes are general lubricants but have poor antiwear characteristics when used to lubricate steel on steel sliding surfaces. Fluorosilicones, such as trifluoropropylmethylpolysiloxanes are much better lubricants for steel on steel but exhibit poor lubrication for steel on brass and steel on aluminum. Thus, the fluorosilicone fluids find only limited use in environments requiring lubrication of metal surfaces other than or in addition to steel on steel.

By the practice of the present invention, the antiwear characteristics of fluorosilicones on steel on brass are greatly enhanced and the thermal stability is increased, thus rendering them suitable for the high temperature lubrication of various metals.

In accordance with the invention, there are provided improved organosilicon compositions comprising of (a) 98 to 99.9 weight percent of an organopolysiloxane fluid containing at least 70 mol percent

$$R_f(R)SiO-$$

units in which R_f is a perfluoroalkylethyl radical of from 3 to 12 carbon atoms, and R is selected from the group consisting of lower alkyl radicals and the phenyl radical; any remaining units being of the formula $R'_3SiO_{1/2}$ or which R' is selected from the group consisting of monovalent hydrocarbon radicals and monovalent halohydrocarbon radicals; and (b) 0.1 to 2 weight percent of liquid polysiloxane consisting essentially of



units wherein R is as defined above, any remaining units being of the formula $R'_3SiO_{1/2}$ wherein R' is as defined above.

As described above, R_f can be any perfluoroalkylethyl radical of no more than 12 carbon atoms, such as

$$CF_3CH_2CH_2-$$

$C_3F_7CH_2CH_2-$, $C_7F_{15}CH_2CH_2-$, $C_8F_{17}CH_2CH_2-$,

$$C_{10}F_{21}CH_2CH_2$$

and the like.

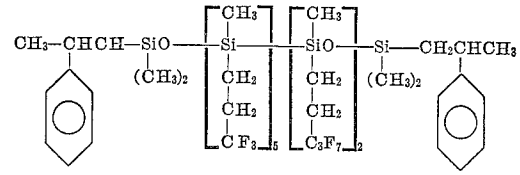
R can be any lower alkyl radical containing from 1 to 6 inclusive carbon atoms, such as methyl, propyl, isopropyl, butyl and hexyl. R can also be a phenyl radical.

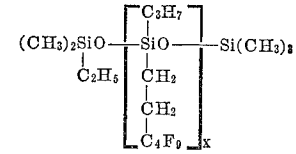
R' can be any monovalent hydrocarbon radical, such as alkyl radicals such as methyl, ethyl, propyl, isopropyl, butyl, pentyl, isopentyl, neopentyl, hexyl, octyl, dodecyl, octadecyl, 3-methylheptyl, 6-butyloctadecyl, tertiary butyl, myricyl and 2,2-diethylpentyl; alkenyl radicals such as, vinyl, allyl, hexenyl, butenyl, 3-octenyl, 4,9-octadecadienyl and 4-nonenyl; alkynyl radicals such as propynyl, heptynyl, butynyl, decynyl; alkenylnyl radicals such as 1-penten-3-ynyl, 2-ethyl-1-buten-3-ynyl; cycloaliphatic radicals such as, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, propylcyclohexyl, 2,4-dimethylcyclopentyl, cyclohexenyl, bicyclo[31.0]hexyl, tricyclo[3.2.1.1^{3,8}]-5-nonenyl, spiro-[4.5]decyl, dispiro[4.1.4.2]-1-tridecenyl, decahydronaphthyl, 2,3-dihydroindyl and 1,2,3,4-tetrahydronaphthyl; aryl radicals such as phenyl, tolyl, xylyl, 3-ethylphenyl, xenyl, naphthyl, anthracyl, pentacenyl, 3,4-methylethylphenyl, 9,9'-bifluoryl and 4-m-terphenyl; and aralkyl radicals such as 2-phenyl-octyl, 3-methyl-2-(4-isopropylphenyl)heptyl, benzyl, 2-ethyltolyl, 2-ethyl-p-cymyl, diphenylmethyl, 4,5-diphenylpentyl, 2-phenylethyl and 2-phenylpropyl.

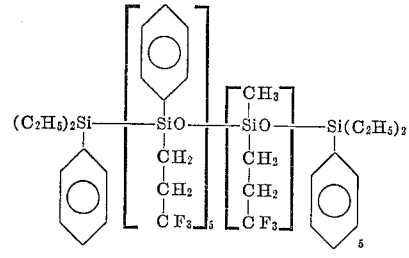
Also included within the scope of R' are monovalent halohydrocarbon radicals, such as aliphatic groups such as chloromethyl, 3-chloropropyl, 3,3,3-trichloropropyl, perfluorovinyl, chlorooctadecyl or radicals of the formula $R_fCH_2CH_2-$ where R_f can be any perfluoroalkyl group such as trifluoromethyl, perfluoroethyl, perfluoroisobutyl, perfluoroheptyl or perfluorooctadecyl; aromatic groups such as dichlorophenyl, tetrabromoxenyl, tetrachlorophenyl, alpha,alpha,alpha-trifluorotolyl or iodonaphthyl; cycloaliphatic groups such as chlorocyclohexyl, bromocyclopentyl or chlorocyclohexenyl and aralkyl groups such as chlorobenzyl, beta-(chlorophenyl)ethyl or beta-(iodophenyl)ethyl or beta-(bromophenyl)propyl.

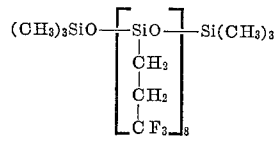
The preferred monovalent hydrocarbon and halohydrocarbon radicals are those having no more than 18 carbon atoms. Especially preferred as R' groups are lower alkyl radicals, the phenyl radical and 2-phenylpropyl radicals.

The above-described fluoroalkylpolysiloxanes are fluids, generally having a viscosity in the range of 20 to 20,000 cs. and include copolymers such as









and the like.

Particularly preferred fluids are the triorganosilyl endblocked 3,3,3 - trifluoropropylmethylpolysiloxanes having a viscosity in the range of about 20 to 1000 cs. when measured at 25° C.

The nitrophenyl-substituted polysiloxanes are known polymers—see U.S. Pat. 3,375,218. The polymers are prepared by nitration of phenylsilanes followed by hydrolysis and condensation. Monofunctional silanes are added to provide endblocking units ($R'_3SiO_{1/2}$) and thus control viscosity of the additive polymer. It is preferred that the fluid polymeric additive has a degree of polymerization of from 3 to 15. Only minor amounts of the additive, from 0.1 to 2 weight percent, preferably from 0.5 to 1.5 weight percent, are necessary to obtain the desired degree of lubricity. The optimum amount will depend upon the nature of the fluorosilicone and its application. Amounts greater than two weight percent can be used, but are generally uneconomical.

Other additives can be utilized in the above compositions without departing from scope of the invention. Thus, the lubricating compositions of the invention may optionally contain corrosion inhibitors, extreme pressure agents, anti-oxidants, dyes and the like. The invention also contemplates the use of thickening agents in combination with the compositions to formulate improved greases. Thickening agents suitable for use in such a grease formulation include fatty acid soaps, carbon black, silica, clay, polytetrafluoroethylene and the like. The thickener should not be one that is reactive with the nitrophenylsiloxane additive. The thickening agent will generally be present in an amount for about 10 to 60 weight percent of the grease compositions.

In addition to enhancing the antiwear properties of fluorosilicones, the nitrophenylsiloxane increases the thermal stability of the fluid. The weight loss at elevated temperatures of additive-containing fluids is significantly decreased. Because of this thermal stability, the compositions of the invention have utility as base stocks in fluorosilicone rubber formulations.

The following example is illustrative and not intended to be limiting of the present invention which is delineated in the claims. In the example, the lubricity characteristics were determined by means of the 4-Ball test. The 4-Ball tests were conducted on a Roxanna wear testing machine wherein a ½ inch diameter steel ball is rotated against three lubricated stationary ½ inch metal balls under various conditions and loads. After testing, the length and width of the scar on each stationary ball is measured and the average of the six measurements is taken as the wear scar diameter. The smaller the wear scar, of course, the better the lubricant.

EXAMPLE

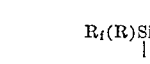
Sufficient trimethylsilyl-endblocked nitrophenylmethylpolysiloxane having a degree of polymerization of about 12 was mixed with trimethylsilyl endblocked 3,3,3 - trifluoropropylmethylpolysiloxane (300 cs.) to form a fluorosilicone composition containing 0.2 weight percent of the additive. The antiwear properties and thermal stability of this composition were compared to the properties of the pure polymer. Results are given below:

4-ball test conditions	Fluorosilicone (scar-min.)	Fluorosilicone + 0.2 wt. percent nitrophenylsiloxane (scar-mm.)
Steel on steel—167° F., 1 hr., 1,200 r.p.m., 40 kg.	0.81	0.43
Steel on steel—167° F., 1 hr., 1,200 r.p.m., 60 kg.	1.47	0.50
Steel on brass—167° F., ½ hr., 1,200 r.p.m., 30 kg.	3.7	1.5
Weight loss (percent) as determined on 10-gram sample in 50 ml. open beaker at 450° F.:		
After 1 day	11.3	4.5
After 7 days	46.4	17.4

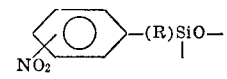
These data demonstrate the effect of the additive on the steel on brass and steel on steel lubrication properties of fluorosilicones at high loads. The additive also reduces the weight loss of fluorosilicones at elevated temperature. These effects are quite unexpected since they were not observed in other silicone lubricants, such as polydimethylsiloxane.

That which is claimed is:

1. A composition consisting essentially of (a) 98 to 99.9 weight percent of an organopolysiloxane fluid containing at least 70 mol percent



units in which R_f is a perfluoroalkylethyl radical of from 3 to 12 inclusive carbon atoms, and R is selected from the group consisting of alkyl radicals of no more than 6 carbon atoms and the phenyl radical; any remaining units being of the formula $R'_3SiO_{1/2}$ which R' is selected from the group consisting of monovalent hydrocarbon radicals and monovalent halohydrocarbon radicals; and (b) 0.1 to 2 weight percent of polysiloxane fluid consisting essentially of



units wherein R is as defined above any remaining units being of the formula $R'SiO_{1/2}$ units wherein R' is as defined above.

2. The composition of claim **1** wherein the organopolysiloxane (a) is triorganosilyl-endblocked 3,3,3 - trifluoropropylmethylpolysiloxane having a viscosity of from 20 to 1000 centistokes at 25° C.

3. The composition of claim **1** wherein the organopolysiloxane (b) has a degree of polymerization in the range of from 3 to 15.

4. The composition of claim **1** where the organopolysiloxane (a) is trimethylsilyl-endblocked 3,3,3 - trifluoropropylmethylpolysiloxane.

5. A lubricant comprising the composition of claim **1** containing sufficient thickening agent to form a grease.

6. The lubricant of claim **5** wherein the thickening agent is present in an amount in the range of from 10 to 60 weight percent, based on the total weight of lubricant.

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U.S. Cl. X.R.

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