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NONFOAMING LUBRICANT COMPOSITION

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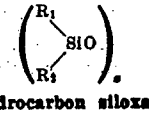
5 Claims. (Cl. 252—33)

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This invention relates to lubricants having reduced foaming tendencies. More particularly, it is concerned with the reduction of the foaming tendencies of compounded hydrocarbon oils such as cutting oils, gear lubricants and the like.

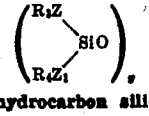
In the machining of metals, as for example, in cutting, forming, grinding, drilling, gear cutting and like operations applied to brass, steel and other metals or alloys, specially compounded lubricants are necessary to reduce friction and remove heat generated thereby. Such lubricants usually comprise mineral oils having compounded or mixed therewith such substances as high molecular weight fats, fatty acids, sulfurized or halogenated fats or fatty acids, sulfurized or halogenated mineral oils or waxes and like materials. In use, these oils are continuously recirculated over the work, being collected in a sump, strained or filtered to remove foreign matter, metal shavings or chips and are returned by a pump to be repeatedly discharged over the area being machined. This is conducive to foaming, but, in general, foaming is not a problem with fresh compounded oils. It has been noted that the tendency for the oil to foam becomes apparent after some use and increases as the oil is continued in service. The foaming tendency of compounded oils is dependent upon a number of factors such as the composition of the oil, the nature of the metal or alloy being worked, the rate of oil recirculation, the amount of air mixed into the oil in its passage over the work or through the recycling pump as well as upon other influences.

I have found that such foams as are encountered in the aforementioned operations are not prevented by means known to be effective in other instances. Polymeric organic silicon compounds, for example, dihydrocarbon siloxane and dihydrocarbon silicates, prepared by ways known to the art (e. g. J. Am. Chem. Soc. 63, 798 (1941)) and represented by the general formulae:



Dihydrocarbon siloxane

and



Dihydrocarbon silicate

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where R_1, R_3 and R_4 are hydrocarbon radicals such as alkyl, cycloalkyl, aryl, aralkyl, alkaryl radicals having less than about 20 carbon atoms and R_2 is hydrogen or a hydrocarbon radical, Z and Z_1 are oxygen, selenium, sulfur or tellurium atoms and x and y are positive integers, preferably 2 or higher, are, when used alone in accordance with the teachings of U. S. 2,375,007, inadequate to prevent the eventual foaming of cutting oils, gear lubricants, E. P. lubricants, etc.

It is an object of this invention to provide nonfoaming lubricants for machining operations. It is a further purpose to provide non-foaming lubricants for gears, transmissions and the like. A still further object is to reduce the foaming tendency of compounded oils such as those containing high molecular weight fats, fatty acids, metal soaps of fatty acids and similar foam-promoting substances. A further purpose is to provide an additive which acts synergistically with such known foam suppressors as polymeric silicon compounds. Another object is to provide additives which enable polymeric silicon compounds, e. g., the dihydrocarbon silicones and dihydrocarbon silicates, to become effective as foam suppressors. An additional object is to provide an improvement in the method of preventing foam formation resulting from admixture of gas with compounded oils coming in contact with metal surfaces, said compounded oil containing fatty compounds and a polymeric organic silicon compound. Another object is to provide a process whereby foam or froth, resulting from admixture of gas with compounded oils containing fatty materials and polymeric organic silicon compounds, is destroyed. Other objects will become apparent as a description of the invention proceeds.

The extraordinary ability of polymerized dihydrocarbon siloxane and dihydrocarbon silicates to prevent or reduce the foaming of certain lubricants in service and which have access to air is well described in U. S. 2,375,007. Ordinarily, from 0.0005 to 0.01% of the silicon compound is ample to prevent the foaming of most oils. I have found, however, as will be more fully brought out below, that polymeric organic silicon com-

pounds are substantially ineffective in preventing the foaming of compounded mineral oils in use. While I am not certain of the reasons underlying this failure to prevent foaming, it appears that soaps formed as a result of reaction between the high molecular weight fats or fatty acids in the compounded oil and the metal or alloy being lubricated are responsible.

The compounded oils with which this invention is concerned vary in manifold respects but one such typical oil has the following composition:

60% mineral oil (SAE 20 grade) sulfurized to contain a minimum of about 2% sulfur by weight and to which has been added 1–3% lard oil
31% mineral oil, 100 S. S. U. viscosity at 100° F.
1% chlorinated paraffin wax (ca. 40% chlorine)
2% sulfurized lard oil (10% sulfur, minimum)
6% No. 1 lard oil.

An oil of this type was used in machining steel and brass. No foam was noted when the oil was first introduced into the lubrication system. As the use of the oil was continued, however, foam appeared and became increasingly voluminous, obscuring the work and causing improper lubrication. To remedy this situation, various quantities of hydrocarbon silicones of varying degrees of polymerization were added to the oil without success. An analysis of the used oil revealed the presence of about 2% of lead fatty acid soap not originally present. In continuing experiments, as will be more fully brought out in connection with a discussion of the data in Table II, it was found that addition to this used cutting oil of a small proportion of a metal soap of a preferentially oil soluble petroleum sulfonic acid, in addition to a small, and lesser, amount of a polymeric organic silicon compound, specifically a dihydrocarbon siloxane, reduced the foaming tendency of the oil to such a degree that the oil compared favorably with fresh oil in performance as a cutting oil and no further work stoppages occurred as a result of foaming. A typical lubricant composition of this type comprises a sulfurized mineral oil of SAE 20 grade containing not less than about 2% combined sulfur, by weight, and a mineral oil of about 100 S. S. U. viscosity at 100° F., and having dissolved therein about 1% of chlorinated paraffin wax containing at least 35% combined chlorine, about 2% of sulfurized lard oil containing a minimum of 10% combined sulfur, about 6% of lard oil, a small amount, less than 0.1% of a dihydrocarbon siloxane, and less than 3% of sodium soaps of oil-soluble petroleum sulfonic acids.

As just mentioned, and contrary to expectations, I have found that the alkali salts of certain sulfonic acids, normally considered foam producers, are remarkably effective in destroying the foam of compounded oils, such as cutting oils containing heavy metal soaps of high molecular weight fatty acids, and if used in conjunction with polymeric organic silicon compounds, e. g., siloxane or silicate polymers, coact with those compounds substantially to prevent the initial formation of foam from such oils.

The alkali petroleum sulfonates which I have found to be most satisfactory are known in the art as mahogany soaps. They are preferentially oil-soluble sulfonates possessing the power of forming emulsions of the oil-in-water type and are made from oil-soluble sulfonic acids which

are formed in the treating of petroleum distillates with sulfuric acid. Considerable quantities of the acids are formed in treating distillates with fuming sulfuric acid for the production of white oils and transformer oils. Those sulfonic acids which remain dissolved in the treated oils are removed at certain levels of acid application by extraction with alcohol, and neutralized usually with caustic either before or following the extraction, to form crude mahogany soaps. Alcohol is removed from the extract by distillation. The resulting crude soap is usually purified by neutralizing the excess caustic soda content with weak sulfuric acid, and desalting by extraction with alcohol to remove most of the water and salts (chiefly sodium sulfate and sodium sulfite) contained in the viscous dark brown liquids.

Various alkali, alkaline earth, amine and alkylolamine soaps of these acids may be prepared by means known in the art, viz, by double decomposition of the alkali soaps or by direct neutralization of the acids with the corresponding metal base or amine and are satisfactory for use in conjunction with polymeric organic silicon compounds as foam inhibitors for use in oils, such as cutting oils, gear lubricants and the like, containing foam producing heavy metal soaps of fatty acids.

The alkali soaps of oil-soluble petroleum sulfonic acids are commonly employed as emulsifying agents in the manufacture of soluble oils and similar products derived from petroleum. In order to prepare consistently high quality emulsifying agents, the several variable which enter into the production of sulfonic acids by sulfuric acid treating of petroleum fractions must be controlled in accordance with practice usually established by trial and error or experience gained over a period of years. Such variables as the source and fraction of crude are important since they determine the predominant chemical nature of the oil, i. e., whether paraffinic, naphthenic or aromatic, and the average molecular weight of the oil, from which sulfonic acids will be derived, and both of these factors exert considerable influence upon the emulsifying power of the finished soaps. The strength of sulfuric acid, temperature of sulfuric acid treatment, manner of application of the sulfuric acid, etc. are equally important and must not be varied from batch to batch if sulfonic acids having uniform properties are desired.

It is general knowledge that a variety of sulfonic acids ranging from water-soluble-oil-insoluble to oil-soluble-water-insoluble are obtainable from petroleum by sulfuric acid treating. The determination of the exact chemical nature of these petroleum sulfonic acids has never been undertaken, due primarily to the complexity of petroleum and consequently of its sulfonic acid derivatives, but I have found it convenient to classify arbitrarily certain groups or mixtures of the acid derivatives according to the relative solubility of their alkali soaps in oil and water as shown in Table I. With reference to Table I, it will be understood that Mahogany B soap may be prepared by treating a fraction of Midcontinent crude having a viscosity of about 350 seconds Saybolt Universal with from 3 to 6 pounds of 104½ (fuming) sulfuric acid per gallon of oil and extracting the treated oil with 50–80% ethyl alcohol at 150–170° F., using a ratio of approximately one volume of dilute alcohol for each four volumes of oil.

TABLE I

Preparation and properties of sodium petroleum sulfonates

Sulfonate Designation	Lbs. 104½ H_2SO_4 per Gal. of Oil	Oil Treated	Source of Sulfonic Acid	Solvent	Relative Solubility of Na Soaps in	
					Oil	Water
Mahogany B	3 to 6	350 SSU-MC	Treated Oil	Alcohol	V. sol.	sl. sol.
Mahogany A	3	100–125 SSU-MC	do	do	V. sol.	sl. sol.
Mahogany AA	3 to 3.5	100–125 SSU-MC	do	do	V. sol.	sol.
Brown	2 to 4	100–125 SSU-MC	Sludge	Cleaners Naphtha	Sol.	sol.
Green	1 to 4	60–125 SSU-MC	do	30% H_2SO_4	Sol.	V. sol.
Detergent	2 to 4	100–125 SSU-MC	do	Benzene	Sl. sol.	V. sol.
Black	8	200–400 SSU-MC	do	30% H_2SO_4	Insol.	V. sol.

The sulfonic acids may be neutralized before or after extraction from the oil, and may be purified by further extraction with dilute alcohol to remove salts and water. It will be seen that this grade of soap is rated as very soluble in oil.

Mahogany A soap is prepared in a manner similar to that used for the B soap but a different fraction of Midcontinent crude and a different amount of sulfuric acid are used. These facts account, in some manner yet to be fully explained, for the slightly greater solubility of the Mahogany A soap in water. Still greater solubility is noted for the AA grade, accompanied by a definite decrease in oil solubility.

Purification of the oil-soluble soaps is generally preceded by reduction of free alkalinity by weak (30%) sulfuric acid addition, followed by air blowing to remove water. Following this, from 1.0 to 1.5 volumes of 60–80% ethyl alcohol is added, the mixture is heated to about 140° F. and settled for 24 to 36 hours. The mixture stratifies into a lower layer consisting predominantly of dilute alcohol and salts and an upper layer of purified mahogany soap containing some dissolved dilute alcohol which is removed by distillation.

Brown, green, detergent and black acids are extracted from sludges resulting from sulfuric acid treating of various oils. The solvents employed to extract brown acids are preferably paraffinic naphthas boiling within the gasoline boiling range. Green acids, extractable from sludge with water or dilute sulfuric acid, are believed to be mixtures of brown, detergent and black acids in indefinite proportions. Detergent acids are sulfonic acids extractable from sludge with aromatic solvents such as benzene and are characterized by the fact that their sodium soaps are soluble in benzene but essentially insoluble in a paraffinic naphtha. The black acids yield sodium soaps which are essentially insoluble in both benzene and naphtha.

The oil and water solubility of the petroleum sulfonates is important in emulsion formation only insofar as it is indicative of the surface activation properties of these soaps. Surface activation in this sense appears to depend upon a double property of the soap, i. e., it must be so constituted that the sulfonic group can readily form a bond with the water phase, and yet not be so overpowering in its hydrophilic character as to weaken the molecule's affinity for the hydrocarbon of the oil phase.

It is believed that some one soap with the correct balance of hydrophilic and hydrophobic properties could be synthesized or prepared from a carefully selected petroleum fraction which would give spontaneous emulsification. None of the sulfonate soaps has this optimum balance in itself but this intermediate property can be realized by the admixture of a too hydrophilic soap with a too hydrophobic soap. Therefore, with these soaps it is necessary and permissible to use blends of the water-soluble and relatively water-insoluble soaps for emulsification.

Sulfonates synthesized as by-products from petroleum, or other similar synthetic sulfonates, may be employed. Aromatics such as benzenes, toluene and the like may be alkylated with olefin polymers, such as propylene and butylene dimers, trimers, tetramers, etc. by known means and sulfonated. The alkali soaps of these acids, having from 9 to 16 carbon atoms in the alkyl chain, might well be substituted for the water-soluble petroleum sulfonates, while those synthetics having from 18 to 30 or more carbon atoms in the alkyl chain can be substituted in most instances for the oil-soluble petroleum sulfonates. It is, therefore, within the scope of this invention to use any combination of the disclosed petroleum sulfonates as well as synthetic sulfonates, which produce emulsions of the oil-in-water type, in conjunction with polymeric organic silicon compounds as agents to cooperate with such silicon compounds to inhibit the foaming of compounded oils.

The method which I employ to assign numerical values to the foaming characteristics of oils consists of measuring 190 ml. of the oil into a 1000 ml. graduated flask, inserting a soapstone, sintered glass or other suitable diffuser of such size that the oil level rises to the 200 ml. mark in the graduate, blowing air through the diffuser for 5 minutes at the rate of 0.2 cubic foot per hour, shutting off the air and recording the volumes of liquid and of foam. After an interval of 10 minutes the respective volumes are again recorded. If the foam breaks to zero before the expiration of 10 minutes, the actual time required for complete disappearance of foam is noted. This procedure was used to collect the data shown in Table II. Observations of this kind may be made at any convenient temperature through the use of constant temperature oil or water baths, in which the graduated cylinder may be immersed. The data in Table II were obtained at room temperature.

The silicon polymer used in the experiments to be described was obtained from the Dow-Corning Corporation and is identified as No. 200, having a viscosity of 1000 centistokes at 25° C. The Dow-Corning Corporation silicone polymer No. 200, otherwise known as DC200 Fluid, are polydimethyl siloxanes having viscosities between 0.65 and one million centistokes. Siloxane polymers of about 1000 centistokes at 25° C. have been found previously to be more effective than those of different viscosity, insofar as the breaking or prevention of ordinary straight mineral oil foams is concerned. Accordingly, as used hereinafter,

in discussing the data of Table II, the term "siloxane" will refere to polydimethyl having a viscosity of 1000 centistokes at 25° C.

In practicing my invention, I may add very small quantities of a polymeric organic silicon compound and mahogany soap to the compounded oil either before the oil is used or during its useful life. Quantities of each may be of the order of magnitude shown in tests 4 and 5 of Table II. A convenient method of incorporating the additives consists of adding to the compounded oil from 0.5 to 2.0%, preferably 1.0%, of an additive concentrate comprising from about 50% to about 70% of a sulfurized mineral oil (SAE 20 grade) containing at least 2% combined sulfur, from about 0.5% to about 2% of lard oil, from 30% to 50% of sodium mahogany soap and 0.05 to 0.2% of the dihydrocarbon siloxane, the latter colloidally dispersed therein.

TABLE II

Test No.	Description of Oil	Time in Minutes since Beginning of Air Blowing	Vol. of Oil in ml.	Vol. of Foam in ml.
1	Used Cutting Oil	5	200	310
		15	200	310
2	97% of No. 1, 3% Sodium Mahogany Soap	5	100	240
		7	212	0
		5	95	355
3	No. 1+0.01% Siloxane	15	205	0
4	No. 1+1.5% Sodium Mahogany Soap and 0.005% Siloxane	5	200	15
		5½	200	Trace
5	No. 1+0.075% Sodium Mahogany Soap and 0.00025% Siloxane	5	200	15
		7	200	Trace
6	No. 1+0.5% Additive Concentrate	5	200	40
		7	200	Trace
7	No. 1+0.1% Additive Concentrate	5	200	25
		7	200	Trace

Referring to Table II, it will be noted from test 1 that a used cutting oil originally similar to that previously described produced 310 ml. of foam which did not reduce in volume after 10 minutes standing. When 3% mahogany soap was added to another sample of the used oil as in test 2, the quantity of foam developed was somewhat less and completely disappeared on standing for 2 minutes. Test 3 shows that 0.01% of siloxane allowed more foaming to occur than did the mahogany soap and that it was more persistent, requiring 10 minutes to disappear. It is desirable, of course, to reduce the formation of foam to a minimum and reference to tests 4 and 5 will show that this object was substantially attained by using mahogany soap and the silicone together, in which case the effect of the two additives is complementary and synergistic. The degree of foam control attained in tests 4 and 5 is regarded as satisfactory for all practical industrial purposes, particularly so in view of the short time interval of 2 minutes required for complete foam disappearance.

In tests 6 and 7, the aforementioned additive concentrate was employed in amounts shown. Results show that the amount of foam permitted to form initially is somewhat greater than was the case when the additives were added directly to the oil, but again, this amount of foam (25–40 ml.) is still very much less than is permitted by the same amount of siloxane alone (test 3) or by approximately the same amount of mahogany soap alone (test 2), and the performance of the concentrate could doubtless be improved by making minor changes in the quantities or ratios of the two additives.

As previously mentioned, I may use any combination of petroleum or synthetic sulfonate which produces oil-in-water emulsions and I may use crude petroleum sulfonates for the same purpose, but I prefer to use petroleum sulfonates purified as herein described.

The results of test 5 are particularly significant and illustrative of the present invention, for the quantities of mahogany soap and siloxane have been reduced far below those quantities employed when the two additives were employed alone, yet the amount of foam formed is much less and breaks rapidly.

In all cases, it is desirable to disperse the antifoam agents thoroughly in the oil.

This invention is equally suitable for the reduction and destruction of foam in systems wherein the gas causing foam is neither oxygen nor air. For example, troublesome foam formation is sometimes encountered in refrigerant compressors utilizing such refrigerants as sulfur dioxide, dichlorodifluoromethane, methyl chloride and the like.

While I have described my invention in terms of its specific application to cutting oils contaminated with a heavy metal soap of a high molecular weight fatty acid as a foaming component, it should be understood that the invention is not so limited, but is equally applicable to lubricating oils originally containing, or compounded with such heavy metal soaps.

I claim:

1. A lubricant composition which is substantially non-foaming in the presence of a high molecular weight fatty compound selected from the group consisting of high molecular weight fats, high molecular weight fatty acids and heavy metal soaps of high molecular weight fatty acids, consisting essentially of a major proportion of a hydrocarbon lubricating oil, a small amount but not more than 0.1%, of a polymeric organic silicon compound selected from the group consisting of a normally liquid polydimethyl siloxane and a normally liquid polydimethyl silicate, and a small amount but not more than 3%, of an alkali soap of a preferentially oil-soluble petroleum sulfonic acid.

2. A lubricant composition which is substantially non-foaming in the presence of a compound selected from the group consisting of high molecular weight fats, high molecular weight fatty acids and heavy metal soaps of high molecular weight fatty acids consisting essentially of a major proportion of a hydrocarbon lubricating oil, from about 0.0005% to about 0.1% of a normally liquid polydimethyl siloxane having a viscosity of about 1000 centistokes at 25° C., and a small amount, but not more than 3%, of an alkali metal soap of a preferentially oil-soluble petroleum sulfonic acid.

3. A lubricant composition which is substantially non-foaming in the presence of a compound selected from the group consisting of high molecular weight fats, high molecular weight fatty acids and heavy metal soaps of high molecular weight fatty acids, consisting essentially of a major proportion of a hydrocarbon lubricating oil, from about 0.0005% to about 0.1% of a normally liquid polydimethyl siloxane having a viscosity of about 1000 centistokes at 25° C., and a small amount but not more than 3%, of an alkaline earth soap of a preferentially oil-soluble petroleum sulfonic acid.

4. A lubricant composition which is substantially non-foaming in the presence of a compound

selected from the group consisting of high molecular weight fats, high molecular weight fatty acids and heavy metal soaps of high molecular weight fatty acids, consisting essentially of a major proportion of a hydrocarbon lubricating oil, from about 0.0005% to about 0.1% of a normally liquid polydimethyl siloxane having a viscosity of about 1000 centistokes at 25° C., and a small amount but not more than 3%, of an amine soap of a preferentially oil-soluble petroleum sulfonic acid.

5. An improved lubricant composition consisting essentially of a sulfurized mineral oil of SAE 20 grade containing not less than about 2% combined sulfur by weight, and a mineral oil of about 100 S. S. U. viscosity at 100° F., and having dissolved therein about 1% of a chlorinated paraffin wax containing at least 35% combined chlorine, about 2% of sulfurized lard oil containing a minimum of 10% combined sulfur, about 6% lard oil, a small amount, less than 0.1%, of a polydimethyl siloxane having a viscosity of about 1000 centistokes at 25° C., and a small amount, less than 3%, of sodium soaps of oil-soluble petroleum sulfonic acids.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,718,335	Cushman et al.	June 25, 1929
1,742,623	Turner et al.	Jan. 7, 1930
1,984,633	De Groote	Dec. 18, 1934
2,252,110	Armendt	Aug. 12, 1941
2,375,007	Larsen	May 1, 1945
2,378,820	Amott	June 19, 1945

FOREIGN PATENTS

Number	Country	Date
825,526	France	Dec. 8, 1937