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ANTIFOAMING COMPOSITION

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This invention relates to liquids having decreased foaming properties. More particularly, it pertains to organic liquids or their aqueous solutions or dispersions possessing decreased foaming properties and other desirable characteristics, which improved properties are contributed to the organic composition by small amounts of certain dissolved or suspended silicon compounds.

The formation of foam or froth, for example in lubrication oil systems, frequently occurs in operations under conditions in which oil and air are agitated together. In particular, foaming takes place in reduction and transmission gears and is an especially serious problem, for example, in aero-engines in which a "dry-sump" lubrication system is employed. In such engines the lubricating oil is supplied by a feed pump to the engine. After use the oil drains to a sump and is withdrawn from the engine by a scavenge pump and returned to the oil reservoir for re-delivery to the engine by the feed pump. The scavenge pump generally has a capacity for handling at least twice as much oil as it actually withdraws from the engine sump and hence it "sucks" several volumes of air with each volume of oil. The resultant mixing of oil and air in the pump causes the oil to be returned to the reservoir largely in the form of a froth. If the froth does not "break" rapidly in the tank it may be taken up and supplied to the engine by the feed pump with the result that the engine receives more air than oil and the bearings are, in effect, starved of lubricant. This condition may cause vapor locking of the pressure pump and a serious drop of the oil pressure. Another objectionable result of frothing in engine lubricants is that it can lead to loss of oil through the vents of the oil reservoir since the tank may be unable to contain the great volume of foam which is much larger than that of the lubricant itself.

It will be understood therefore that great benefit may be obtained from the use of an anti-foaming agent dissolved in lubricating oil, especially when the agent has no adverse effect on the lubricant or engine and manifests itself only by its action in causing rapid dispersal of the foam or preventing foam formation. In addition to their special application to aviation engines, such anti-foaming additives may also be added advantageously to lubricating oils used in other spark-ignition engines as well as to lubricants for other machines including compression-ignition or Diesel engines.

These compounds may also be advantageously

used in connection with other additives. Thus, most commonly used lubricating oil bases or undoped oils will foam under certain conditions and this tendency is accentuated by the addition of numerous additives, useful for other purposes, such as anti-oxidants, extreme pressure agents, detergents, corrosion inhibitors and the like. Hence, where in the past the amount of these other additives had to be held to a minimum due to their aggravation of the foaming problem, they may now be employed in larger and more useful quantities to produce a better product by the simultaneous employment of the present anti-foaming agents.

Detergents for lubricating oils normally employed in concentrations of about 0.25 to 5% which may cause foaming comprise the oil-soluble salts of various bases with detergent forming acids. Such bases include metal as well as organic bases. Metal bases include those of the alkali metals, Cu, Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Pb, Cr, Mn, Fe, Ni, Co, etc. Organic bases include various nitrogen bases as primary, secondary, tertiary and quaternary amines.

Examples of detergent forming acids are the various fatty acids of, say, 10 to 30 carbon atoms, wool fat acids, paraffin wax acids (produced by oxidation of paraffin wax), chlorinated fatty acids, aromatic carboxylic acids including aromatic fatty acids, aromatic hydroxy fatty acids, paraffin wax benzoic acids, various alkyl salicylic acids, phthalic acid mono esters, aromatic keto acids, aromatic ether acids; diphenols as di-(alkylphenol) sulfides and disulfides, methylene di-(alkylphenols); sulfonic acids such as may be produced by treatment of alkyl aromatic hydrocarbons or high boiling petroleum oils with sulfuric acid; sulfuric acid mono esters; phosphoric acid mono and di esters, including the corresponding thio phosphoric acids; phosphonic and arsonic acids, etc.

Non-metallic detergents which may cause foaming include compounds such as the phosphatides, e.g. lecithin; certain fatty oils as rapeseed oils; voltolized fatty or mineral oils.

Particularly bad foamers are the alkali earth phosphate di esters, including the thiophosphate di esters; the alkali earth diphenolates, specifically the calcium and barium diphenol mono and poly sulfides; and lecithin.

Anti-oxidants comprise several types, for example, alkyl phenols such as 2,4,6-trimethyl phenol, pentamethyl phenol, 2,4-dimethyl-6-tertiary butyl phenol, 2,4-dimethyl-6-octyl phenol, 2,6-ditertiary butyl-4-methyl phenol, 2,4,6-triter-

tiary butyl phenol, etc.; amino phenols as benzyl amino phenols; amines such as dibutyl phenylene diamine, diphenyl amine, phenyl alpha naphthyl amine, phenyl beta naphthyl amine, dinaphthyl amines; various sulfurized compounds, as sulfurized sperm oil or jojoba oil, sulfurized olefin polymers, paraffin wax polysulfides, ethylene bis-phenyl sulfide, etc.

Corrosion inhibitors which may cause some foaming comprise various dicarboxylic acids of 16 and more carbon atoms, alkali metal and alkali earth salts of sulfonic acids and fatty acids, etc.

The use of these anti-foaming agents is not limited to their employment in lubricating oils but they may be utilized with benefit in any organic medium in which it is desired to reduce foaming or frothing as well as pressure failure or vapor locking in pressure pumps caused by such foaming or frothing, and related phenomena. For example, these additives may be incorporated advantageously in various refined and semi-refined hydrocarbon compositions, such as turbine oil, spray oils, cleaning fluids, special-boiling-point solvents, Diesel fuels, gasoline, kerosene, etc.

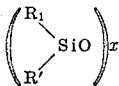
Particular reference may also be made to their use in animal fats and oils, vegetable fats and oils, photographic developers, both natural and synthetic oils, perfumes, paints, cellulose acetate, various resins, latex (i. e., solutions or suspensions of natural or synthetic rubber), etc.

These anti-foaming agents may also be employed in connection with aqueous dispersions of organic material as for instance in the viscose spinning baths utilized in the manufacture of cellulosic materials of artificial origin such as yarns of rayon, artificial silk and the like.

Accordingly, it is a principal object of this invention to reduce foaming or frothing of liquids normally tending to foam and froth. Another purpose is to produce improved liquid compositions adapted to use in pressure pumps in circulatory systems to which air or other gas has access. A further object is to provide improved lubricating oils of reduced foaming tendencies. Another purpose is to produce new and useful aviation lubricating oil compositions. Other objects will be apparent from the present description.

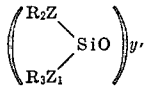
It has now been found that the above-described foam-reducing properties may be obtained in organic liquids or their aqueous solutions or dispersions by the incorporation therein of small amounts of organic silicon compounds of the following classes:

I



Dihydrocarbon silicone

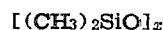
II



Dihydrocarbon silicate

in which R_1 , R_2 and R_3 are hydrocarbon radicals such as alkyl, cycloalkyl, aryl, aralkyl, alkaryl radicals preferably having less than about 20 carbon atoms; R' is hydrogen or a hydrocarbon radical; Z and Z_1 are oxygen, sulfur, selenium or tellurium atoms; and x and y are positive integers preferably 2 or higher. With regard to y it is believed that it should preferably be not higher

than about 6. The first formula above may be illustrated by dimethyl silicone:



The second formula is illustrated by di-ethyl silicate:



The two R 's and the two Z 's of the above formulae may be identical or different in each monomer and such monomeric units may be polymerized with identical or different monomeric units.

Among the many radicals represented by the several R 's, especial reference may be made to methyl, ethyl, normal and iso propyl; normal, iso, secondary and tertiary butyl; the various amyl, hexyl, heptyl, octyl and homologous groups. Also of value are such radicals as cyclopentyl, cyclohexyl, phenyl, benzyl, tolyl, naphthyl and the like. These hydrocarbon radicals may also be substituted with chlorine. Dialkyl silicones constitute a preferred group of anti-foaming additives for lubricating compositions, particularly those in which the alkyl radicals have 5 or less carbon atoms.

The amounts of the silicon compounds required for reducing foaming are generally below 0.1%. Normally, amounts ranging from about 0.0005 to 0.01% are sufficient but higher concentrations may be used when necessary.

These compounds as a group are very sparingly soluble in many solvents, but in these they are readily colloiddally dispersable. Colloidal dispersions, even of higher polymers, in most solvents are very stable.

If an ebullioscopic or cryoscopic determination of the molecular weight of these materials is attempted in various organic solvents in which they are soluble, there is evidence of considerable molecular association depending on the particular solvent to which they are added, the concentration and temperature, etc. Therefore it is impossible to ascertain the true molecular weight of these compounds. The type and degree of polymerization may also be altered by the method of preparation, environment, and related conditions. They may be prepared by ways known to the art (e. g. 63 J. A. C. S. 798 (1941)). Because of these uncertainties, it is quite impossible to state definitely the degree of polymerization which a certain silicon compound may have and which may be optimum for foam reduction.

Certain other silicon compounds, not included, have been found to possess little or no anti-foaming ability. This was especially notable with tetra hydrocarbon silicones such as tetra-benzyl silicon also with glycol silicate, cetyl silicic acid, etc. In some instances, differences in the degree of polymerization of one and the same silicon compound may vary its anti-foaming properties, some polymers being more effective than others. In the case of the silicones of Formula I above, a relatively high degree of polymerization is desirable, whereas in the case of the silicon esters of Formula II a low degree of polymerization is more desirable. Also it appears that the insoluble but colloiddally dispersable compounds are the most active anti-foamers for a given medium. As a rule liquid silicon compounds are more easily dispersed by simple means than solids and hence are preferred.

The foaming properties of mineral oils containing anti-foaming silicon compounds were evaluated by methods described below. Two

specific procedures were employed on high-viscosity aircraft oils, one for determining foaming properties at high temperature (210° F.) and the other at low (ambient) temperature (82.4° F.). Foam is produced and observed over a period of time. The resulting measurement is thus chiefly one of foam stability or "defoaming" (evolution of air and water vapor), but the initial increase of the total volume also gives an indication of foam-forming tendencies.

The high-temperature tests were conducted as follows: A 10 ml. sample of oil is measured into a 50 ml. graduated Pyrex test tube (22.5 mm. internal diameter) which is then immersed in an illuminated glass walled thermostatically controlled oil bath (of the type employed with Ostwald viscosimeters) at 98.9° C. (210° F.). A stirrer (consisting of a motor-driven two-bladed propeller) is inserted in the tube to such a depth that the bottom of the blade is at the 7 ml. point and, when temperature equilibrium has been reached, is operated at 3100 R. P. M. in such manner that the circulation is directed downward at the center. After 30 seconds, 0.1 ml. of distilled water is added from a hypodermic-type syringe and stirring continued for another 30 seconds, at which point the stirrer is removed. Readings of the height (in ml.) of the interface, which soon appears, and the topmost level are taken at intervals, generally for ten minutes. The volume of the lower layer of separated oil and of the upper layer of foam (determined by difference) are plotted as a function of time, the zero being taken when stirring is stopped.

The low-temperature tests were conducted as follows: A 100-g. sample is weighed into an ordinary liter Pyrex beaker (104 mm. internal diameter) and stirred at room temperature for 5 minutes by means of a motor-driven "Kaidette" twin-mixer egg beater, stirrer blade speed 800 R. P. M. This is mounted so that the bottom of the stirrer is 3.4 mm. above the center inside bottom of the beaker. The 120-vis. at 210° F. aviation oil tested assumed a depth of 18.0 mm. in the beaker (i. e. 14.6 mm. above the bottom of the stirrer).

The resulting foam is allowed to stand for 15 seconds, and 10 grams of the foam are then carefully poured into a 50 ml. graduated Pyrex test tube mounted on a balance pan so that the operation takes 25 seconds. After standing for another 20 seconds, the tube is immersed in a thermostatically controlled bath at 28° C. and observations are made on the volumes of the two layers which form. The total volume occupied initially by the 10 grams poured is a measure of reciprocal foam density; this indicates the tendency of an oil to form foam, which is information supplementary to the stability determination.

EXAMPLE I

By these procedures an undoped 120 vis. at 210° F. aviation oil gave an interface height after 11 minutes of 5.5 ml. in the low temperature test, and 11 ml. after 10 minutes in the high temperature test. In comparison, the same oil containing 0.01% dimethyl silicone polymer (made by Grignard reaction) showed a volume of separated oil of 13.3 ml. under the low temperature conditions and 11.3 ml. under the high temperature conditions. The corresponding volumes of foam for the same lengths of time were 21.5

ml. and 2.0 ml. for the undoped oil, and 2.0 ml. and 0 ml. for the dimethyl silicone-containing oil.

EXAMPLE II

Similar tests were made on the same grade oil containing 1.5% of a barium diphenol-sulfide-type additive commonly employed in heavy-duty or Diesel lubricating oils for its detergent and anti-oxidant properties. This compounded oil, without any added silicone compound, under the above tests showed a volume of separated oil, at the end of 11 min., of 0.1 ml. under the low temperature conditions and 6.1 ml. after 10 minutes in the high temperature test. When 0.01% of the above dimethyl silicone had been added to this compounded oil, the volume of separated oil was 14.3 ml. after 11 minutes (cold test) and 6.4 ml. after 10 minutes (hot test). The corresponding volumes of foam were 28.3 ml. (11 min., cold) and 16.7 ml. (10 min., hot) for the compounded oil, and 2.8 ml. (11 min., cold) and 17.6 ml. (10 min., hot) for the compounded oil containing 0.01% dimethyl silicone polymer.

It is thus evident that the barium diphenol sulfide additive, though admittedly imparting other desirable qualities, increases the foaming characteristics of the oil. And even this increased foaming tendency is notably overcome by the present silicon additives.

Likewise, the silicon compounds will eliminate in large measure the foaming properties imparted to organic compositions by innumerable other additives and combinations of additives necessary to impart other desirable properties to the organic solutions.

EXAMPLE III

In another test carried out as Example I, using the same aero lubricating oil, but employing a dimethyl silicone of considerably higher viscosity at a concentration of 0.005%, results were as follows:

Test

	High temperature		Low temperature	
	Separated oil	Foam	Separated oil	Foam
No silicone.....	11.0	2.0	5.5	21.5
0.005% silicone.....	11.0	1.0	12.1	0.9

EXAMPLE IV

The test of Example III was repeated with the same aero oil but containing 1.5% of a barium ditertiary amyl phenol disulfide (as per Example II). Results were as follows:

Test

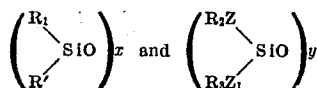
	High temperature		Low temperature	
	Separated oil	Foam	Separated oil	Foam
No silicone.....	6.1	16.7	0.1	28.3
0.005% silicone.....	10.7	3.1	12.0	1.0

We claim as our invention:

1. A composition of matter of reduced foaming properties comprising an organic liquid having foaming tendencies and a small amount, less than 0.1%, of an active defoaming compound selected

from the group consisting of polymerized dihydrocarbon silicones and dihydrocarbon silicates.

2. A composition of matter of reduced foaming properties comprising an organic liquid having foaming tendencies and a small amount, less than 0.1%, of an active defoaming compound having a formula selected from the group consisting of



wherein R_1 , R_2 and R_3 are hydrocarbon radicals having less than 20 carbon atoms; R' is hydrogen or a hydrocarbon radical of less than 20 carbon atoms; Z and Z_1 are elements selected from the group consisting of oxygen, sulfur, selenium and tellurium; and x and y are positive integers of at least 2.

3. The composition of claim 1 wherein said liquid is a hydrocarbon oil.

4. The composition of claim 1 wherein said liquid is an aqueous solution of an organic substance.

5. The composition of claim 1 wherein said liquid is a colloidal dispersion of an organic substance.

6. The composition of claim 1 wherein said active compound is insoluble and colloiddally dispersed in said organic liquid.

7. The composition of claim 1 wherein the active compound is a liquid.

8. The composition of claim 1 in which the active compound is a dialkyl silicone whose alkyl radicals contain not more than 5 carbon atoms.

9. The composition of claim 1 in which the active compound is dimethyl silicone.

10. The composition of claim 1 in which the active compound is diethyl silicate.

11. An improved mineral lubricating oil containing, colloiddally dispersed, from about 0.005 to 0.01% of a dialkyl silicone which is insoluble in said lubricating oil.

12. The composition of claim 11 in which the lubricating oil is a turbine oil.

13. The composition of claim 11 in which the lubricating oil is an aviation lubricating oil.

14. A heavy duty motor oil of improved anti-foaming properties consisting essentially of a mineral lubricating oil and containing an active amount of a detergent tending to increase foaming and, colloiddally dispersed, a small amount, less than 0.1%, of an active defoamer selected from the group consisting of polymerized dihydrocarbon silicones and dihydrocarbon silicates.

15. The lubricating oil of claim 14 wherein the detergent is a diphenate of an alkali earth metal.

16. The lubricant of claim 14 wherein the detergent is an alkali earth diphenol sulfide.

17. The lubricating oil of claim 14 wherein the detergent is a barium salt of a diphenol sulfide.

18. The lubricant of claim 14 wherein the detergent is lecithin.

19. A heavy duty motor oil of improved anti-foaming properties consisting essentially of a mineral lubricating oil and containing an active amount of an alkali earth diester phosphate and colloiddally dispersed, a small amount, less than 0.1%, of an active defoamer selected from the group consisting of polymerized dihydrocarbon silicones and dihydrocarbon silicates.

20. The lubricating oil of claim 19 wherein the phosphate is an alkali earth diester thio phosphate.

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DISCLAIMER

2,375,007.—Robert G. Larsen, Albany, and Hyman Diamond, Berkeley, Calif. ANTI-FOAMING COMPOSITION. Patent dated May 1, 1945. Disclaimer filed Apr. 7, 1947, by the assignee, Shell Development Company.

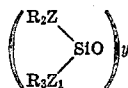
Hereby enters this disclaimer to claims 8, 9, 11, 12, and 13 of said patent;

And further disclaims from claim 1 any composition of matter which does not contain a polymerized dihydrocarbon silicate as an active defoaming compound, except where the organic liquid referred to in said claim is an aqueous solution of an organic substance;

From claims 3, 5, 6, and 7 any composition of matter which does not contain a polymerized dihydrocarbon silicate as an active defoaming compound;

From claims 14, 15, 16, 17, 18, 19, and 20 any motor oil which does not contain a polymerized dihydrocarbon silicate as an active defoamer;

And from claim 2 any composition of matter which does not contain an active defoaming compound corresponding to the formula



wherein R_2 , R_3 , Z , Z_1 and y are as defined in said claim.

[Official Gazette May 6, 1947.]