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PREVENTION OF FOAMING OF HYDROCARBON OILS

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13 Claims. (Cl. 252—49.6)

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This invention relates to the prevention of foaming of hydrocarbon oils, particularly mineral oils and lubricants containing them.

This application is a continuation-in-part of our co-pending application, Serial Number 478,154, filed on March 5, 1943, for Prevention of foaming of hydrocarbon oils.

Hydrocarbon oils and oil compositions containing them tend to foam or froth when agitated in the presence of gases or vapors, such as air, steam, oil vapor, products of combustion, and the like. The amount of foam or froth varies with the conditions under which the oil compositions are agitated, as well as the character of the composition. Under some conditions, the volume of foam or froth produced is many times that of the original oil, and even with mild agitation, substantial amounts of foam are produced in many oil compositions. In preparing and using such oils and oil compositions commercially, they are subjected to agitation under a wide range of conditions and frequently undesirable amounts of foam or froth are produced.

Various means of combating such foaming of oils and oil compositions have been proposed. For instance, mechanical devices have been proposed for destroying or breaking foam as it is formed. Usually such devices have been cumbersome or inefficient, or both, and they are not generally used commercially. Likewise, the incorporation of certain oil-soluble compounds in the oil has been proposed as a means for preventing foaming; such compounds being called "anti-foam agents." Unfortunately, no agent of this type has been found which is completely satisfactory in commercial practice; and their effectiveness sometimes diminishes rapidly in use or they must be added to the oil in such amounts that the desirable properties of the oil are impaired, or they are objectionable for other reasons.

Among the objects achieved by this invention is the provision of an improved method of preventing foaming of hydrocarbon oils, particularly mineral oils and oil compositions containing them, in which the normal foaming tendency of the oil is effectively abated or suppressed for long periods of use without deleteriously affecting the other properties of the oil.

Another object achieved by the present invention is the provision of new and improved antifoam agents and compositions capable of abating and inhibiting foaming of hydrocarbon oils and oil compositions when dispersed therein in minute amounts.

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A further object achieved by the present invention is the provision of new and improved oil compositions, particularly improved mineral oils and lubricants, having marked resistance to foaming and other advantageous properties including resistance to emulsification and containing minute amounts of an oil-insoluble antifoam agent finely dispersed therein.

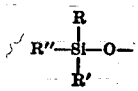
We have discovered that foaming of hydrocarbon oils, particularly mineral oils and compositions containing them, can be effectively suppressed or prevented without substantial modification of the desirable properties of such oils by forming in the oil a stable, fine dispersion of a small amount of a substantially oil-insoluble liquid condensation product of an organo-silicon oxide compound having a low interfacial tension toward the oil. We have found that hydrocarbon oil compositions containing such liquid organo-silicon oxide condensation products as a stable, finely dispersed phase are markedly resistant to foaming even under the most violent conditions encountered in commercial practice. The presence of the finely dispersed insoluble liquid phase in the oil apparently causes the films of the oil foam to rupture, thereby quickly destroying the foam. In fact, in most cases, its presence so rapidly breaks the oil foam that substantially all foam is destroyed as fast as it is formed.

In the practice of this invention, various oil-insoluble liquid organo-silicon oxide condensation products having a low interfacial tension toward oil and capable of being stably and finely dispersed in the oil may be employed as antifoam agents. These oil-insoluble liquid organo-silicon oxide condensation or polymerization products possess the property of a low interfacial tension toward hydrocarbon oils in marked degree, and are particularly advantageous for the purpose of our invention because they are capable of being stably and finely dispersed in such oils. The interfacial tension of such liquid organo-silicon oxide condensation products toward hydrocarbon oils can be measured on a special type DuNouy tensiometer. The condensation products having low tensions have proved most useful as foam suppressing agents.

The organo-silicon oxide condensation products contemplated for use according to this invention are composed primarily of a plurality of silicon atoms linked together through oxygen atoms, each silicon atom having attached to it at least one organic radical either directly or through an oxygen atom, and they may contain

one or more other substituents, such as hydroxyl groups or halides. Typical organo-silicon oxide condensation products which have been found suitable for the purposes of our invention include for example the liquid organo-siloxanes and the liquid organo-silicate condensation products.

The organo-siloxanes are sometimes referred to as the organo-silicone polymers or condensation products as a result of the fact that they are principally composed of organo-silicone residues. They vary in composition depending upon the materials from which they are produced and the method of production. They are usually produced as condensation or polymerization products of the organo-silicols including the mono-silicols, disilicols and trisilicols and mixtures of these silicols. The organo-silicone residues from these three silicols are of three different types. The silicone residue of the mono-silicols may be represented generically by the formula



in which R, R' or R'' represent similar or dissimilar organic radicals such as alkyl, aryl, aralkyl, alkaryl or heterocyclic groups. The silicone residue of the disilicols may be represented generically by the formula



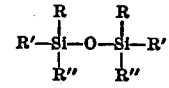
in which R and R' represent similar or dissimilar organic radicals such as alkyl, aryl, aralkyl, alkaryl or heterocyclic groups. The silicone residue of the trisilicols may be represented by the formula



in which R represents an organic radical such as an alkyl, aryl, aralkyl, alkaryl or heterocyclic group.

The organo-siloxanes or organo-silicone condensation products may contain any one or all three of the above types of silicone residues depending upon whether they are produced from pure silicols or mixtures of two or three of the mono-, di- and trisilicols. The condensation products obtainable may be straight chain, cyclic or cross polymerization products and include both solids and liquids. The liquid organo-siloxanes or organo-silicone condensation products have been found most advantageous for the purposes of our invention.

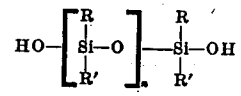
The organo-mono-silicols when polymerized alone can form only the dimer having the generic formula



in which R, R' and R'' represent similar or dissimilar organic radicals such as alkyl, aryl, alkaryl, aralkyl and heterocyclic groups. These compounds are generally liquid and are effective anti-foam agents. They are, however, somewhat soluble in hydrocarbon oil compositions and are for this reason somewhat less effective than other organo-siloxanes. However, the condensation products of organo-mono-silicols in admixture with diols and triols are particularly valuable

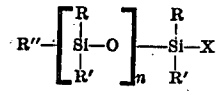
for the purposes of our invention. The presence of mono-silicols tends to prevent excessive formation of resinous solids rather than liquid condensation products.

The oily liquid condensation products obtained by polymerization of organo-silane diols are particularly advantageous anti-foam agents for the present purposes. The organo-disilicol compounds when polymerized alone tend to produce predominantly straight chain polymerization products which may be generically represented by the following formula:

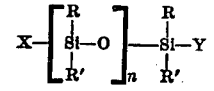


wherein R represents an organic radical, such as alkyl, aryl, aralkyl, alkaryl or heterocyclic group, R' is a similar or dissimilar organic radical and n may be one or higher depending upon the number of organo-silicon oxide residues in the complex molecule resulting from the condensation and dehydration of the organo-silane diol.

When the organo-silane diols are polymerized in the presence of an organo-silane-monol the monol tends to substitute at the end of the chain in place of at least one hydroxyl group and produce compounds having the formula

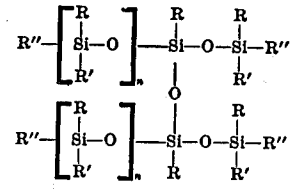


in which R, R' and R'' represent similar or dissimilar organic radicals such as the alkyl, aryl, aralkyl, alkaryl or heterocyclic group, X may be such an organic radical or a hydroxyl group and n may be one or higher. Similarly other terminal groups may be substituted in these compounds in which case the generic structural formula may be represented by



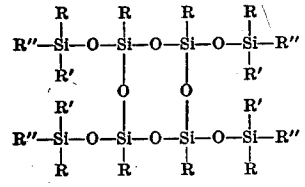
in which R and R' represent similar or dissimilar organic radicals as above and X and Y represent similar or dissimilar organic radicals or inorganic substituents such as hydroxyl radicals, halides or the like and n may be one or higher.

The condensation products obtained from pure organo-silane triols are generally resinous solids because of the extensive cross polymerization which takes place. However, liquid condensation products suitable for the purposes of our invention may be obtained from mixtures of trisilicols with mono- or disilicols or both. In such mixtures cross polymerization is more limited and there may be obtained suitable oil insoluble liquid condensation products containing for example cross polymerization products having a formula of the following type:



in which R, R' and R'' may be similar or dissimilar alkyl, aryl, aralkyl, alkaryl or heterocyclic group and n may be one or more. It will be understood that this formula is merely illustrative of cross polymerization products suitable for the

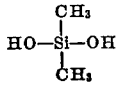
purposes of our invention and such products may take other forms in which two or more cross linkings between polymers are established. Such compounds may take a form in which they resemble cyclic compounds for example:



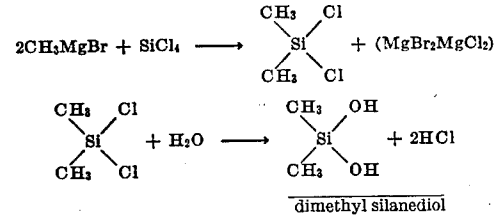
in which R, R' and R'' may be similar or dissimilar alkyl, aryl, aralkyl, alkaryl or heterocyclic groups.

The molecular weight and other properties of the organo-siloxanes or silicone condensation products vary with the extent of the dehydration and condensation of the silicols from which they are produced and with the particular organic radicals present. While some of them are resinous or rubbery solids, others are oily liquids. For the purposes of the present invention, we have found the liquid condensation products particularly effective. These viscous oily liquids, in general, have low surface tensions and low interfacial tensions toward hydrocarbon oils. They also have low solubility in hydrocarbon oils and are readily dispersible in such oils, particularly mineral lubricating oils. In general, we find the condensation products containing simple organic radicals, such as methyl, ethyl and short-chain alkyl groups, most advantageous for the purposes of our invention, as they have exceedingly small solubility in most hydrocarbon oils.

For example, we have found that the oily liquid condensation products of the methyl silicols are, in general, good anti-foam agents. The liquid condensation products of di-methyl-silane diol are most advantageous for this purpose. However, very good results have also been obtained from condensation products of mixtures containing tri-methyl-silane monol, di-methyl-silane diol and methyl-silane triol. Di-methyl-silane diol has the following formula:



It is customarily produced from silicon tetrachloride through the Grignard reaction as follows:



dimethyl silanediol

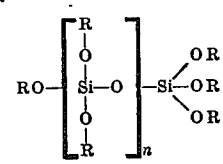
In this reaction all of the silicon tetrachloride may not be converted to the di-methyl-silane diol. The product may then consist of a mixture of tri-methyl-silane monol, di-methyl-silane diol and methyl-silane triol. This reaction product may be polymerized directly to produce satisfactory antifoam agents for the purpose of our invention. Alternatively, intermediate separation may be effected so that polymers of the individual silicols may be produced.

As a class, these liquid condensation products are for all practical purposes substantially oil-insoluble. They are also substantially insoluble

in water and aqueous solutions. On the other hand, they can be readily dispersed in hydrocarbon oils to form stable dispersions containing extremely fine particles of oil-insoluble liquid. In fact, we have prepared oil compositions containing such oil-insoluble liquids dispersed therein, in which the majority of the dispersed particles range from 2.0 to 0.3 microns or less. Such fine dispersions of these condensation products in oils are very stable and are markedly resistant to foaming. Oil compositions containing from 5 to 100 parts per million of these compounds finely dispersed therein yield little or no foam when subjected to drastic foaming tests. In fact, compositions containing as low as 0.05 part per million of a dispersed siloxane condensation product showed a measurable resistance to foaming.

The liquid condensation products of the methyl-silicols described above are merely illustrative of this type of anti-foam agent. The liquid condensation products of other organo-silicols are also effective in suppressing foaming of hydrocarbon oils and may be employed as the anti-foam agent. The amount used should be sufficiently in excess of the solubility of the compounds in the oil to give the required amount of dispersed liquid phase necessary to prevent foaming under service conditions. For this reason, the liquid siloxanes which are substantially oil-insoluble are most advantageous. While we have found that the compounds containing the simple organic radicals, such as methyl, ethyl and short-chain alkyl groups, are especially advantageous for the present purposes, satisfactory results can also be obtained with organo-siloxanes containing other organic radicals, such for example as aryl siloxanes, alkaryl siloxanes and substituted aryl siloxanes. Diphenyl siloxanes have produced particularly good results, and good anti-foam properties have also been obtained with condensation products such as methyl phenyl siloxanes and di-chlorphenyl siloxane.

Another class of liquid organo-silicon oxide condensation products which we have found useful as foam inhibitors includes the organo-silicate condensation products represented by the probable formula:



in which R represents an organic radical such as an alkyl, aryl, aralkyl, alkaryl or a heterocyclic group and n may be one or higher depending upon the number of organo-silicate residues in the complex molecule of the condensation product.

These compounds may be obtained as the polymerized hydrolysis products of the esters of ortho silicic acid by controlled hydrolysis of the tetra orthosilicate esters with water. Hydrolysis and condensation or polymerization take place simultaneously with the formation of liquid products which are in general substantially insoluble in hydrocarbon oils and have little or no interfacial tension toward such oils. Normally mixtures of products in various degrees of polymerization are first obtained. These mixtures may be used directly as anti-foam agents. It is generally more advantageous, however, to isolate the higher liquid polymerization products from the total products. We have found that the effectiveness

of these organo-silicate condensation products in preventing foam formation increases with increased molecular weight and boiling point. Also, the higher condensation products are less soluble in the hydrocarbon oils. Consequently, we find it advantageous to use the higher boiling liquid fractions of the products. Separation of the desired fractions may be accomplished by vacuum distillation of the total reaction products.

These organo-silicate condensation products are also effective foam inhibitors in very low concentration and although they are substantially insoluble in hydrocarbon oils, they are readily dispersible in such oils to form compositions containing stable, fine dispersions of the organo-silicate condensation products in hydrocarbon oils, which are substantially resistant to foam formation, without deleteriously modifying the advantageous properties of the oil. In general, we find the organo-silicate condensation products containing simple organic radicals, such as methyl, ethyl and short-chain alkyl groups most advantageous as they have exceedingly small solubility in most hydrocarbon oils. For example, we have found that a fraction of the total reaction products obtained on hydrolysis and polymerization of tetramethyl orthosilicate and fractionation at 220° to 240° C. at 0.75 mm., which consists predominantly of a condensation product in which n is of the order of 3, is markedly effective in concentrations as low as 0.1 per cent and less. A similar fraction obtained by hydrolysis and polymerization of tetraethyl orthosilicate and fractionation of the products to recover the compounds boiling above 290° C. at 1 mm., proved effective in concentrations as low as 0.005 per cent and less.

The particle size of the insoluble liquid dispersed in the hydrocarbon oil has a marked effect upon the resistance to foaming so imparted to the oil compositions. In general, we have found that oil compositions containing dispersions of our new oil-insoluble, anti-foam agents in which the liquid particles are about 2.0 microns and less in size are particularly advantageous for the present purposes. Such oil compositions are very stable in storage and under service conditions, and they have a high resistance to foaming which they retain over long periods of use.

Further, since good resistance to foaming can be readily obtained with exceedingly small proportions of our new anti-foam agents finely dispersed in the hydrocarbon oil, the anti-foam agents of our invention do not deleteriously modify the other properties of such compositions. Accordingly, the desired foam-resisting properties can be imparted to such oils without impairing their effectiveness as lubricants or for other intended uses.

In the commercial practice of this invention, oil compositions may be produced directly in which the anti-foam agent is present in the desired small amount and fine dispersion. However, in certain embodiments of the invention, oil compositions initially containing relatively coarse dispersions and relatively high concentrations of the anti-foam agents may be first prepared and the desired finely dispersed agent concentration may be produced in the hydrocarbon oil during use by agitation thereof in the lubricating system, such as by gear pumps and other mechanisms Such production of the desired fine dispersions in situ in the oil during use is sometimes advantageous. Of course, the amount of anti-foam agent and the fineness of the dispersion necessary to prevent foaming in a given case vary somewhat with the particular oil and agent employed as well as the service conditions to which the oil composition is subjected.

In preparing our improved oil compositions, the oil-insoluble anti-foam agent may be incorporated in the oil or oil composition by any suitable method capable of producing a stable fine dispersion of the liquid agent in the oil. For example, the anti-foam agent may be dissolved in a light hydrocarbon or other suitable solvent, such as mineral seal oil, gasoline, naphtha, hexane and benzene, and this solution may be introduced into the hydrocarbon oil to which it is desired to give anti-foam properties. The anti-foam agents of our invention are substantially soluble in these solvents at normal temperatures, and after such a solution has been formed it may be incorporated in the hydrocarbon oil or oil composition or crude oil, simply by mixing and agitating the solution therewith. A fine dispersion of the anti-foam agent in the oil is thus obtained. A convenient solution for such use would contain 1.0 per cent of active anti-foam agent. To add 0.001 per cent anti-foam agent to the final oil would require the addition of 0.1 per cent of the solution of anti-foam agent. Where it is desired to form directly a dispersion of the anti-foam agent in the oil, various commercial colloid mills may be employed to disperse finely the liquid agent in the oil. In this way, stable fine dispersions, wherein the size of the dispersed liquid particles is within the range of 2.0 to 0.3 microns or less, are readily obtained. Also, gear pumps may be employed to disperse the liquid anti-foam agent in the oil. The use of such gear pumps is advantageous in many embodiments of this invention, particularly those wherein fine dispersions of the anti-foam agents are produced in situ in the oil. Other methods and apparatus may also be employed in dispersing these agents in oils or oil compositions.

It is sometimes advantageous to first disperse the liquid anti-foam agent in part of the oil and then add this concentrate dispersion to the remainder of the oil. Such concentrate dispersions can be readily prepared as stable uniform compositions. For instance, a mixture of oil and anti-foam agent in the desired proportions may be continuously circulated through a gear pump until a stable concentrate containing a uniform dispersion of the agent in the desired particle size is obtained. Thus, standardized concentrates can be prepared which can be added to lubricating compositions as needed. In such case, the desired amount of concentrate is added to the hydrocarbon oil composition and the mixture is agitated until uniform.

Also, such concentrates are themselves valuable anti-foam compositions. As they contain a preformed, dispersed, insoluble liquid phase of the desired particle size, they quickly break oil foams, as well as suppress foaming in general. For instance, when added to oil or oil compositions which have foamed, they rapidly destroyed the foam present and stopped further foaming. In such cases, they can be quickly blended with oils, oil compositions, and crude oil and uniformly incorporated therein before serious foaming occurs.

For such purposes, oil concentrates containing from 100 to 2000 parts per million of finely dispersed liquid organo-silicon oxide condensation products are advantageous. By adding from 0.1 to 10 parts of such concentrates to 100 parts of

mineral lubricating oils, improved lubricants having marked resistance to foaming are readily and easily obtained.

One particularly advantageous field of use for the anti-foam agents of our invention is in lubricants for internal combustion engines, such as automotive, aviation, Diesel and like engines, because we have found that even under the high temperature of operation of these engines, these compounds retain their foam-inhibiting properties. In lubricating such engines, appreciable foaming of the motor oil seriously interferes with effective lubrication. For instance, aviation oils (either straight or compounded oils) tend to foam at the low barometric pressures encountered at high altitudes. Also in lubricating such engines, particularly aviation engines, the lubricating oil is circulated under pressure through the parts to be lubricated. In doing so gear pumps are usually employed in supplying pressure oil to the engine and returning the oil from the engine sumps to the reservoir tank. In such systems, the scavenger pump is usually of such capacity as to maintain the engine sump in a substantially dry condition. With such dry sump systems, the scavenger pump frequently pumps large volumes of air with the oil, this air becoming dispersed in the oil. Under such conditions, excessive foam often leads to loss of the oil from the engines and impairs the lubrication. By the present invention, such foaming can be readily overcome or suppressed. For example, an appropriate amount of our liquid anti-foam agents can be introduced into the circulating oil and dispersed therein by the gear pumps, or oil concentrates of the anti-foam agents can be intermittently injected into the oil and uniformly dispersed therein by such gear pumps whenever substantial amounts of foam appear in the system. Further, such foaming can be prevented and the engine effectively lubricated at all times by employing an improved lubricant containing these liquid anti-foam agents dispersed therein from the beginning.

While our anti-foam agents and improved motor oils are particularly advantgeous in lubricating engines wherein the oil is circulated under pressure by means of such gear pumps, they are also useful and advantageous in lubricating certain types of engines using splash lubrication. Also, modern Diesel engine oils usually contain relatively large amounts of additives of the detergent or detergent-dispersion type. It has been found that such additives promote foaming. Accordingly, many Diesel oils foam badly. By the present invention, such foaming is effectively prevented and improved anti-foaming Diesel oils readily obtained.

Another advantageous field of use is in gear lubricants, particularly for transmission gears of automotive equipment and the like. In lubricating such gears, the oil composition is violently agitated by the rotating gears and substantial amounts of foam are formed. This foam interferes with the lubrication and cooling of the gears. By the present invention, this foaming and its attendant difficulties in gear lubricants are effectively prevented and overcome.

Still another field of use for the products of our invention is in the light oils used in steam turbines. With these light oils, agitation may produce considerable foaming. By the present invention, such foaming of light oils is effectively prevented. Furthermore, there is often a tendency for steam turbine oils to emulsify with the water with which they are mixed. We have found that the anti-foam agents of our invention have an additional advantage in this use, because they generally increase the resistance of such oils to emulsification.

Our improved anti-foaming agents also may be advantageously added to crude oil to prevent foaming in pipe lines, storage tanks and the like, particularly such oils as are produced in western Venezuela. Concentrations of the order of 0.00005 per cent or 0.5 parts per million are quite effective in suppressing foaming in crude oils. It is usually advantageous to add the anti-foam agent to the crude oil in solution in a solvent such as one of those indicated above, because of the small amount of anti-foam used in a large volume of crude. Good results can be obtained when the anti-foam agent is added to the crude oil when the crude oil is being fed from the wellhead to a gas separator. The agitation secured at this point is sufficient for distributing the solution of anti-foam agents through the crude oil. The effect of adding such solutions of our anti-foam agents is that existing tankage and equipment for handling such crudes can, for its capacity, about double its throughput. Our new anti-foam agents and compositions are also useful in other oil compositions and effectively prevent the foaming thereof. Indeed, they are useful and advantageous in any hydrocarbon oil or oil composition in which they are substantially insoluble whether used as a lubricant or not, and in which it is desired to prevent foaming. However, they are particularly effective in combating foaming in mineral lubricating oils and lubricants.

The relative effectiveness of various organosilicon oxide anti-foam agents of our invention in preventing foaming in different hydrocarbon oils and oil compositions may be demonstrated by means of the following foaming test in which the oil or oil composition is controllably aerated under fixed conditions, so that the results obtained in a series of tests are directly comparable.

In carrying out this test, 200 cc. of the oil are placed in a tall graduate and air, in the form of fine bubbles, is passed upwardly through this column of oil at a controlled rate of 0.2 cubic feet per hour by means of a diffuser positioned in the bottom of the graduate. The graduate is closed with a suitable cover provided with air inlet and outlet tubes. The inlet tube extends to the bottom of the graduate and has a diffuser fixedly mounted on the lower end. Air is passed down through this tube and through the fine pores of the diffuser into the oil. In this way, uniform fine air bubbles are introduced at the bottom of the oil column. The fine air bubbles pass up through the column of oil agitating it and forming foam. The volume of foam formed at the top of the oil column can be readily and accurately measured on the graduate.

By this test, the time to form a given amount of foam may be noted and recorded and the amount of foam formed in a given time from the start of air flow through the oil may be measured and recorded. Either of these measurements gives a numerical value proportioned to the overall average rate of foaming. One or both of these values can be conveniently used to compare and evaluate the respective foaming properties of different oils and oil compositions.

In the above test, the foaming characteristics of the oil or oil composition tested are usually determined at room temperature under atmospheric pressure. However, if desired, similar

foaming tests can be made at other temperatures and pressures as desired. For instance, foaming tests may be made at higher or lower temperatures by placing the graduate containing the oil in a thermostatically controlled bath maintained at the desired temperature. In fact, this is usually done even when the tests are made at room temperatures, the bath and oil in the graduate being brought to a standard temperature, usually 80–90° F., before aerating the oil. The foaming test may be made at reduced pressures by connecting the air outlet of the graduate to a suitable low pressure reservoir maintained at the pressure desired.

In the following specific examples, there are illustrated by means of this foaming test the advantageous results obtained by incorporating in a mineral lubricating oil the organo-silicon oxide anti-foam agents of our invention.

Example I

In this example, a commercial liquid condensation product of dimethyl silane diol was used as the anti-foam agent, and it was incorporated in a highly refined paraffinic lubricating oil of SAE 50 grade.

The selected dimethyl silicon oxide condensation product was a viscous oily liquid having a molecular weight of about 2000 and a viscosity (S. U. S.) of approximately 30,000 at 100° F. Its composition by chemical analysis was as follows:

Carbon, percent	Hydrogen, percent	Silicon, percent	Oxygen, percent (by difference)
32.0	8.15	35.5	24.35

It had a low interfacial tension toward the selected oil and was practically insoluble although it was readily dispersible in the selected oil.

In dispersing this liquid anti-foam agent in the lubricating oil, a concentrated oil dispersion was first prepared. In doing so, 0.1 part of the di-methyl silicon oxide compound was added to 99.9 parts of the oil by weight, and this mixture was continuously circulated through a gear pump until a fine dispersion containing dispersed liquid particles varying from less than 0.3 to 2.0 microns was obtained. Next, one part of this concentrate was added to 99 parts of the selected paraffinic lubricating oil and this oil mixture was agitated with a suitable stirrer until a uniform composition was obtained. The non-foaming lubricating oil so obtained contained 10 parts of the liquid anti-foam agent per million parts of oil. The inspection properties of this improved non-foaming oil composition were substantially the same as those of the base oil, as shown in the following table:

Composition	Base oil	Base oil+10 P. P. M. anti-foam agent
Gravity, API	29.6	29.6
Viscosity SUV at—		
100° F	1,065	1,081
210° F	96.4	97.4
Color, NPA	3—	3—
Ash, percent	0.01	0.01
Precipitation No	0.05	0.05
Neutralization No	0.03	0.02

To compare the foaming properties of the base oil and the oil containing the dimethyl silicon

oxide compound, samples (200 ml.) of the two oils were subjected to the above-described foam test at 78° F. The results were as follows:

Composition	Time, minutes	Vol. of foam, ml.
1. Base oil	0	0
	1	140
	3	365
	4	440
	5	510
	6	550
	8	645
	10	755
	12	835
2. Base oil+10 P. P. M. anti-foam agent	0	0
	1	0
	5	0
	10	0
	15	0
	20	0
	25	0

As shown by the above test, this oil containing the anti-foam agent of our invention is effectively rendered non-foaming.

Example II

In this example a methyl siloxane product was produced from silicon tetrachloride and tested as an anti-foam agent.

The methyl silicone polymer was prepared as follows:

Silicon tetrachloride dissolved in an equal volume of ether was mixed at a temperature between −10° C. and 0° C. with methyl magnesium chloride in ether in a ratio of one mol of silicon tetrachloride to each two mols of methyl magnesium chloride. Near the end of the mixing, the temperature was allowed to rise slowly until the ether refluxed gently. After all the methyl magnesium chloride had been added, heat was applied and the mixture was refluxed for one hour. After the reaction product stood overnight, it was poured over cracked ice to hydrolyze the methyl silicon chlorides. The ether solution of the hydrolyzed reaction products was then washed with water and with sodium thiosulfate solution until neutral and until all of the free chlorine had been removed. The ether was then evaporated and the methyl silicol product recovered. No attempt was made to recover the individual silicols from the methyl silicol mixture thus obtained.

The methyl silicol mixture was then dissolved in benzene and about 20 per cent by weight of 9 N sulfuric acid was added. This mixture was heated on a steam bath for about five to ten minutes. After about two hours the benzene layer was separated from the sulfuric acid, was washed with water and treated with small portions of activated charcoal on the steam bath over a period of three-quarters of an hour. The activated charcoal was filtered off and the benzene was evaporated in about two hours by heating over a steam bath in a current of air. The last traces of benzene were removed under vacuum to recover the methyl silicone polymerization products or methyl siloxanes.

The methyl siloxane product on analysis gave the following results:

Percent carbon	Percent hydrogen	Percent silicon
28.25	7.26	39.70
28.10	7.20	39.49

These results show a higher silicon to carbon ratio than the theoretical for a dimethyl silicone polymer indicating the presence of other methyl silicone polymers.

The methyl siloxane product thus obtained was tested for its effectiveness as an anti-foam agent by the foam test above described. When incorporated in the same base oil in corresponding concentrations the synthetic methyl siloxane product showed substantially the same foam suppressing power as the commercial dimethyl silicone polymer used in Example I.

Example III

In this example methyl-o-silicate condensation products were prepared by partial hydrolysis of tetra methyl-o-silicate, and were tested as anti-foam agents.

The preparation of the methyl-o-silicate polymer or condensation product was carried out as follows:

Freshly distilled tetra methyl-o-silicate was mixed with alcohol containing about 4.5 per cent of water, in such proportion as to provide about 0.8 mol of water per mol of silicate. The mixture was then heated at refluxing temperature for two hours. The alcohol and unchanged tetra methyl orthosilicate were then distilled off at atmospheric pressure. The condensation products were then fractionally distilled at 0.75 mm. pressure at temperatures between 120° and 240° C. The fractions boiling between 200° and 220° C., between 220° and 240° C. and the residue boiling above 240° C. were tested as anti-foam agents. The tests of the respective fractions as anti-foam agents were made in comparison with the uncondensed tetra methyl-o-silicate and with the commercial dimethyl siloxane used above in Example I. The results of these tests are shown in the following table.

Material tested	Percentage in base oil required for equivalent results
Dimethyl siloxane	0.0005
Tetramethyl-o-silicate	Not effective
Silicate condensation product B. P. 200–220° C./0.75 mm	0.25
Silicate condensation product B. P. 220–240° C./0.75 mm	0.1 to 0.25
Silicate condensation product B. P. above 240° C./0.75 mm	0.08

These results indicate that the higher boiling liquid methyl orthosilicate polymers are the more effective anti-foam agents but that the methyl silicate polymers are substantially less effective than the methyl siloxanes as anti-foam agents.

Example IV

In this example tetra ethyl-o-silicate condensation products were prepared by partial hydrolysis of tetra ethyl-o-silicate and tested as anti-foam agents. The same method of preparation as is above described for the preparation of the methyl-o-silicate condensation products was used.

The fractions of the condensation products boiling between 200° and 240° C./1 mm., 280°–290° C./1 mm., and above 290° C./1 mm. were tested as anti-foam agents in comparison with uncondensed tetra ethyl-o-silicate and with the commercial dimethyl siloxane described in Example I. The following results were obtained:

Material tested	Percentage in base oil required for equivalent results
Dimethyl siloxane	0.0005
Tetra ethyl-o-silicate	Not effective
Ethyl silicate condensation product B. P. 200–240° C./1 mm	1.0
Ethyl silicate condensation product B. P. 280–290° C./1 mm	0.5
Ethyl silicate condensation product B. P. above 290° C./1 mm	0.005

These results indicate also that the higher boiling fractions of the ethyl-o-silicate condensation products are the more effective anti-foam agents.

While our invention has been described above with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such illustrative examples and embodiments, and may be variously practiced within the scope of the claims herein made.

What we claim is:

1. A composition of matter of reduced foaming properties comprising an organic liquid having foaming tendencies and a small amount, less than 0.1 per cent, of an active defoaming compound comprising a dehydration silicon oxide condensation product.

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

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

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

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

6. 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, colloidally dispersed, a small amount, less than 0.1 per cent, of an active defoamer comprising a dehydration silicon hydroxide condensation product.

7. A process of suppressing foaming in hydrocarbon oils and hydrocarbon oil compositions which comprises producing in the oil a stable fine dispersion of a liquid organo-silicon oxide condensation product in an amount corresponding to at least 0.5 parts per million of the oil but insufficient to substantially modify the desirable properties of the oil.

8. A process of suppressing foaming in hydrocarbon oils and hydrocarbon oil compositions which comprises producing in the oil a stable fine dispersion of a liquid organo-silicon oxide condensation product in an amount corresponding to from 0.5 to 100 parts per million of the oil.

9. A process as claimed in claim 8, wherein the dispersion of liquid organo-silicon oxide condensation product comprises predominantly particles of 2.0 microns and less in size.

10. A process of suppressing foaming in hydrocarbon oils and oil compositions containing them, comprising forming in said oil a stable fine dispersion of a liquid organo-silicon oxide condensation product having a low interfacial tension toward said oil in an amount corresponding to at least 5 parts per million of said oil and insufficient to deleteriously modify other desirable

properties of the oil, by incorporating in said oil a solution of said liquid organo-silicon oxide condensation product in a lighter hydrocarbon than said oil in which said organo-silicon oxide condensation product is substantially more soluble than in said oil, said solution containing 100 to 2000 parts per million of said liquid organo-silicon oxide condensation product.

11. A hydrocarbon oil composition of reduced foaming properties comprising a hydrocarbon oil having foaming tendencies and an organo-silicon oxide condensation product stably dispersed in said oil in a small amount, not less than 0.5 parts per million, insufficient to substantially modify the desirable properties of said oil.

12. A hydrocarbon oil composition of reduced foaming properties comprising a hydrocarbon oil having foaming tendencies and from 0.5 to 100 parts per million of a liquid organo-silicon oxide condensation product stably dispersed in said oil.

13. A composition adapted to impart foam-resisting properties to hydrocarbon oils and compositions containing them when added thereto in an amount corresponding to 0.1 to 100 parts per hundred, comprising a hydrocarbon liquid containing from 100 to 2000 parts per million of a liquid organo-silicon oxide condensation product.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,375,007	Larsen et al.	May 1, 1945
2,345,155	Dennison et al.	Apr. 11, 1944
2,242,400	Loane et al.	Mar. 20, 1941
2,129,281	Lincoln et al.	Sept. 6, 1938

OTHER REFERENCES

Chemical & Metallurgical Engineering, Aug. 1944, pp. 109 and 136. (Copy in Div. 50.)

Certificate of Correction

Patent No. 2,416,503. February 25, 1947.

CHARLES E. TRAUTMAN ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 14, lines 31 and 48, for "dehydration" read *dihydrocarbon*; column 16, line 16, for the patent number "2,345,155" read *2,346,155*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of April, A. D. 1947.

[SEAL]

LESLIE FRAZER,
First Assistant Commissioner of Patents.