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2,772,238

FOAM-INHIBITED LUBRICATING OILS

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7 Claims. (Cl. 252—48.2)

This invention pertains to lubricating oil compositions containing new compounds which inhibit foaming (especially where excessive foaming occurs) and rusting. In particular, the lubricating compositions described herein have new sulfur-containing compounds (i. e., bis(alkylphenyl polyethylene glycol ether) sulfides) incorporated therein.

This application is a continuation-in-part of application Serial No. 308,950, filed September 10, 1952 (and now abandoned).

When air is mixed with oil, a certain amount of foam may be created; the amount of foam depending, among other things, upon the character of the oil and the type of service in which the oil is employed. Usually, under ordinary service conditions, mineral oils uncompounded with a chemical additive do not readily form a foam. On the other hand, many compounded oils tend to form a stable foam, a foam more stable than the base oils from which they are compounded. For example, petroleum lubricating oils compounded with metal naphthenates, higher metal alcoholates, higher metal alkyl phenates and metal salts of fatty acids foam more than the corresponding base oils. Oils containing many other additives cause more foam than is formed by the base oils per se.

In certain types of service, such as where there is little or no agitation, trouble due to foaming is encountered only in very exceptional cases. On the other hand, certain drastic types of service, involving extremely violent intermixture of oil and air or combustion gases, may produce an objectionable amount of foam with many oils. However, between the extremes of service causing little foaming of any oil and service causing much foam of many oils, there are types of service and certain oils which, when used in combination, cause considerable difficulty. As stated, certain compounded oils exhibit a greater tendency to foam than the base oils, and when these compounded oils are used in certain types of lubricating systems involving greater agitation of the oil and greater intermixture with gases than the ordinary crankcase lubrication of automobiles, the greatest practical difficulty is encountered.

The dry sump lubrication system employed in many aircraft engines is illustrative of the type of lubrication system which, when used with compounded lubricating oils having a strong tendency to foam, causes practical difficulty. In this system, oil from the moving parts of the motor is collected in the crankcase and pumped from there to an external tank or sump by a scavenging pump. Oil from this sump is pumped back to the motor in the usual manner by an oil pump. The foaming difficulty arises from the fact that the scavenging pump operates at excess capacity; it pumps faster than required to pump all of the available oil in the crankcase. Therefore, it pumps a great deal of air along with the oil, and this at a rapid rate, with the result that air is entrained in the

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oil and a foam is formed. As a consequence, excessive foaming occurs when oils such as the aforementioned compounded oils are used. Among the disadvantages resulting therefrom are the loss of oil through the breather pipes, insufficient lubrication because of the presence of air in the oil supplied to the motor, etc.

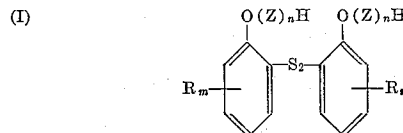
Oil also forms a more persistent foam if it contains water (as in solution) and is then heated and suddenly subjected to a very low pressure, as for instance, in the oil of an airplane engine powering an airplane from a low altitude to an altitude of 40,000 feet at a high speed.

In other instances, as in the lubrication of gears with heavy oils, foaming difficulties may also be encountered.

Thus, it is an object achieved by the present invention to inhibit the foaming of oils.

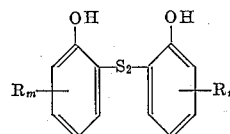
According to the present invention, it has been discovered that certain oil-soluble alkylphenyl polyethylene glycol ether sulfides are effective as foam inhibitors in lubricating oil compositions. The lubricating oil compositions of this invention comprise oils of lubricating viscosity and certain alkylphenyl polyethylene glycol ether sulfides.

The oil-soluble alkylphenyl polyethylene glycol ether sulfides described herein are prepared by the reaction of alkyl phenol sulfides with ethylene oxide and are characterized by the formula:



wherein the R's are straight-chain or branched-chain, saturated or unsaturated, essentially hydrocarbonaceous radicals, each having from 1 to 30 carbon atoms (i. e., less than 31 carbon atoms), the m's are numbers each having a value from 1 to 3, Z represents an ethylene oxide group ($\text{---CH}_2\text{CH}_2\text{---O---O---}$), and the n's are numbers each having a value from about 8 to about 17.

Alkylphenol sulfides used in the preparation of the compounds of Formula I hereinabove are represented by the following formula:



wherein R and m have the same representations as set forth hereinabove.

By essentially hydrocarbonaceous radical is meant those radicals which are composed mainly of hydrogen and carbon, and includes such radicals which contain, in addition, minor amounts of substituents, such as chlorine, bromine, oxygen, sulfur, nitrogen, etc., which do not substantially affect their hydrocarbon character.

Examples of suitable hydrocarbonaceous radicals include alkyl radicals such as butyl, butenyl, pentyl, pentenyl, hexyl, octyl, decyl, dodecyl, dodecenyl, hexadecyl, eicosyl, triacontyl, etc.; radicals derived from petroleum hydrocarbons, such as white oil, wax, olefin polymers (e. g., polypropylene and polybutylene), etc.

The lubricating oils in which the bis(alkylphenyl polyethylene glycol ether) sulfides of this invention may be incorporated include a wide variety of lubricating oils such as naphthenic base, paraffin base, and mixed base mineral oils, other hydrocarbon lubricants, e. g., lubricating oils derived from coal products, and synthetic oils, e. g., alkylene polymers (such as polymers of propylene,

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butylene, etc., and mixtures thereof), alkylene oxide type polymers, dicarboxylic acid esters, liquid esters of acids of phosphorus, alkyl benzenes, oils containing silicon, etc. Synthetic oils of the alkylene oxide type polymers which may be used include those exemplified by the alkylene oxide polymers (e. g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing alkylene oxides, e. g., propylene oxide, in the presence of water or alcohols, e. g., ethyl alcohol; esters of alkylene oxide type polymers, e. g., acetylated propylene oxide polymers prepared by acetylating propylene oxide polymers containing hydroxyl groups; polyethers prepared from the alkylene glycols (e. g., ethylene glycol), etc. The polymeric products prepared from the various alkylene oxides and alkylene glycols may be polyoxyalkylene diols or polyalkylene glycol derivatives; that is, the terminal hydroxyl group can remain as such, or one or both of the terminal hydroxyl groups can be removed during the polymerization reaction by etherification or esterification.

Synthetic oils of the dicarboxylic acid ester type include those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkenyl succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc. Examples of dicarboxylic acid ester synthetic oils include dibutyl adipate, dihexyl adipate, di-2-ethylhexyl sebacate, di-n-hexyl fumaric polymers, etc.

Synthetic oils of the type of liquid esters of acids of phosphorus include the diesters of phosphoric acid, e. g., tricresyl phosphate; the esters of phosphonic acid, e. g., diethyl ester of "white oil" phosphonic acid, (or other such esters as obtained by reacting alkane phosphonyl chlorides with hydroxy-containing compounds such as phenols and aliphatic alcohols as described in Jensen and Clayton U. S. Patent No. 2,683,168).

Synthetic oils containing silicon include the liquid esters of silicic acid and the polysiloxanes. The liquid esters of silicic acid and the polysiloxanes include those exemplified by tetra(methyl-2-butyl) silicate, tetra(4-methyl-2-pentyl) silicate, tetra(1-methoxy-2-propyl) silicate, tetra(2-ethylhexyl) silicate, hexa(4-methyl-2-pentoxo) disiloxane, poly(methyl siloxane), poly(methylphenyl siloxane), etc.

The above base oils may be used individually as such or in various combinations (whenever miscible or whenever made so by the use of mutual solvents).

Depending upon the use and the solubility of the compounds of this invention, they may be used in oils in amounts of 10% or more, such as from 0.001% to 10%. In certain instances it may be advantageous to use solubilizing agents. When used to inhibit foaming, for example, the compounds of this invention may be used in oils in amounts of 0.001% to 1%, by weight. On the other hand, when the compounds of this invention are used in lubricating oils to inhibit rust, they may be used in amounts of 0.25% to 4%, or as much as 10%, by weight.

The new compounds used herein as foam and rust inhibitors according to this invention are normally prepared by heating alkyl phenol sulfides with ethylene oxide in the presence of base catalysts.

Such basic substances effective as catalysts in the preparation of the new compounds of this invention include the alkali metal oxides and hydroxides, alkaline earth metal oxides and hydroxides, etc.

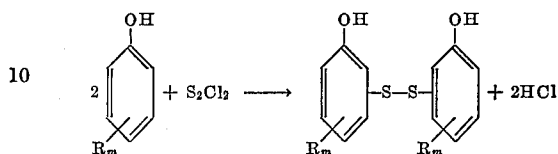
The molar ratio of ethylene oxide to alkyl phenol sulfide herein is dependent upon the number of ethylene oxide units desired in the finished product; the greater the value of the molar ratio of ethylene oxide to the phenol sulfide, the greater the number of ethylene oxide units in the product.

The following examples illustrate the preparation of the compounds of this invention.

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Example 1.—Preparation of di(tetrapropylenephenol disulfide

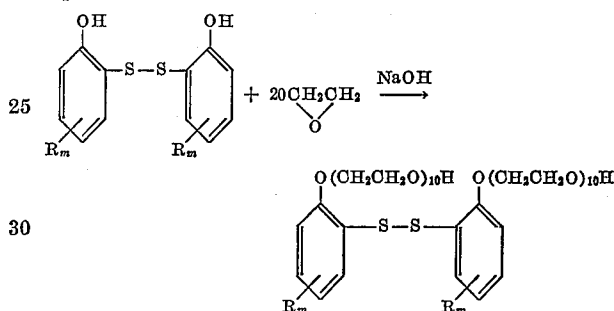
The di(tetrapropylenephenol) disulfide which was used in the preparation of the di(tetrapropylenephenyl decaethylene glycol ether) disulfide of Example 2 hereinbelow was obtained as follows:



wherein R represents the tetrapropylene radical, and m is a number having a value from 1 to 3.

Example 2.—Preparation of bis(ditetrapropylenephenyl decaethylene¹ glycol ether) disulfide

This preparation takes place according to the following equation:



A mixture of 100 g. of bis(ditetrapropylenephenol) disulfide and 0.80 g. of C. P. sodium hydroxide was charged to a reaction flask and heated to a temperature of 150° C. After the flask had been purged with nitrogen, then purged with ethylene oxide, the temperature was increased to 200° C. The reaction vessel was closed, and during a period of about 20 hours, a total of 90.8 g. of ethylene oxide reacted with the bis(ditetrapropylenephenol) disulfide. The reaction mixture was finally heated at 150° C. for 1½ hours.

Example 3.—Preparation of bis(ditetrapropylenephenyl polyethylene glycol ether) disulfide

A mixture of 307 g. of bis(ditetrapropylenephenol) disulfide and 1.2 g. of sodium hydroxide was charged to a reaction vessel. The reaction vessel was purged first with nitrogen, then with ethylene oxide, after which excess ethylene oxide was added. The reaction temperature was maintained between about 220° C. to 230° C.

At various intervals during the reaction period, samples of the reaction product were removed from the reaction mixture and analyzed. The following table presents data as to the number of ethylene oxide units present in the composition at various stages during the reaction period.

TABLE I

Sample No.	Average No. of Ethylene Oxide Units
1	4.4
2	6.3
3	9.9
4	14.8
5	20
6	24

The foam and rust inhibitors of this invention (which also include the monosulfides) are exemplified as follows: di(amyphenyl octaethyleneglycol ether) disulfide, bis-(diamylphenyl decaethyleneglycol ether) disulfide, bis-

¹ The number of ethylene oxide units is an average of 10, the range being from about 8 to about 12.

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(triarylphenyl decaethyleneglycol ether) disulfide, bis-(triarylphenyl polyethyleneglycol ether) disulfide, di-(hexylphenyl octaethyleneglycol ether) disulfide, di(octylphenyl pentadecaethyleneglycol) disulfide, di(octylphenyl hexadecaethyleneglycol ether) disulfide, di-(octylphenyl dodecaethyleneglycol ether) disulfide, di(decylphenyl pentadecaethyleneglycol ether) disulfide, bis(didodecylphenyl hexadecaethyleneglycol ether) disulfide, di(cetylphenyl decaethyleneglycol ether) disulfide, bis(dicetylphenyl pentadecaethyleneglycol ether) disulfide, etc.

As stated hereinabove, the new compounds herein are useful to inhibit the formation of foam in excessively foaming lubricating oil compositions. The data set forth hereinbelow in Table II, which were obtained according to the procedure set forth in the ASTM D892-46T Foam Test, show the effectiveness of these compounds in inhibiting foam formation. This test is described as follows:

The test oil was poured into a clean 1000 ml. cylinder until the liquid level reached the 180 ml. mark. The test sample was heated rapidly to 200° F. by placing the cylinder in a heating bath, after which the cylinder was immersed to the 900 ml. mark in a separate bath maintained at 200° F. By means of the diffuser stone, air was blown through the test sample for five minutes at the rate of 94 ml. per minute, and the volume of foam recorded. The volume of foam was again recorded after a ten-minute settling period.

The reference oil was a California solvent-refined paraffin-base oil containing a sulfurized calcium alkylphenate, a sulfurized diparaffin sulfide, and a calcium alkylphenyl dithiophosphate. The abbreviations in Table II are identified as follows:

F. T.=Foam volume, ml. at end of 5-minute blowing period.

F. S.=Foam volume, ml. at end of 10-minute settling period.

DTP=Ditetrapropylenephenyl.

TABLE II

Test No.	Oil Description	F. T.	F. S.
1.....	Reference Oil.....	800	590
2.....	Reference Oil+0.10% Bis (DTP decaethyleneglycol ether) disulfide.	20	0
3.....	Reference Oil+0.10% Bis (DTP pentadecaethyleneglycol ether) disulfide.	50	0

¹ The number of ethylene oxide units is an average of 10, the range being from about 8 to about 12.

² The number of ethylene oxide units is an average of 15, the range being from about 13 to about 17.

The compounds of this invention are also useful in fuel oils (i. e., hydrocarbon fuel oils). In the operation of pressure atomizing type burners and diesel engines, difficulties are encountered in the formation of deposits which gradually plug filters and strainers in the fuel systems. These deposits are composed, in part, of products of deterioration from the fuel. When small amounts of the new compounds of this invention are added to fuel oils, the sedimentary materials are dispersed and held in suspension, thus avoiding the formation of deposits which gradually plug the filters and strainers.

Furthermore, when fuel oils are placed in storage tanks or tankcars, they normally become contaminated with water. This water, either salt water or fresh water, is usually held in suspension, forming an emulsion. This emulsion is broken when small amounts of the new compounds of this invention are incorporated in the fuel oils. The emulsion is broken and the water coalesces, resulting in a clean phase separation.

This invention is not limited in its application to those oils which, because of certain salt-like compounding agents, form viscous, plastic surfaces. This invention is applicable broadly to the inhibition of oil foaming wherever it occurs and comprises the addition of my foam inhibiting agents to any oil which foams excessively.

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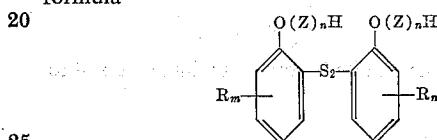
In addition to the alkylphenyl polyethyleneglycol ether sulfides, the lubricating oil compositions of this invention can contain oxidation inhibitors, pour point depressants, extreme pressure agents, grease thickening agents, coloring agents, etc.

As used herein, the term "excessive" with regard to foaming means that the "foam volume" at the end of the 10-minute period was above about 100 ml.

It may be desirable to incorporate larger amounts of the bis(alkylphenyl polyethyleneglycol ether) sulfides in oil than specified herein. For example, for shipping purposes, it is advantageous to incorporate as much as 50% of the additives of this invention in oil. Whenever necessary, solubilizing agents may be used.

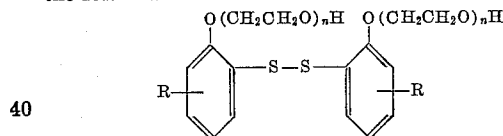
I claim:

1. A foam inhibited lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and an alkylphenyl polyethyleneglycol ether sulfide of the formula



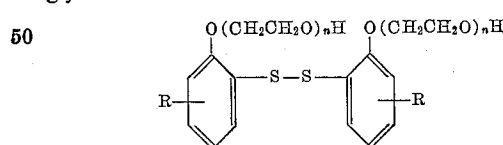
wherein R represents an aliphatic group containing less than 31 carbon atoms, Z is an ethylene oxide group, *m* is a number having a value from 1 to 3, and *n* is a number having a value from about 8 to about 17, in an amount sufficient to inhibit foaming of said oil composition.

2. A foam-inhibited lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and, in an amount sufficient to inhibit the formation of foam, an alkylphenyl polyethyleneglycol ether sulfide of the formula



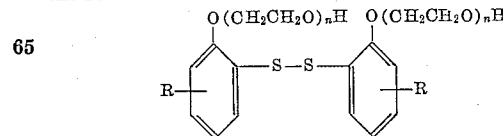
wherein R represents an alkyl group containing from 8 to 16 carbon atoms, and *n* is a number having a value from about 8 to about 17.

3. A foam-inhibited lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and from 0.01% to 2.0% of an alkylphenyl polyethyleneglycol ether sulfide of the formula



wherein R represents an alkyl group containing from 8 to 16 carbon atoms, and *n* is a number having a value from about 8 to about 17.

4. A foam-inhibited lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and, in an amount sufficient to inhibit the formation of foam, an alkylphenyl polyethyleneglycol ether sulfide of the formula

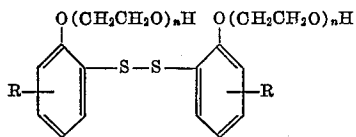


wherein R represents an alkyl group containing from 8 to 16 carbon atoms, and *n* is a number having a value from about 8 to about 12.

5. A foam-inhibited lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and, in an amount sufficient to inhibit the formation of

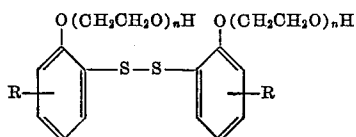
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foam, an alkylphenyl polyethyleneglycol ether sulfide of the formula



wherein R represents an alkyl group containing from 8 to 16 carbon atoms, and n is a number having a value from about 13 to about 17.

6. A foam-inhibited lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and from 0.01% to 2.0% of an alkylphenyl polyethyleneglycol ether sulfide of the formula

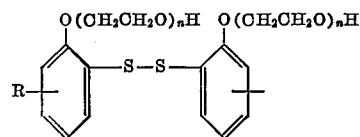


wherein R represents an alkyl group containing from 8 to

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16 carbon atoms, and n is a number having a value from about 8 to about 12.

7. A foam-inhibited lubricating oil composition comprising a major proportion of an oil of lubricating viscosity and from 0.01% to 2.0% of an alkylphenyl polyethyleneglycol ether sulfide of the formula



wherein R represents an alkyl group containing from 8 to 16 carbon atoms, and n is a number having a value from about 13 to about 17.

References Cited in the file of this patent

UNITED STATES PATENTS

20	2,306,354	Cook	Dec. 22, 1942
	2,629,743	Burnette et al.	Feb. 24, 1953
	2,681,315	Tongberg et al.	June 15, 1954