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POLYALKYLENE SULFIDES, SULFOXIDES AND SULFONES

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ABSTRACT OF THE DISCLOSURE

Long hydrocarbon chain-containing sulfur derivatives (sulfides, sulfoxides and sulfones and polysubstituents thereof) find use as detergents in lubricating oils.

This invention concerns novel sulfur derivaties which find use as detergents in lubricating oils. More particularly, this invention concerns novel sulfur derivatives having one long chain hydrocarbon radical which find use as detergents in lubricating oils.

A development of major importance in the lubricating oil additive field has been the introduction of ashless detergents, that is, metal free compounds which are capable of reducing varnish and sludge deposits in internal combustion engines. An important advantage of these ashless detergents is the avoidance of the ash formed by the metal salt detergents on decomposition. Thus, valve and combustion chamber deposition with accompanying octane requirement increase can be minimized through their use.

A variety of lower molecular weight ashless detergents have been reported in the patent literature. See for example U.S. Patent No. 3,018,251, which discloses acylated polyamines; U.S. Patent No. 2,764,551, which discloses polyesters containing amino groups; U.S. Patnet No. 2,887,452, which discloses urethanes; and U.S. Patent No. 2,371,333, which discloses esters of pentaerythritol, to mention a few.

It has now been found that sulfur-containing compounds of from about 25 to 250 carbon atoms having (1) from 1 to 3 sulfur-containing functionalities of the formula

$$—S(O)_n—$$

wherein n is a cardinal number of from 0 to 2, at the same end of the molecule; and

(2) an uninterrupted chain of at least 20 carbon atoms, preferably 25 carbon atoms, can be used as ashless detergents in lubricating oils. Alternatively, the compounds of this invention have a long aliphatic hydrocarbon chain as one part of the molecule and joined to this chain is a functionality having from 1 to 3 thioether group bonded only to carbon, i.e., —C—S—C; wherein from 0 to 2 oxygens may be bonded to the sulfurs by coordinate covalent bonds.

Bonded to the short chain radical bonded to sulfur may be substitutents which are inert (the substituents do not interfere with the preparation of the products or enhance or detract from the products' utility) or do impart desirable properties to the product. Illustrative of such substituents are hydroxy, lower alkoxy, amino, lower alkyl amino and di(lower alkyl)amino.

The molecule may be described by the following formula

$$X\{A[S(O)_nX']_m\}$$

wherein X is an aliphatic hydrocarbon radical of from about 20 to 245 carbon atoms, A is a polyvalent (di-, tri- or tetra-substituted) hydrocarbon radical of from 1 to 7 carbon atoms, usually an aliphatic hydrocarbon radical,

X' is a hydrocarbon radical of from 1 to 8 carbon atoms, or a substituted hydrocarbon radical of from 1 to 12 carbon atoms (see above), n is a cardinal number of from 0 to 2 and m is an integer of from 1 to 3, usually of from 1 to 2.

The molecule may be further described, somewhat more narrowly, by the following formula

$$R(S(O)_nR^1)_m$$

wherein R is an aliphatic hydrocarbon group, either saturated or having aliphatic unsaturation (e.g., olefinic unsaturation) of from about 20 to 245, usually 25 to about 150 carbon atoms, the sulfur substituent(s) being toward the end of the molecule (not more than 6 carbon atoms from a terminal carbon atom), R^1 is a hydrocarbyl radical of from about 1 to 8 carbon atoms, more usually of from about 1 to 3 carbon atoms or substituted hydrocarbyl radical of from 1 to 12 carbon atoms and having from 0 to 1 atoms of row 2 of the Periodic Table of atomic number 7 to 8, i.e., oxygen or nitrogen (hydrocarbyl is a monovalent organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., alkaryl or aralkyl, and may have aliphatic unsaturation, e.g., ethylenic), n is a cardinal number of from 0 to 2, m is an integer of from 1 to 3, usually 1 to 2; when m is 2, the two R^1's may be joined together to form a ring with the sulfurs to which the two R^1's are attached together with the intervening carbon atoms. When m is two or three, the sulfur substituents will be separated by not more than four carbon atoms and usually not more than two carbon atoms.

Compounds wherein m is 1 have the following formula

$$R^2S(O)_nR^3$$

wherein R^2 is aliphatic hydrocarbyl of from about 25 to 150 carbon atoms, preferably of from about 30 to 75 carbon atoms, R^3 is hydrocarbyl of from 1 to 8 carbon atoms, preferably hydrocarbyl of from 1 to 3 carbon atoms and particularly preferred alkyl of from 1 to 3 carbon atoms and n is a cardinal number of from 0 to 2 or substituted hydrocarbyl as indicated previously for P', preferably substituted alkyl of from 1 to 8 carbon atoms and 1 atom of atomic number 7 to 8.

When m is 2 or 3, the compounds have the following formula

$$R^4[A^1(S[O]_nR^5)_m]$$

wherein R^4 is aliphatic hydrocarbyl of from about 25 to 150 carbon atoms, more usually of from about 30 to 75 carbon atoms, R^5 is hydrocarbyl of from 1 to 8 carbon atoms, more usually hydrocarbyl of from 1 to 3 carbon atoms and preferably alkyl of from 1 to 3 carbon atoms and when the two R^5's are taken together, hydrocarbylene of from 1 to 8 carbon atoms, preferably alkylene of from 1 to 3 carbon atoms and n is a cardinal number of from 0 to 2 (hydrocarbylene is a divalent radical composed solely of carbon and hydrogen and otherwise the same as the definition of hydrocarbyl) and A^1 is a polyvalent (tri- or tertavalent) aliphatic hydrocarbon radical whose valences are satisfied by R^4 and $S[O]_nR^5$ and is of from 1 to 7 carbon atoms, usually of from 1 to 2 carbon atoms. R^5 can also be substituted hydrocarbyl as indicated for R^3.

As already indicated, two sulfur atoms will be separated by not more than four carbon atoms, and usually not more than two carbon atoms; preferably, two sulfur atoms are separated by from 1 to 2 carbon atoms.

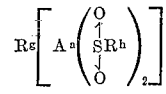
As is evident from the above formulae, the compounds of this invention are either mono-, di- or tri-thioethers, sulfoxides or sulfones, wherein 1 or more functionalities may be present. That is, the same molecule may have a

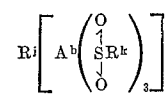
sulfide and a sulfoxide or sulfone functionality. The following formulae illustrate the various functionalities and indicate also the preferred sub-genera.

(I) R^aSR^b

(II) 

(III) 

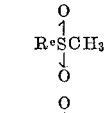
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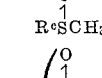
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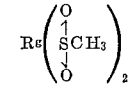
wherein R^a, R^c, R^e, R^g and R^j are aliphatic monovalent hydrocarbon radicals of from about 30 to 75 carbon atoms, preferably of from 30 to 60 carbon atoms, R^b, R^d, R^f, R^h and R^k are aliphatic radicals of from 1 to 6 carbon atoms, preferably alkyl radicals of from 1 to 3 carbon atoms; A^a and A^b are polyvalent aliphatic radicals of from 1 to 2 carbon atoms whose valences are satisfied by R^g, SO_2R^h and R^j, SO_2R^k, respectively.

Particularly preferred are the thiomethyl compounds of the following formulae:

(I) R^aSCH_3

(II) 

(III) 

(IV) 

wherein R^a, R^c, R^e and R^g are as defined previously.

Illustrative of the various compounds of this invention are the following: polyisobutenyl methyl sulfide, polyethylenyl methyl sulfide, polypropenyl methyl sulfide, poly-1-butenyl methyl sulfide, polyisobutenyl ethyl sulfide, polyisobutenyl hexyl sulfide, polypentenyl cyclohexyl sulfide, polypropenyl tolyl sulfide, polyisobutenyl methyl sulfoxide, polyisobutenyl phenyl sulfoxide, polypropenyl butyl sulfoxide, polyisobutenyl methyl sulfone, polyisobutenyl ethyl sulfone, polyisobutenyl di(methylsufenyl) methane, polyethenyl di(ethylsufonyl) methane, 2-polyisobutenyldithiolan-1,3, 2-polypropenyldithiolan-1,3, 2-polyisobutenyl-1,1,3,3-tetraoxodithiolan-1,3, 2-polyisobutenyl-1-oxodithiolan-1,3, polyisobutenyl tris(methylsulfonyl)methane, polypropenyl tri(ethylsulfonyl)methane, etc. (The polyalkenyl groups can be either saturated or unsaturated having olefinic unsaturation and are from about 25 to 150 carbon atoms.)

As already indicated, inert substituents may be present in the molecule. The substituents for the most part are hydroxyl, amino and lower alkyl derivatives thereof. Illustrative of compositions having these substituents are polypropenyl 2-hydroxyethyl sulfide, polyisobutenyl 2-ethoxyethyl sulfide, polyisobutenyl 3-isopropoxyethyl sulfoxide, polyisobutenyl 2-aminoethyl sulfone, polyisobutenyl N,N-diethylaminopropyl sulfide, polyethylenyl N,N-dimethylaminoethyl sulfone, polyisobutenyl p-anisyl sulfide, polypropenyl p-aminophenyl sulfone, etc.

Individual substituents are illustrated by amino, hydroxy, dimethylamino, pentylamino, ethoxy, propoxy, hexyloxy, etc.

The compounds of this invention can be prepared in a variety of ways according to known synthetic organic procedures. The sulfides can be prepared by combining the desired alkali metal sulfide with the polyalkenyl halide, e.g., chloride or bromide. Preferably, the bromide is used since it appears to provide superior results in the engine.

The polyalkenyl halides can be obtained by polymerizing olefins from about 2 to 5 carbon atoms to a polymer of the desired molecular weight. Illustrative olefins are ethylene and propylene. Various methods known in the art may be used, e.g., Lewis acid catalysts. The resulting polymer will have residual unsaturation which can be used as the active site for introduction of the halogen. Halogen may be introduced either ionically or free radically.

The respective sulfoxides and sulfones can then be prepared by using a variety of oxidizing agents, hydrogen peroxide being the most convenient. The reaction is generally carried out in the presence of a carboxylic acid, which aids the oxidation of the sulfide to the sulfoxide or the sulfone.

The derivatives having more than one sulfur-containing functionality can be prepared from disubstituted methanes, when the methylene group is activated by a sulfonyl group, by preparing derivatives of a polyalkenyl aldehyde, by forming the thiomercaptal, or other similar means.

The method of preparation is not critical to this invention and any convenient means known in the art for preparing the desired compounds may be used.

The following examples are offered by way of illustration and not by way of limitation.

EXAMPLE A

Preparation of polyalkenyl halides

(1) Into a reaction flask was introduced 1,350 g. of polyisobutene (1.5 moles, approximately 900 molecular weight), the mixture cooled to about −20° C. and a solution of 240 g. (1.5 moles) of bromine in 750 ml. of carbon tetrachloride added over a period of 4 hours, while maintaining the temperature below −10° C. The mixture was then allowed to warm to room temperature with stirring and the solvent removed by heating to 100° C. at a pressure of 10 mm. Hg. The residue was then analyzed for bromine. Weight percent Br=9.46, indicating an equivalent weight of 846.

(2) Into a reaction flask was introduced 1,800 g. of polyisobutent (2 moles, approximately 900 molecular weight) and 1.5 liters of benzene and the solution cooled to 0° C. Over an 8-hour period, 142 g. of chlorine (2.0 moles) was bubbled into the benzene solution while maintaining the temperature at about 0° C. An aliquot was taken and heated to 100° C. at 5 mm. Hg to remove any volatile material and the residue analyzed. Weight percent Cl=4.01, theory 3.9.

EXAMPLE 1

Preparation of polyisobutenyl methyl sulfide

A. Into a reaction flask was introduced 162 g. (2.4 moles) of a 95 weight percent aqueous potassium hydroxide solution and then diluted with 500 ml. of absolute ethanol. The solution was cooled with an ice bath, the flask fitted with an acetone-Dry Ice condenser and then 106 g. (2.4 moles) of methyl mercaptan added to the solution. To the resulting potassium methyl mercaptide was added 1,267 g. (1.2 moles, approximately 93 weight percent of the bromide) of polyisobutenyl bromide (prepared as described in Example A–1) in 1 liter of benzene. The addition of the benzene solution was at a rate which maintained the temperature below 36° C. After all of the benzene solution was added, the mixture was stirred and then refluxed overnight.

The benzene phase was separated from the ethanolic phase, washed with water until neutral and then dried over sodium sulfate. The benzene was stripped in vacuo yielding 995 g. Analysis: Weight percent S=2.55, theoretical=3.55; percent Br=0.727.

B. Into a reaction flask was introduced 132 g. of 85 weight percent aqueous potassium hydroxide, 400 ml. of absolute ethanol, the solution cooled in an ice bath and

96 g. (2 moles) of methyl mercaptan added. The resulting potassium methyl mercaptide solution was then diluted with 400 ml. of dioxane and 200 ml. of diethyl ether.

A benzene solution (1,172 g.) containing 80 weight percent polyisobutenyl chloride (approximately 900 molecular weight, 4.01 weight percent Cl) was diluted with 400 ml. of diethyl ether and the solution added to the above mixture. The reaction mixture was then heated to reflux for one hour, the heating stopped and the mixture allowed to stand overnight.

The reaction mixture was then repeatedly washed until neutral to pH paper, dried over anhydrous sodium sulfate, filtered through Celite and the volatile material removed in vacuo. Yield: 841 g. Analysis (percent): Sl= 1.98 (theory, 3.37%), Cl=1.44. Molecular weight (ThermoNAM)=1022.

EXAMPLE 2

Preparation of a polyisobutenyl methyl sulfoxide

A. Into a reaction flask was introduced 1,207 g. (0.925 mole) of polyisobutenyl methyl sulfide (prepared as described in Example 1–A) and 1 liter of methylene chloride, the mixture cooled at 20° C. and a solution of 104.8 g. (0.925 mole) of 30 percent hydrogen peroxide added over a period of 1 hour. At the end of this time, 10 ml. of glacial acetic acid was added and the mixture was heated to reflux (50° C.) and methylene chloride distilled off. Benzene (100 ml.) was then added to assist the removal of water, a vacuum of 1 to 2 mm. Hg being applied when the pot temperature reached 100° C. The residue weighed 1,200 g. Analysis: Weight percent S=2.01; molecular weight (ThermoNAM)=1,013.

B. Into a reaction flask was introduced 841 g. of the product of Example 1–B, one liter of benzene, and 10 ml. of glacial acetic acid. To this mixture was slowly added 59 ml. of 30 weight percent aqueous hydrogen peroxide. At the end of the addition, the mixture was heated to 48° C. for a short time and then allowed to stand overnight.

After diluting the reaction mixture with one liter of ether, the ethereal solution was washed with water until neutral to pH paper, dried over anhydrous sodium sulfate and then stripped of volatile materials in vacuo. Analysis (percent): S=1.80, Cl=1.40. Molecular weight (ThermoNAM)=994.

EXAMPLE 3

Preparation of a polyisobutenyl sulfone

Into a reaction flask was introduced 900 g. of sulfide prepared as described in Example 1 (0.542 mole of sulfide, the remaining material being inert) 1.2 liters of benzene and 250 cc. of glacial acetic acid. To this mixture was added 184.5 ml. of 30 weight percent aqueous hydrogen peroxide. At the end of the addition, the mixture was heated at reflux for 1 hour and allowed to stir overnight. To this mixture was then added 61.5 ml. of 30 weight percent hydrogen peroxide and heated to reflux and held at this temperature for 8 hours. An infrared spectrum of the product indicated the presence of sulfone. The reaction mixture was then washed with water until neutral to pH paper, dried over anhydrous sodium sulfate, filtered through Celite and the solvent stripped. Analysis: Weight percent S=1.63 (theoretical=1.89%).

EXAMPLE 4

Preparation of polyisobutenyl bis(methylsulfonyl)methane

Into a reaction flask was introduced 950 ml. of absolute ethanol and 23 g. of sodium dissolved in the ethanol. To the sodium ethoxide solution was then added 172 g. of bis-di(methylsulfonyl)methane, after which was added 1,000 g. of polyisobutenyl bromide (prepared as described in Example A–1) dissolved in 1.5 liters of benzene and the reaction mixture maintained at a temperature of about 50° C. The temperature was then raised to reflux (71° C.) and maintained for 7.5 hours. At the end of this time, the reaction was allowed to cool, diluted with ether and washed with water. After drying the solution, it was filtered and the volatile material removed in vacuo. Analysis: Weight percent S=0.71 (theory= 6.39).

EXAMPLE 5

Preparation of a polyisobutenyl sulfone having a hydroxyl substituent

A. Into a reaction vessel was introduced 80 g. (2.0 moles) sodium hydroxide and 250 ml. of absolute ethanol, followed by the dropwise addition of 2-mercaptoethanol.

To the mercaptide prepared above was added 520 g. of polyisobutenyl bromide (approximate molecular weight =550) in 500 ml. of benzene and the mixture was then heated at reflux for 18 hours. After allowing the mixture to cool, the mixture was filtered and then extracted with 3 aliquots of 250 ml. of water. The solution was then neutralized by the addition of 10 ml. conc. HCl and then washed with water until the washings were neutral to pH paper. After drying over anhydrous sodium sulfate, the volatile material was removed in vacuo. Yield=442 g. Analysis (percent): S=3.79, 3.75. Molecular weight (ThermoNAM)=467.

B. Into a reaction flask was introduced 442 g. (0.848 mole, approximate molecular weight 520) of polyisobutenyl 2-hydroxyethyl sulfide, prepared as described above, 500 ml. of benzene and 20 ml. of glacial acetic acid. To this mixture was then added 287 g. (2.55 moles) of 30 percent hydrogen peroxide, the temperature rapidly rising to 60° C. After the addition of the hydroperoxide was completed, the mixture was stirred for an additional 3 hours and then heated at reflux for an additional 2 hours. The infrared spectrum of an aliquot of the reaction mixture from which the solvent had been removed indicated the presence of sulfone. The reaction mixture was then diluted with 500 ml. of ether, the organic phase separated from the aqueous phase, and then the organic phase washed with water until neutral to pH paper. After drying the organic phase over anhydrous sodium sulphate, the volatile materials were removed in vacuo. The residue weighed 411 g. Analysis: Weight precent S=2.95%; molecular weight (ThermoNAM)=594.

EXAMPLE 6

Preparation of polyisobutenyl 2-aminoethyl sulfide

A. To 111 g. (0.982 mole) of 2-aminoethanethiol hydrochloride was added 500 ml. of absolute ethanol and 50 ml. water, followed by the slow addition of 129.4 g. (1.97 moles) of 85 weight percent aqueous KOH while cooling the reaction mixture in an ice bath.

To the above mixture was then added 1,163 g. of polyisobutenyl bromide (82.7 weight percent active, 0.982 mole, approximately 900 molecular weight) and one liter of ether, the resulting mixture allowed to stand overnight, followed by heating at reflux throughout the following day. After allowing the mixture to cool, the mixture was washed with water until neutral to pH paper, dried over anhydrous sodium sulfate, filtered through Celite and then the volatile materials stripped in vacuo. Analysis (percent): S=1.41, 1.42, N=0.76, 0.75, Br=1.75. Molecular weight (ThermoNAM)=1,139.

Preparation of polyisobutenyl 2-aminoethyl sulfoxide

B. To a mixture of 911 g. (0.492 mole) of the sulfide prepared above, one liter of benzene and 100 ml. of glacial acetic acid cooled in an ice bath, 55 ml. of 30 weight percent aqueous hydrogen peroxide was added over a one hour period. After stirring for an additional two hours, the reaction mixture was diluted with pentane, washed with water, the acetic acid extracted with dilute

base, and then repeatedly washed, adding methanol to minimize the emulsion. After distilling the benzene-water azeotrope, the residue was diluted with pentane, extracted with ethanol, and the two phases stripped of volatiles.

Raffinate: Yield, 552 g. Analysis (percent): S=0.29, N=0.32, 0.30.

Extract: Yield, 274 g. Analysis (percent): S=1.43, N=0.73, 0.71.

EXAMPLE 7

Alternative method of preparation polyisobutenyl methyl sulfide

Methyl disulfide (113 g., 1.2 moles) in 750 ml. of methyl chloride was cooled to −10° C. while maintaining a nitrogen atmosphere, followed by the addition of 85 g. (1.2 moles) of chlorine over a two hour period. The resulting mixture was added to 630 g. (2.0 moles) of polyisobutene (approximately 315 molecular weight) in 500 ml. methylene chloride at −20° C. After completion of the addition, volatile material was stripped in vacuo at 100° C., the residue treated with Norite, an activated charcoal, for 1 hour at 100° C. and the charcoal removed by filtration. Yield=536 g. Analysis (percent): S=3.53 (theory=6.9), Cl=3.25.

A number of other compounds were prepared according to methods described in the previous example. While some variations in the solvent or temperature occurred, these were not found to significantly affect the products obtained or their subsequent performance in the engine. The high molecular weight olefin used was polyisobutene, either of 450 molecular weight or of about 900 molecular weight. Both the chloride and bromide were used, which ever one being indicated. The sulfur analysis is reported both with the sulfide and, when applicable, the oxidized sulfur compound. The compounds are all polyisobutenyl methyl sulfides and their sulfoxide derivatives.

TABLE I

Ex. No.	Polyisobutene [1]	Halide	Wt. percent sulfur: Sulfide	Wt. percent sulfur: Sulfoxide	Molecular weight (ThermoNAM) [2]
8	A	Br	1.78	1.84, 1.88	----------
9	A	Br	1.67	1.61, 1.64	----------
10	B	Br	3.98	----------	----------
11	A	Cl	1.98	1.80	994
12	B	Cl	2.77, 2.87	2.84	484
13	B	Cl	2.18, 2.22	1.59	460
14	B	Br	4.09	----------	----------
15	B	Br	4.23	3.79, 3.73	590
16 [3]	B	Br	3.85	2.30	518

[1] Polyisobutene having approximate molecular weight: A—900; B—450.
[2] Commercial differential diffusion method for molecular weight determination.
[3] After preparing the sulfoxide, the product was purged with nitrogen, and then heated at 100° C. for 30 minutes at 10 mm. Hg. The analysis is for the product after the thermal treatment.

As already indicated, the compounds of this invention find use as dispersants and detergents in lubricating oils. The compounds of this invention find particular use in diesel engines, demonstrating excellent results under the high temperatures at which diesel engines operate. When compounded with a lubricating oil for use in an engine, the compounds of this invention will be present in at least about 0.1 weight percent and usually not more than 10 weight percent, more usually in the range of about 1 to 5 weight percent.

The compounds, however, can be prepared as concentrates, due to their excellent compatibility with oils. As concentrates, the compounds of this invention will generally range from about 10 to 70 weight percent, more usually from about 20 to 50 weight percent of the total composition.

Usually included in the oils are other additives, such as extreme pressure agents, rust inhibitors, antioxidants, oiliness agents, foam inhibitors, viscosity index improvers, pour point depressants and occasionally other detergents. Usually, these will be present in the range from about 0.01 to 10 weight percent, more usually from about 0.5 to 5 weight percent of the composition and generally each of the additives will be present in the range from about 0.01 to 5 weight percent of the composition.

A preferred aspect in using the compounds of this invention in lubricating oils is to include in the oil from about 10 to 50 mM./kg. of a zinc O,O-dihydrocarbyl phosphorodithioate, wherein the hydrocarbyl groups are from about 4 to 30 carbon atoms. Usually, the hydrocarbyl groups will be alkyl or alkaryl groups. Other phosphorodithioates may also be used with advantage.

The lubricating fluids which may be used with the compounds of this invention (hereinafter referred to as oils) may be derived from natural or synthetic sources. Oils generally have viscosities of from about 35 to 50,000 Saybolt Universal seconds (SUS) at 100° F. Among natural hydrocarbonaceous oils are paraffin base, naphthenic base, asphaltic base and mixed base oils. Illustrative of synthetic oils are: hydrocarbon oils, such as polymers of various olefins, generally of from 2 to 6 carbon atoms, and alkylated aromatic hydrocarbons; and non-hydrocarbon oils, such as polyalkylene oxides, aromatic ethers, carboxylate esters, phosphate esters and silicon esters. The preferred media are the hydrocarbonaceous media, both natural and synthetic.

The above oils may be used individually or together, whenever miscible or made so by the use of mutual solvents.

In order to demonstrate the excellent effectiveness of the compounds of this invention as detergents and dispersants in lubricating oils, the compounds were tested in the 1-G Caterpillar Test (MIL-L-45199 conditions). The oil used was a Mid-Continent SAE 30 oil and 12 mM./kg. of zinc dialkylphenyl phosphorodithioate (the alkyl groups were polypropylene of about 12 carbon atoms) was included.

TABLE II

Ex. No.	Wt. percent of detergent in oil [1]	Groove deposits [2]	Land deposits [3]	Underhead deposits
1-A	10	44-44-0-0	190-105-110	4.5
2-A	10	78-14-0-0	385-35-40	6.7
3	5	63-15-1-0.5	700-150-120	5.7
4	4	31-15-1-1	450-125-105	5.5
5-B	4	49-6-1-1	520-105-50	3.5
8	5	53-8-.9-.4	370-10-10	----------
9	4	53-12-0-0	365-15-15	8.0
10	4	86-2-1-0	85-50-30	9.0
11	5	72-13-0.5-0.5	470-60-35	6.2
12	5.75	60-10-5-3	615-620-670	3.5
13	5	82-13-1.5-1	655-515-325	3.5
14	4	70-12-1-0	155-30-50	9.4
15	4	44-8-1-1	210-30-20	7.5
16	4	30-15-1-0	485-70-25	7.5

[1] The weight percent is based on the total non-volatile product obtained, which generally contains about 50 to 75% of the sulfur-containing product. Therefore, all the values should be reduced by from ¼ to ½ to indicate the weight percent of active material.
[2] The groove deposits are rated on a scale of 0 to 100; 0 is completely clean, while 100 is completely filled. Base oil containing the indicated amount of phosphorodithioate is rated as 93-15-5-3.
[3] The land deposits are rated on a basis of 0 to 800; 0 is completely clean and 800 is completely black. Base oil containing the indicated amount of phosphorodithioate is rated as 500-800-370.
[4] The underhead deposits are rated on a scale of 0 to 10; 0 is completely black, while 10 is clean.

It is evident from the above table that the sulfides, sulfoxides and sulfones all provide excellent detergency under the stringent conditions of the 1-G Caterpillar Test. Of particular note is the extremely clean underhead obtained in most of the examples. Moreover, it is possible that the presence of polyisobutenyl halide is detrimental to maintaining clean pistons. By removing the undesirable halides from the compounds of this invention, further improvement in operating efficiency in the engine could presumably be obtained.

As will be evident to those skilled in the art, various modifications on this invention can be made or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure.

I claim:

1. A composition of the formula:

$$X(A[S(O)_nX']_m)$$

wherein X is an aliphatic hydrocarbon radical of from about 30 to 245 carbon atoms, A is a polyvalent aliphatic hydrocarbon radical of from 1 to 2 carbon atoms, X' is selected from the group consisting of an alkyl radical of from 1 to 8 carbon atoms and a substituted alkyl radical having from 1 to 12 carbon atoms and 1 oxygen atom as its only heteroatom, *n* is a cardinal number of from 0 to 2 and *m* is an integer of from 1 to 3.

2. A composition according to claim 1 wherein *m* is 1.

3. A composition according to the formula:

$$R^2S(O)_nR^3$$

wherein R^2 is alkyl or alkenyl of from about 30 to 150 carbon atoms, R^3 is alkyl of from 1 to 8 carbon atoms and *n* is a cardinal number of from 0 to 2.

4. A composition according to claim 3 wherein R^3 is alkyl of from 1 to 3 carbon atoms and *n* is 1.

5. A composition according to claim 8 wherein R^5 is substituted alkyl of from 1 to 8 carbon atoms and *n* is 0.

6. A composition according to claim 8 wherein R^5 is substituted alkyl of from 1 to 8 carbon atoms and *n* is 1.

7. A composition according to the formula:

$$R^4[A^1(S[O]_nR^5)_m]$$

wherein R^4 is alkyl or alkenyl of from about 25 to 150 carbon atoms, R^5 is alkyl of from 1 to 8 carbon atoms, A^1 is a polyvalent aliphatic hydrocarbon radical of from 1 to 2 carbon atoms, *n* is a cardinal number of from 0 to 2, with the proviso that two R^5's can be taken together to form a hydrocarbylene radical of from 1 to 8 carbon atoms, and *m* is an integer of from 2 to 3.

8. A composition according to the formula:

$$R^4[A^1(S[O]_nR^5)_m]$$

wherein R^4 is alkyl or alkenyl of from about 25 to 150 carbon atoms, R^5 is substituted alkyl of from 1 to 12 carbon atoms and 1 atom of atomic number 8 as its only heteroatom, A^1 is a polyvalent aliphatic hydrocarbon radical of from 1 to 2 carbon atoms, *n* is a cardinal number of from 0 to 2, with the proviso that two R^5's can be taken together to form a divalent radical of from 1 to 8 carbon atoms, and *m* is an integer of from 2 to 3.

9. Polyisobutenyl methyl sulfoxide, wherein said polyisobutenyl group is of from about 30 to 150 carbon atoms.

10. Polyisobutenyl methyl sulfone, wherein said polyisobutenyl group is of from about 30 to 150 carbon atoms.

11. Bis(methylsulfonyl)polyisobutenyl methane, wherein said polyisobutenyl group is of from about 30 to 150 carbon atoms.

12. Polyisobutenyl 2-hydroxyethyl sulfone, wherein said polyisobutenyl group is of from about 30 to 150 carbon atoms.

13. Polyisobutenyl tris(methylsulfonyl)methane, wherein said polyisobutenyl group is of from about 30 to 150 carbon atoms.

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