Title: LUBRICANT COMPOSITION COMPRISING ANTI-FOAM AGENTS

Technical Field

This invention relates to lubricant compositions. The lubricant compositions may be particularly suitable for lubricating diesel engines.

Background

Historically, diesel engines, especially heavy duty diesel engines, have utilized 15W-40 multi-grade lubricants and higher viscosity grades. However, the demand for enhanced fuel economy is driving the marketplace to lower viscosity oils. This has led to increases in air entrainment with some engines resulting in "overflow" of the oil and shutdown of the engine. Air entrainment may arise from various mechanical sources, including mechanical flaws such as cracks or leaking parts or seals, or from the crankshaft splashing in oil in the oil pan, particularly if an excess of oil is present.

Antifoam agents are known, and in certain end-use applications (e.g., transmission fluids), mixtures of antifoam agents have been used. For instance, U.S. Patent 6,251,840, Ward et al., June 26, 2001, discloses a lubricating/functional fluid which exhibits in use improved antiwear and antifoaming properties. The improvements are said to result from use of 2,4-dimercapto1,3,4-thiadiazole and derivatives thereof together with silicone and/or fluorosilicone antifoam agents.

Summary

The problem, therefore, is to provide a multigrade lubricant composition with a relatively low viscosity that can be used to lubricate a diesel engine, optionally provide for enhanced fuel economy, and avoid foaming and/or air entrainment problems. This invention provides a solution to this problem.

The present invention thus provides a lubricant composition, comprising: an oil of lubricating viscosity; a detergent; a dispersant; a first anti-foam agent comprising a polydimethyl siloxane having a kinetic viscosity (absent solvent) at 25°C in the range from about 10,000 to about 50,000 mm^2/s (cSt); a second anti-foam agent comprising a polydimethyl siloxane having a kinetic viscosity (absent solvent) at 25°C in the range from about 80,000 to about 120,000 mm^2/s (cSt); and a third anti-foam agent comprising a fluorinated polysiloxane having a

kinematic viscosity (absent solvent) at 25°C in the range from about 50 to about 500 mm^2/s (cSt).

In one embodiment, the invention relates to a multigrade lubricant composition, comprising: an oil of lubricating viscosity; a detergent; a dispersant; a viscosity index improver; a first anti-foam agent, the first anti-foam agent being derived from a first anti-foam composition comprising a polydimethyl siloxane dispersed or dissolved in an aromatic oil or a naphthenic hydrocarbon solvent, to provide a first anti-foam composition, the first anti-foam composition having a kinetic viscosity at 25°C (absent solvent) in the range from about 10,000 to about 50,000 cSt; a second anti-foam agent, the second anti-foam agent being derived from a second anti-foam composition comprising a polydimethyl siloxane dispersed or dissolved in an aromatic oil or a naphthenic hydrocarbon solvent to provide a second anti-foam composition, the second anti-foam composition having a kinetic viscosity at 25°C (absent solvent) in the range from about 80,000 to about 120,000 cSt; and a third anti-foam agent, the third anti-foam agent being derived from a third anti-foam composition comprising a fluorinated polysiloxane dispersed or dissolved in an aliphatic solvent or a solvent comprising a ketone (e.g., aliphatic ketone) having about 5 to about 16 carbon atoms, the third anti-foam composition having a kinematic viscosity at 25°C (absent solvent) in the range from about 50 to about 500 cSt.

The present invention also provides a method of lubricating an engine, comprising: supplying to the engine the lubricant composition described herein.

Detailed Description

All ranges and ratio limits disclosed in the specification and claims may be combined in any manner. It is to be understood that unless specifically stated otherwise, references to "a," "an," and/or "the" may include one or more than one, and that reference to an item in the singular may also include the item in the plural.

The terms "hydrocarbyl" and "hydrocarbon," when referring to groups attached to the remainder of a molecule, refer to groups having a purely hydrocarbon or predominantly hydrocarbon character within the context of this invention. Such groups include the following:

(1) Purely hydrocarbon groups; that is, aliphatic, alicyclic, aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and

alicyclic groups, and the like, as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic group). Examples include methyl, octyl, cyclohexyl, phenyl, etc.

(2) Substituted hydrocarbon groups; that is, groups containing non-hydrocarbon substituents which do not alter the predominantly hydrocarbon character of the group. Examples include hydroxy, nitro, cyano, alkoxy, acyl, etc.

(3) Hetero groups; that is, groups which, while predominantly hydrocarbon in character, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Examples include nitrogen, oxygen and sulfur.

In general, no more than about three substituents or hetero atoms, and in one embodiment no more than one, will be present for each 10 carbon atoms in the hydrocarbyl or hydrocarbon group.

The term "lower" as used herein in conjunction with terms such as hydrocarbyl, alkyl, alkenyl, alkoxy, and the like, is intended to describe such groups which contain a total of up to 7 carbon atoms.

The term "oil-soluble" refers to a material that is soluble in mineral oil to the extent of at least about 0.5 gram per liter at 25°C.

The term "TBN" refers to total base number. This is the amount of acid (perchloric or hydrochloric) needed to neutralize a material's basicity, expressed as milligrams of KOH per gram of sample.

The term "TAN" refers to total acid number. This is the amount of base (NaOH or KOH) needed to neutralize a material's acidity, expressed as milligrams of KOH per gram of sample.

The inventive lubricant composition may comprise one or more base oils which may be present in a major amount. The lubricant composition may have a viscosity of up to about 12.5 cSt at 100°C, or from about 3.8 to about 12.5 cSt at 100°C, or from about 4.1 to about 12.5 cSt at 100°C, or from about 5.6 to about 12.5 cSt at 100°C.

The lubricant composition may have an SAE Viscosity Grade of 0W-20, 0W-30, 5W-20, 5W-30, 10W-20, 10W-30, 15W-20 or 15W-30.

The oil of lubricating viscosity may be referred to as a base oil. The base oil may be selected from any of the base oils in the group definitions as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows:

Base Oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group I	>0.03	and/or	<90	80 to 120
Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	≥120
Group IV	All polyalphaolefins (PAO)			
Group V	All others not included in Groups I, II, III, or IV			

The base oil may contain less than about 300 ppm sulfur and/or at least about 90% saturate content, determined by test procedure described in ASTM D2007. The base oil may have a viscosity index of at least about 120.

Groups I, II and III are mineral oil base stocks. The base oil may comprise natural or synthetic lubricating oils and mixtures thereof. Mixture of mineral oil and synthetic oils, particularly polyalphaolefin oils and ester oils, may be used. In certain embodiments, the oil of lubricating viscosity comprises a Group III oil. It is sometimes observed that lubricant based on Group III oils may have a greater tendency for foam formation than those prepared with Group I or II oils, and therefore, in such formulations, the present invention may be particularly efficacious.

Natural oils may include animal oils and vegetable oils (e.g. castor oil, lard oil, and other vegetable acid esters) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid treated mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic-naphthenic types. Hydrotreated or hydrocracked oils may be included within the scope of useful oils.

Base oils derived from coal or shale may be useful. Synthetic lubricating oils may include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins and mixtures thereof, alkylbenzenes, polyphenyl, (e.g., biphenyls, terphenyls, and alkylated polyphenyls), alkylated diphenyl ethers and alkylated diphenyl sulfides and their derivatives, analogs and homologues thereof. Alkylene oxide polymers and interpolymers and derivatives thereof, and those where terminal hydroxyl groups have been modified by, for

example, esterification or etherification, may constitute other classes of known synthetic lubricating oils that can be used. Another suitable class of synthetic lubricating oils that may be used comprises the esters of dicarboxylic acids and those made from about C_5 to about C_{12} monocarboxylic acids and polyols or polyol ethers.

Other suitable synthetic lubricating oils may include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, silicon-based oils such as the poly-alkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils, silahydrocarbons and silicate oils.

Hydrotreated naphthenic oils may be used. Synthetic oils may be used, such as those produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. The base oil may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid procedures.

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove may be used. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Rerefined oils may be obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. The rerefined oils often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

The amount of oil in a fully formulated lubricant will typically be the amount remaining to equal 100 percent after the remaining additives are accounted for. Typically this may be from about 60 to about 99 percent by weight, or from about 70 to about 97 percent, or from about 80 to about 95 percent, or from about 85 to about 93 percent by weight. The lubricant composition may be delivered as a concentrate, in which case the amount of oil is typically reduced and the concentrations of the other components are correspondingly increased. In such cases the amount of oil may be from about 30 to about 70 percent by weight, or from about 40 to about 60 percent by weight.

(such as boric acid), urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. The post-treated dispersant may be borated. The post-treated dispersant may result from a reaction of the dispersant with a dimercaptothiadiazole. The post-treated dispersant may result from a reaction of the dispersant with phosphoric or phosphorous acid.

The dispersant may be present in the lubricant composition at a concentration in the range from about 0.01 wt % to about 20 wt %, or from about 0.1 wt % to about 15 wt %, or from about 0.1 wt % to about 10 wt %, or from about 1 wt % to about 6 wt %, or from about 1 to about 3 wt % of the lubricating composition.

The lubricant composition may further include one or more viscosity index improvers, which may be referred to as viscosity modifiers. The presence of a viscosity index improver is typically characteristic of a multigrade lubricant composition. Viscosity modifiers may include hydrogenated styrene-butadiene rubbers, ethylene-propylene copolymers, polymethacrylates, polyacrylates, hydrogenated styrene-isoprene polymers, hydrogenated diene polymers, poly(alkyl styrenes), polyolefins, esters of maleic anhydride-olefin copolymers (such as those described in International Application WO 2010/014655), esters of maleic anhydride-styrene copolymers, or mixtures or two or more thereof. The viscosity index improver may be present in the lubricant composition at a concentration in the range of about 0 to about 20 wt%, or from about 2 to about 10 wt%.

The inventive lubricant composition may employ the combination of three anti-foam agents to reduce or eliminate the problem of foaming that results when operating certain heavy duty diesel engines and converting from a higher viscosity grade (e.g., 15W-40) lubricant composition to a lower viscosity grade (e.g., 10W-30) lubricant in order to provide for enhanced fuel economy. It may be particularly useful to prevent foaming in diesel engines having a power output of greater than about 750 kW (1000 horsepower (hp)), such as greater than about 1120 kW (1500 hp) or 1500 kW (2000 hp) or 2240 kW (3000 hp), and up to, for instance about 15,000 kW (20,000 hp) or to 7500 kW (10,000 hp).

The first anti-foam agent may be, or may be derived from, a first anti-foam composition which may comprise a polydimethyl siloxane. The siloxane may be dispersed or dissolved in an aromatic oil or a naphthenic solvent or oil, and typically in a naphthenic hydrocarbon solvent. A naphthenic hydrocarbon typically comprises a significant amount of saturated, cyclic hydrocarbon species (naphthenes), such as at least about 10 percent by weight thereof, or at least about 20 or 30 or 40 or 50 or 60 percent thereof, and up to about 90 or 80 or 70 percent. Certain amount of aromatic hydrocarbon content may also be present, such as about 2 to 50 or about 5 to 40 or about 10 to 30 percent. An example of a naphthenic hydrocarbon solvent is petroleum naphtha. The first anti-foam composition may be provided as a solution or dispersion comprising from about 1 to about 50 wt% of the polydimethylsiloxane, or from about 5 wt% to about 25 wt%, or about 10 wt% in the solvent, diluent, or oil. The first anti-foam composition, as provided, may comprise from about 50 wt% to about 99 wt% of the solvent, diluent, or oil, or from about 75 wt% to about 95 wt%, or about 90 wt% of the solvent, diluent, or oil. The first anti-foam composition may have a kinematic viscosity at 25°C in the range from about 10,000 to about 50,000 mm^2/s (cSt), or from about 20,000 to about 40,000 mm^2s (cSt), or about 30,000 mm^2/s (cSt) (these values referring to the polydimethylsiloxane in the absence of solvent or diluent). The concentration of the first anti-foam agent (i.e., the polydimethyl siloxane) in the lubricant composition may be in the range from about 50 to about 500 parts per million by weight (ppm), or from about 100 to about 300 ppm, or about 200 ppm. The foregoing amounts are based on the polydimethylsiloxane plus solvent/diluent as conventionally provided; corresponding amounts for the neat anti-foam agent may be, for instance, about 5 to about 50 ppm or about 10 to about 30 ppm or about 15 to about 25 ppm or about 20 ppm

The second anti-foam agent may be, or may be derived from, a second anti-foam composition which may comprise a second polydimethyl siloxane. The second polydimethyl siloxane may be dispersed or dissolved in an aromatic oil or a naphthenic solvent or oil, and typically in a naphthenic hydrocarbon solvent. The second anti-foam composition may be provided as a solution or dispersion comprising from about 1 wt% to about 50 wt% of the polydimethylsiloxane, or

from about 5 wt% to about 25 wt%, or about 12.5 wt% in the solvent, diluent, or oil. The second anti-foam composition, as provided, may comprise from about 50 wt% to about 99 wt% of the solvent, diluent, or oil, or from about 75 wt% to about 95 wt%, or about 87.5 wt% of the solvent, diluent, or oil. The second anti-foam additive composition may have a kinematic viscosity at 25°C in the range from about 80,000 to about 120,000 mm^2/s (cSt), or from about 90,000 to about 110,000 mm^2/s (cSt), or about 100,000 mm^2/s (cSt), (these values referring to the polydimethylsiloxane in the absence of solvent or diluent). The concentration of the second anti-foam agent (i.e., the polydimethyl siloxane) in the lubricant composition may be in the range from about 5 to about 100 ppm, or from about 10 to about 30 ppm, or about 15 ppm. The foregoing amounts are based on the polydimethylsiloxane plus solvent/diluent; corresponding amounts for the neat anti-foam agent may be, for instance, about 0.6 to about 13 ppm, or about 1.2 to about 3.8 ppm, or about 1.5 to about 2.5 ppm, or about 1.9 ppm.

The third anti-foam agent may be, or may be derived from, a third anti-foam composition. The third antifoam agent may comprise a fluorinated polysiloxane which may be dispersed or dissolved in an aliphatic solvent, or in a ketone solvent, or mixtures thereof. The ketone solvent may comprise a ketone having about 5 to about 16 carbon atoms, such as 6 to 12 carbon atoms or 8 carbon atoms. The fluorinated polysiloxane may be a poly(3,3,3-trifluropropyl methyl siloxane). The solvent may be methylbutyl ethyl ketone (5-methyl-3-heptanone). The third anti-foam composition may comprise from about 5 wt% to about 95 wt% of the fluorinated polysiloxane, or from about 65 wt% to about 85 wt%, or about 75 wt%. The third anti-foam composition may comprise from about 5 wt% to about 95 wt% of the solvent, or from about 15 wt% to about 40 wt%, or about 25 wt% of the oil. The third anti-foam composition may have a kinematic viscosity at 25°C in the range from about 50 to about 500 mm^2/s (cSt), or from about 100 to about 500 mm^2/s (cSt), or from about 200 to about 400 mm^2/s (cSt), or about 300 mm^2/s (cSt) (these values referring to the fluorinated polysiloxane in the absence of solvent or diluent). The concentration of the third anti-foam agent (i.e., the fluorinated polysiloxane) in the lubricant composition may be in the range from about 5 to about 95 ppm, or from about 20 to about 60 ppm, or about 40 ppm. The foregoing amounts are based on the fluorinated polysiloxane plus

solvent/diluent as conventionally provided; corresponding amounts for the neat anti-foam agent may be, for instance, about 3.7 to about 71 ppm or about 15 to about 45 ppm or about 25 to about 35 ppm, or about 30 ppm.

All three of the anti-foam agents will be present, although optionally additional anti-foam agents may be present. Each of the three anti-foam agents described above may be present in an amount of about 1% or more by weight of the total anti-foam package (oil/solvent free basis). In certain embodiments, the first and third listed anti-foam agents may each independently be present at about 10 % or more or 15 % or more of the total antifoam package and the second anti-foam agent may be present at about 1 % or more, or 1.5 % or more, or 2 % or more. In certain embodiments, the total amount of silicon-containing anti-foam agents may be an amount to deliver about 5 to 20, or 10 to 18, or 12 to 15 ppm silicon to the lubricant.

The lubricant composition may comprise other performance additives. These may include one or more metal deactivators, friction modifiers, antiwear agents, corrosion inhibitors, dispersant viscosity modifiers, extreme pressure agents, antioxidants, demulsifiers, pour point depressants, seal swelling agents, mixtures of two or more thereof, and the like.

The antioxidants may include sulfurized olefins, diarylamines, hindered phenols, molybdenum compounds (such as molybdenum dithiocarbamates), hydroxyl thioethers, or mixtures thereof. The antioxidant may be present at a concentration in the range from about 0 wt % to about 15 wt %, or about 0.1 wt % to about 10 wt %, or about 0.5 wt % to about 5 wt %, or about 0.5 wt % to about 3 wt % of the lubricant composition.

The diarylamine may be phenyl alpha-naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenylnapthylamine, or mixtures thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, di-octylated diphenylamine, di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In one embodiment the diphenylamine may include nonyl diphenylamine, or dinonyl

Claims

1. A lubricant composition, comprising:

an oil of lubricating viscosity;

a detergent;

a dispersant;

a first anti-foam agent comprising a polydimethyl siloxane having a kinetic viscosity (absent solvent) at 25°C in the range from 10,000 to 50,000 mm^2/s (cSt);

a second anti-foam agent comprising a polydimethyl siloxane having a kinetic viscosity (absent solvent) at 25°C in the range from 80,000 to 120,000 mm^2/s (cSt); and

a third anti-foam agent comprising a fluorinated polysiloxane having a kinematic viscosity (absent solvent) at 25°C in the range from 50 to 500 mm^2/s (cSt).

2. The composition of claim 1 wherein the composition is a multigrade composition, further comprising a viscosity index improver

3 The composition of claim 1 or claim 2 wherein the composition further comprises an antiwear agent.

4. The composition of any one of the preceding claims wherein the composition further comprises an antioxidant.

5. The composition of any one of the preceding claims wherein the composition further comprises a friction modifier.

6. The composition of any one of the preceding claims wherein the composition further comprises a pour point dispersant.

7. The composition of any one of the preceding claims wherein the composition further comprises one or more metal deactivators, corrosion

inhibitors, dispersant viscosity modifiers, extreme pressure agents, demulsifiers, seal swelling agents, or a mixture of two or more thereof.

8. The composition of any one of the preceding claims wherein the lubricant composition has a kinematic viscosity at 100°C of up to about 12.5 cSt.

9. The composition of any one of the preceding claims wherein the lubricant composition has an SAE Viscosity Grade of 0W-20, 0W-30, 5W-20, 5W-30, 10W-20, 10W-30, 15W-20, or 15W-30.

10. The composition of any one of the preceding claims wherein the oil of lubricating viscosity comprises a Group III oil.

11. The composition of any one of the preceding claims wherein the detergent comprises an overbased calcium sulfonate, an overbased calcium phenate, or a mixture thereof.

12. The composition of any one of the preceding claims wherein the dispersant comprises a polyisobutene substituted succinimide, a borated polyisobutene substituted succinimide, or a mixture thereof.

13. The composition of any one of the preceding claims wherein the viscosity index improver comprises an ethylene propylene copolymer.

14. The composition of any one of the preceding claims wherein the first anti-foam agent is provided to the lubricant in the form of a solution or dispersion of from 1 to 50% by weight of the polydimethyl siloxane in a solvent.

15. The composition of claim 14 wherein the solvent comprises a naphthenic hydrocarbon solvent.

16. The composition of any one of the preceding claims wherein the second anti-foam agent is provided to the lubricant in the form of a solution or dispersion of from 1 to 50% by weight of the polydimethyl siloxane in a solvent.

17. The composition of claim 16 wherein the solvent comprises a naphthenic hydrocarbon solvent.

18. The composition of any one of the preceding claims wherein the fluorinated polysiloxane of the third anti-foam agent comprises poly(3,3,3-trifluropropyl methyl siloxane).

19. The composition of any one of the preceding claims wherein the third anti-foam agent is provided to the lubricant in the form of a solution or dispersion of from 5 to 95 % by weight of the fluorinated polysiloxane in a solvent.

20. The composition of claim 19 wherein the solvent comprises a ketone having 5 to 16 carbon atoms.

21. The composition of any one of the preceding claims wherein the lubricant composition has a sulfur content of about 1% by weight or less.

22. The composition of any one of the preceding claims wherein the lubricant composition has a phosphorus content of about 0.2% by weight or less.

23. The composition of any one of the preceding claims wherein the lubricant composition has a metal content as measured by sulfated ash in the range from 0.3 to 1.2% by weight sulfated ash.

24. The composition of any one of the preceding claims wherein the amount of the first anti-foam agents is 5 to 50 ppm, the amount of the second antifoam agent is 0.6 to 13 ppm, or the amount of the third antifoam agent is 3.7 to 71 ppm, or in which each such antifoam agent is present in the aforesaid amounts.

25. The composition of any one of the preceding claims wherein the lubricant composition has a chlorine content of up to about 100 ppm.

26. A method of lubricating an engine, comprising: supplying to the engine the lubricant composition of any one of the preceding claims.

27. The method of claim 26 wherein the engine is a diesel engine having an output of at least about 750 kW (1000 horsepower).

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Summary

The problem, therefore, is to provide a multigrade lubricant composition with a relatively low viscosity that can be used to lubricate a diesel engine, optionally provide for enhanced fuel economy, and avoid foaming and/or air entrainment problems. This invention provides a solution to this problem.

The present invention thus provides a lubricant composition, comprising: a Group III oil of lubricating viscosity; a detergent; a dispersant; 5 to 50 ppm of a first anti-foam agent comprising a polydimethyl siloxane having a kinetic viscosity (absent solvent) at 25°C in the range from 10,000 to 50,000 mm^2/s (cSt); 0.6 to 13 ppm of a second anti-foam agent comprising a polydimethyl siloxane having a kinetic viscosity (absent solvent) at 25°C in the range from 80,000 to 120,000 mm^2/s (cSt); and 3.7 to 35 ppm of a third anti-foam agent comprising a

fluorinated polysiloxane having a kinematic viscosity (absent solvent) at 25°C in the range from 50 to 500 mm^2/s (cSt).

In one embodiment, the invention relates to a multigrade lubricant composition, comprising: a Group III oil of lubricating viscosity; a detergent; a dispersant; a viscosity index improver; 5 to 50 ppm of a first anti-foam agent, the first anti-foam agent being derived from a first anti-foam composition comprising a polydimethyl siloxane dispersed or dissolved in an aromatic oil or a naphthenic hydrocarbon solvent, to provide the first anti-foam composition, the first anti-foam composition having a kinetic viscosity at 25°C (absent solvent) in the range from 10,000 to 50,000 cSt; 0.6 to 13 ppm of a second anti-foam agent, the second anti-foam agent being derived from a second anti-foam composition comprising a polydimethyl siloxane dispersed or dissolved in an aromatic oil or a naphthenic hydrocarbon solvent to provide the second anti-foam composition, the second anti-foam composition having a kinetic viscosity at 25°C (absent solvent) in the range from 80,000 to 120,000 cSt; and 3.7 to 35 ppm of a third anti-foam agent, the third anti-foam agent being derived from a third anti-foam composition comprising a fluorinated polysiloxane dispersed or dissolved in an aliphatic solvent or a solvent comprising a ketone (e.g., aliphatic ketone) having 5 to 16 carbon atoms, the third anti-foam composition having a kinematic viscosity at 25°C (absent solvent) in the range from 50 to 500 cSt.

The present invention also provides a method of lubricating an engine, comprising: supplying to the engine the lubricant composition described herein.

Detailed Description

All ranges and ratio limits disclosed in the specification and claims may be combined in any manner. It is to be understood that unless specifically stated otherwise, references to "a," "an," and/or "the" may include one or more than one, and that reference to an item in the singular may also include the item in the plural.

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(1) Purely hydrocarbon groups; that is, aliphatic, alicyclic, aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and

alicyclic groups, and the like, as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic group). Examples include methyl, octyl, cyclohexyl, phenyl, etc.

(2) Substituted hydrocarbon groups; that is, groups containing non-hydrocarbon substituents which do not alter the predominantly hydrocarbon character of the group. Examples include hydroxy, nitro, cyano, alkoxy, acyl, etc.

(3) Hetero groups; that is, groups which, while predominantly hydrocarbon in character, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Examples include nitrogen, oxygen and sulfur.

In general, no more than about three substituents or hetero atoms, and in one embodiment no more than one, will be present for each 10 carbon atoms in the hydrocarbyl or hydrocarbon group.

The term "lower" as used herein in conjunction with terms such as hydrocarbyl, alkyl, alkenyl, alkoxy, and the like, is intended to describe such groups which contain a total of up to 7 carbon atoms.

The term "oil-soluble" refers to a material that is soluble in mineral oil to the extent of at least about 0.5 gram per liter at 25°C.

The term "TBN" refers to total base number. This is the amount of acid (perchloric or hydrochloric) needed to neutralize a material's basicity, expressed as milligrams of KOH per gram of sample.

The term "TAN" refers to total acid number. This is the amount of base (NaOH or KOH) needed to neutralize a material's acidity, expressed as milligrams of KOH per gram of sample.

The inventive lubricant composition may comprise one or more Group III base oils which may be present in a major amount. The lubricant composition may have a viscosity of up to about 12.5 cSt at 100°C, or from about 3.8 to about 12.5 cSt at 100°C, or from about 4.1 to about 12.5 cSt at 100°C, or from about 5.6 to about 12.5 cSt at 100°C.

The lubricant composition may have an SAE Viscosity Grade of 0W-20, 0W-30, 5W-20, 5W-30, 10W-20, 10W-30, 15W-20 or 15W-30.

A base oil is generally any of the base oils in the group definitions as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows:

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Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	≥120
Group IV	All polyalphaolefins (PAO)			
Group V	All others not included in Groups I, II, III, or IV			

The base oil may contain less than about 300 ppm sulfur and/or at least about 90% saturate content, determined by test procedure described in ASTM D2007. The base oil may have a viscosity index of at least about 120.

The oil of lubricating viscosity in the present invention is a Group III base oil.

Groups I, II and III are mineral oil base stocks. Mixture of mineral oil and synthetic oils, particularly polyalphaolefin oils and ester oils, may be used. It is sometimes observed that lubricant based on Group III oils may have a greater tendency for foam formation than those prepared with Group I or II oils.

Natural oils may include mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid treated mineral lubricating oils of the paraffinic, naphthenic, or mixed paraffinic-naphthenic types. Hydrotreated or hydrocracked oils may be included within the scope of useful oils.

Group III base oils derived from coal or shale may be useful.

Hydrotreated naphthenic oils may be used. Synthetic oils may be used, such as those produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. The base oil may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid procedures.

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove may be used. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Rerefined oils may be obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. The rerefined oils often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

The amount of oil in a fully formulated lubricant will typically be the amount remaining to equal 100 percent after the remaining additives are accounted for. Typically this may be from about 60 to about 99 percent by weight, or from about 70 to about 97 percent, or from about 80 to about 95 percent, or from about 85 to about 93 percent by weight. The lubricant composition may be delivered as a concentrate, in which case the amount of oil is typically reduced and the concentrations of the other components are correspondingly increased. In such cases the amount of oil may be from about 30 to about 70 percent by weight, or from about 40 to about 60 percent by weight.

(such as boric acid), urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids such as terephthalic acid, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds. The post-treated dispersant may be borated. The post-treated dispersant may result from a reaction of the dispersant with a dimercaptothiadiazole. The post-treated dispersant may result from a reaction of the dispersant with phosphoric or phosphorous acid.

The dispersant may be present in the lubricant composition at a concentration in the range from about 0.01 wt % to about 20 wt %, or from about 0.1 wt % to about 15 wt %, or from about 0.1 wt % to about 10 wt %, or from about 1 wt % to about 6 wt %, or from about 1 to about 3 wt % of the lubricating composition.

The lubricant composition may further include one or more viscosity index improvers, which may be referred to as viscosity modifiers. The presence of a viscosity index improver is typically characteristic of a multigrade lubricant composition. Viscosity modifiers may include hydrogenated styrene-butadiene rubbers, ethylene-propylene copolymers, polymethacrylates, polyacrylates, hydrogenated styrene-isoprene polymers, hydrogenated diene polymers, poly(alkyl styrenes), polyolefins, esters of maleic anhydride-olefin copolymers (such as those described in International Application WO 2010/014655), esters of maleic anhydride-styrene copolymers, or mixtures or two or more thereof. The viscosity index improver may be present in the lubricant composition at a concentration in the range of about 0 to about 20 wt%, or from about 2 to about 10 wt%.

The inventive lubricant composition employs the combination of three anti-foam agents to reduce or eliminate the problem of foaming that results when operating certain heavy duty diesel engines and converting from a higher viscosity grade (e.g., 15W-40) lubricant composition to a lower viscosity grade (e.g., 10W-30) lubricant in order to provide for enhanced fuel economy. It may be particularly useful to prevent foaming in diesel engines having a power output of greater than about 750 kW (1000 horsepower (hp)), such as greater than about 1120 kW (1500 hp) or 1500 kW (2000 hp) or 2240 kW (3000 hp), and up to, for instance about 15,000 kW (20,000 hp) or to 7500 kW (10,000 hp).

The first anti-foam agent may be, or may be derived from, a first anti-foam composition which may comprise a polydimethyl siloxane. The siloxane may be dispersed or dissolved in an aromatic oil or a naphthenic solvent or oil, and typically in a naphthenic hydrocarbon solvent. A naphthenic hydrocarbon typically comprises a significant amount of saturated, cyclic hydrocarbon species (naphthenes), such as at least about 10 percent by weight thereof, or at least about 20 or 30 or 40 or 50 or 60 percent thereof, and up to about 90 or 80 or 70 percent. Certain amount of aromatic hydrocarbon content may also be present, such as about 2 to 50 or about 5 to 40 or about 10 to 30 percent. An example of a naphthenic hydrocarbon solvent is petroleum naphtha. The first anti-foam composition may be provided as a solution or dispersion comprising from about 1 to about 50 wt% of the polydimethylsiloxane, or from about 5 wt% to about 25 wt%, or about 10 wt% in the solvent, diluent, or oil. The first anti-foam composition, as provided, may comprise from about 50 wt% to about 99 wt% of the solvent, diluent, or oil, or from about 75 wt% to about 95 wt%, or about 90 wt% of the solvent, diluent, or oil. The first anti-foam composition may have a kinematic viscosity at 25°C in the range from about 10,000 to about 50,000 mm^2/s (cSt), or from about 20,000 to about 40,000 mm^2s (cSt), or about 30,000 mm^2/s (cSt) (these values referring to the polydimethylsiloxane in the absence of solvent or diluent). The concentration of the first anti-foam agent (i.e., the polydimethyl siloxane) in the lubricant composition may be in the range from about 50 to about 500 parts per million by weight (ppm), or from about 100 to about 300 ppm, or about 200 ppm. The foregoing amounts are based on the polydimethylsiloxane plus solvent/diluent as conventionally provided; corresponding amounts for the neat anti-foam agent are, for instance, about 5 to about 50 ppm or about 10 to about 30 ppm or about 15 to about 25 ppm or about 20 ppm

The second anti-foam agent may be, or may be derived from, a second anti-foam composition which may comprise a second polydimethyl siloxane. The second polydimethyl siloxane may be dispersed or dissolved in an aromatic oil or a naphthenic solvent or oil, and typically in a naphthenic hydrocarbon solvent. The second anti-foam composition may be provided as a solution or dispersion comprising from about 1 wt% to about 50 wt% of the polydimethylsiloxane, or

from about 5 wt% to about 25 wt%, or about 12.5 wt% in the solvent, diluent, or oil. The second anti-foam composition, as provided, may comprise from about 50 wt% to about 99 wt% of the solvent, diluent, or oil, or from about 75 wt% to about 95 wt%, or about 87.5 wt% of the solvent, diluent, or oil. The second anti-foam additive composition may have a kinematic viscosity at 25°C in the range from about 80,000 to about 120,000 mm^2/s (cSt), or from about 90,000 to about 110,000 mm^2/s (cSt), or about 100,000 mm^2/s (cSt), (these values referring to the polydimethylsiloxane in the absence of solvent or diluent). The concentration of the second anti-foam agent (i.e., the polydimethyl siloxane) in the lubricant composition may be in the range from about 5 to about 100 ppm, or from about 10 to about 30 ppm, or about 15 ppm. The foregoing amounts are based on the polydimethylsiloxane plus solvent/diluent; corresponding amounts for the neat anti-foam agent are, for instance, about 0.6 to about 13 ppm, or about 1.2 to about 3.8 ppm, or about 1.5 to about 2.5 ppm, or about 1.9 ppm.

The third anti-foam agent may be, or may be derived from, a third anti-foam composition. The third antifoam agent may comprise a fluorinated polysiloxane which may be dispersed or dissolved in an aliphatic solvent, or in a ketone solvent, or mixtures thereof. The ketone solvent may comprise a ketone having about 5 to about 16 carbon atoms, such as 6 to 12 carbon atoms or 8 carbon atoms. The fluorinated polysiloxane may be a poly(3,3,3-trifluropropyl methyl siloxane). The solvent may be methylbutyl ethyl ketone (5-methyl-3-heptanone). The third anti-foam composition may comprise from about 5 wt% to about 95 wt% of the fluorinated polysiloxane, or from about 65 wt% to about 85 wt%, or about 75 wt%. The third anti-foam composition may comprise from about 5 wt% to about 95 wt% of the solvent, or from about 15 wt% to about 40 wt%, or about 25 wt% of the oil. The third anti-foam composition may have a kinematic viscosity at 25°C in the range from about 50 to about 500 mm^2/s (cSt), or from about 100 to about 500 mm^2/s (cSt), or from about 200 to about 400 mm^2/s (cSt), or about 300 mm^2/s (cSt) (these values referring to the fluorinated polysiloxane in the absence of solvent or diluent). The concentration of the third anti-foam agent (i.e., the fluorinated polysiloxane) in the lubricant composition may be in the range from about 5 to about 95 ppm, or from about 20 to about 60 ppm, or about 40 ppm. The foregoing amounts are based on the fluorinated polysiloxane plus

solvent/diluent as conventionally provided; corresponding amounts for the neat anti-foam agent are, for instance, 3.7 to 35 ppm or about 15 to about 35 ppm or about 25 to about 35 ppm, or about 30 ppm.

All three of the anti-foam agents will be present, although optionally additional anti-foam agents may be present. Each of the three anti-foam agents described above may be present in an amount of about 1% or more by weight of the total anti-foam package (oil/solvent free basis). In certain embodiments, the first and third listed anti-foam agents may each independently be present at about 10 % or more or 15 % or more of the total antifoam package and the second anti-foam agent may be present at about 1 % or more, or 1.5 % or more, or 2 % or more. In certain embodiments, the total amount of silicon-containing anti-foam agents may be an amount to deliver about 5 to 20, or 10 to 18, or 12 to 15 ppm silicon to the lubricant.

The lubricant composition may comprise other performance additives. These may include one or more metal deactivators, friction modifiers, antiwear agents, corrosion inhibitors, dispersant viscosity modifiers, extreme pressure agents, antioxidants, demulsifiers, pour point depressants, seal swelling agents, mixtures of two or more thereof, and the like.

The antioxidants may include sulfurized olefins, diarylamines, hindered phenols, molybdenum compounds (such as molybdenum dithiocarbamates), hydroxyl thioethers, or mixtures thereof. The antioxidant may be present at a concentration in the range from about 0 wt % to about 15 wt %, or about 0.1 wt % to about 10 wt %, or about 0.5 wt % to about 5 wt %, or about 0.5 wt % to about 3 wt % of the lubricant composition.

The diarylamine may be phenyl alpha-naphthylamine (PANA), an alkylated diphenylamine, or an alkylated phenylnapthylamine, or mixtures thereof. The alkylated diphenylamine may include di-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, di-octylated diphenylamine, di-decylated diphenylamine, decyl diphenylamine and mixtures thereof. In one embodiment the diphenylamine may include nonyl diphenylamine, dinonyl diphenylamine, octyl diphenylamine, dioctyl diphenylamine, or mixtures thereof. In one embodiment the diphenylamine may include nonyl diphenylamine, or dinonyl

Claims

1. A lubricant composition, comprising:

a Group III oil of lubricating viscosity;

a detergent;

a dispersant;

5 to 50 ppm of a first anti-foam agent comprising a polydimethyl siloxane having a kinetic viscosity (absent solvent) at 25°C in the range from 10,000 to 50,000 mm^2/s (cSt);

0.6 to 13 ppm of a second anti-foam agent comprising a polydimethyl siloxane having a kinetic viscosity (absent solvent) at 25°C in the range from 80,000 to 120,000 mm^2/s (cSt); and

3.7 to 35 ppm of a third anti-foam agent comprising a fluorinated polysiloxane having a kinematic viscosity (absent solvent) at 25°C in the range from 50 to 500 mm^2/s (cSt).

2. The composition of claim 1 wherein the composition is a multigrade composition, further comprising a viscosity index improver

3 The composition of claim 1 or claim 2 wherein the composition further comprises an antiwear agent.

4. The composition of any one of the preceding claims wherein the composition further comprises an antioxidant.

5. The composition of any one of the preceding claims wherein the composition further comprises a friction modifier.

6. The composition of any one of the preceding claims wherein the composition further comprises a pour point dispersant.

7. The composition of any one of the preceding claims wherein the composition further comprises one or more metal deactivators, corrosion

inhibitors, dispersant viscosity modifiers, extreme pressure agents, demulsifiers, seal swelling agents, or a mixture of two or more thereof.

8. The composition of any one of the preceding claims wherein the lubricant composition has a kinematic viscosity at 100°C of up to 12.5 cSt.

9. The composition of any one of the preceding claims wherein the lubricant composition has an SAE Viscosity Grade of 0W-20, 0W-30, 5W-20, 5W-30, 10W-20, 10W-30, 15W-20, or 15W-30.

10. The composition of any one of the preceding claims wherein the detergent comprises an overbased calcium sulfonate, an overbased calcium phenate, or a mixture thereof.

11. The composition of any one of the preceding claims wherein the dispersant comprises a polyisobutene substituted succinimide, a borated polyisobutene substituted succinimide, or a mixture thereof.

12. The composition of any one of the preceding claims wherein the viscosity index improver comprises an ethylene propylene copolymer.

13. The composition of any one of the preceding claims wherein the first anti-foam agent is provided to the lubricant in the form of a solution or dispersion of from 1 to 50% by weight of the polydimethyl siloxane in a solvent.

14. The composition of claim 13 wherein the solvent comprises a naphthenic hydrocarbon solvent.

15. The composition of any one of the preceding claims wherein the second anti-foam agent is provided to the lubricant in the form of a solution or dispersion of from 1 to 50% by weight of the polydimethyl siloxane in a solvent.

16. The composition of claim 15 wherein the solvent comprises a naphthenic hydrocarbon solvent.

17. The composition of any one of the preceding claims wherein the fluorinated polysiloxane of the third anti-foam agent comprises poly(3,3,3-trifluropropyl methyl siloxane).

18. The composition of any one of the preceding claims wherein the third anti-foam agent is provided to the lubricant in the form of a solution or dispersion of from 5 to 95 % by weight of the fluorinated polysiloxane in a solvent.

19. The composition of claim 18 wherein the solvent comprises a ketone having 5 to 16 carbon atoms.

20. The composition of any one of the preceding claims wherein the lubricant composition has a sulfur content of 1% by weight or less.

21. The composition of any one of the preceding claims wherein the lubricant composition has a phosphorus content of 0.2% by weight or less.

22. The composition of any one of the preceding claims wherein the lubricant composition has a metal content as measured by sulfated ash in the range from 0.3 to 1.2% by weight sulfated ash.

23. The composition of any one of the preceding claims wherein the lubricant composition has a chlorine content of up to 100 ppm.

24. A method of lubricating an engine, comprising: supplying to the engine the lubricant composition of any one of the preceding claims.

25. The method of claim 24 wherein the engine is a diesel engine having an output of at least about 750 kW (1000 horsepower).