

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 616 635 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

07.01.1999 Bulletin 1999/01

(21) Application number: **93921434.2**

(22) Date of filing: **09.09.1993**

(51) Int Cl.⁶: **C10M 159/18**, C10M 133/16,
C10M 149/00, C10L 1/14,
C10L 10/00, C10M 167/00
//(C10M167/00, 133:16, 133:56,
143:06, 159:18), C10N10:12,
C10N30:04, C10N40:25

(86) International application number:

PCT/US93/08471

(87) International publication number:

WO 94/06897 (31.03.1994 Gazette 1994/08)

(54) FUEL COMPOSITION FOR TWO-CYCLE ENGINES

BRENNSTOFFZUSAMMENSETZUNG FÜR ZWEITAKTMOTOREN

COMPOSITION DE CARBURANT POUR MOTEURS DEUX-TEMPS

(84) Designated Contracting States:
CH DE FR GB LI SE

(30) Priority: **11.09.1992 US 943844**

(43) Date of publication of application:
28.09.1994 Bulletin 1994/39

(73) Proprietor: **Chevron Chemical Company LLC**
San Francisco, CA 94105 (US)

(72) Inventors:

- **CALLIS, Glenn, E.**
Walnut Creek, CA 94598 (US)

- **SABOURIN, Edward, T.**
Novato, CA 94947 (US)

(74) Representative: **Nash, David Allan et al**
Haseltine Lake & Co.,
Imperial House,
15-19 Kingsway
London WC2B 6UD (GB)

(56) References cited:

US-A- 3 219 666	US-A- 3 405 064
US-A- 4 164 473	US-A- 4 263 152
US-A- 4 266 945	

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 616 635 B1

Description**BACKGROUND OF THE INVENTION**

5 The present invention relates to a fuel composition for two-cycle internal combustion engines which comprises a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising a lubricating oil and an additive formulation containing a molybdenum/sulfur complex of a basic nitrogen compound.

Over the past several decades the use of spark-ignited two-cycle (two-stroke) internal combustion engines including rotary engines such as those of the Wankel type has steadily increased. They are presently found in power lawn
10 mowers and other power-operated garden equipment, power chain saws, pumps, electrical generators, marine out-board engines, snowmobiles, motorcycles, and the like.

The increasing use of two-cycle engines coupled with increasing severity of the conditions in which they have operated has led to an increasing demand for oils to adequately lubricate such engines. Among the problems associated with lubrication of two-cycle engines are piston ring sticking, rusting, lubrication failure of connecting rods and main
15 bearings and the general formation on the engine's interior surface of carbon and varnish deposits. The formation of varnish is a particularly vexatious problem since the build-up of varnish on piston and cylinder walls is believed to ultimately result in ring sticking which leads to failure of the sealing function of piston rings. Such seal failure causes loss of cylinder compression which is particularly damaging in two-cycle engines because they depend on suction to draw the new fuel charge into the exhausted cylinder. Thus, ring sticking can lead to deterioration in engine performance, and unnecessary consumption of fuel and/or lubricant. Spark plug fouling and engine port plugging problems
20 also occur in two-cycle engines.

A variety of compounds have been proposed as additives for fuel-lubricating oil mixtures to be used in two-cycle internal combustion engines. For example, U.S. Patent No. 4,708,809 to Davis discloses a lubricant composition for two-cycle engines comprising a major amount of an oil of lubricating viscosity and a minor amount of at least one alkyl
25 phenol having at least one hydrocarbon-based group of at least 10 aliphatic carbon atoms. Preferably, such lubricant composition will also contain a detergent-dispersant additive selected from (i) a neutral or basic metal salt of an organic sulfur acid, phenol or carboxylic acid, (ii) a hydrocarbyl-substituted amine, (iii) an acylated, nitrogen-containing compound having a substituent of at least 10 aliphatic carbon atoms, (iv) a nitrogen-containing condensate of a phenol, aldehyde and amino compound, and (v) an ester of a substituted polycarboxylic acid.

U.S. Patent No. 4,724,091 to Davis discloses a lubricant composition for two-cycle engines comprising a major amount of an oil of lubricating viscosity and a minor amount of a mixture of at least one alkyl phenol and at least one amino phenol, each phenol having at least one hydrocarbon-based group of at least about 10 aliphatic carbon atoms. Preferably, this composition will additionally contain a detergent-dispersant additive.
30

U.S. Patent No. 4,740,321 to Davis et al. discloses a lubricant composition for two-cycle engines comprising a major amount of an oil of lubricating viscosity and a minor amount of at least one sulfurized alkyl phenol or metal salt thereof having at least one hydrocarbon-based group of at least 10 aliphatic carbon atoms. This lubricant composition will also preferably contain a detergent-dispersant additive.
35

U.S. Patent No. 4,705,643 to Nemo discloses a lubricating oil composition for two-cycle engines comprising a lubricating oil and an ashless detergent additive which is the hydrolyzed reaction product of an aliphatic branched chain carboxylic acid of 16 to 20 carbon atoms and a polyamine of at least 3 amine groups. Preferably, the ashless detergent additive is the hydrolyzed reaction product of isostearic acid and tetraethylenepentamine.
40

U.S. Patent No. 4,994,196 to Kagaya et al. discloses a two-cycle engine oil composition comprising a base oil and a calcium phenate detergent additive, wherein the base oil is a mixture of (a) a copolymer of an alpha-olefin with an ester of a dicarboxylic acid and (b) an ester of pentaerythritol and a fatty acid.
45

U.S. Patent No. 3,888,776 to Silverstein discloses a two-cycle engine lubricant which comprises a major amount of a polypropylene glycol and minor amounts of a sulfurized oxymolybdenum organophosphorodithioate, a finely divided molybdenum disulfide and a halogenated hydrocarbon detergent, such as 1,1,1-trichloroethylene, orthodichlorobenzene, perchlorinated biphenyl, and the like.

Molybdenum/sulfur complexes of basic nitrogen compounds have previously been described in the art as useful antioxidant additives for lubricant compositions finding application, for example, as crosshead diesel engine lubricants, automobile and railroad crankcase lubricants, lubricants for heavy machinery, greases for bearings, and the like.
50

For example, U.S. Patent No. 4,263,152 to King et al. discloses an antioxidant additive for lubricating oils which is prepared by combining an acidic molybdenum compound, a polar promoter, a basic nitrogen-containing compound and a sulfur source to form a molybdenum and sulfur-containing complex. Similar molybdenum-containing antioxidant additives are disclosed in U.S. Patent Nos. 4,285,822; 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195; and 4,259,194. However, none of these patents teaches or appreciates the use of such antioxidant additives, or lubricating oils containing such additives, in admixture with fuels in two-cycle engines. Furthermore, none of these patents teaches or appreciates that such antioxidant additives would be effective deposit control agents or would reduce piston sticking
55

when utilized in fuel-lubricating oil mixtures in two-cycle engines.

Moreover, as taught in the aforementioned U.S. Patent No. 4,708,809, the unique problems and techniques associated with the lubrication of two-cycle engines has led to the recognition by those skilled in the art of two-cycle engine lubricants as a distinct lubricant type.

Accordingly, the present invention is directed to minimizing the problems of varnish build-up and ring sticking in two-cycle engines through the provision of effective additives for fuel-lubricating oil combinations which eliminate or reduce two-cycle engine varnish deposits and piston ring seal failure.

SUMMARY OF THE INVENTION

The present invention provides a fuel composition for two-cycle engines comprising a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising:

(A) a major amount of a base oil of lubricating viscosity, and

(B) a minor amount of an additive formulation comprising:

(1) from 0.05 to 15 % by weight of a sulfurized molybdenum-containing composition prepared by (i) reacting an acidic molybdenum compound and a basic nitrogen compound selected from the group consisting of a succinimide, a carboxylic acid amide, a hydrocarbyl monoamine, a hydrocarbyl polyamine, a Mannich base, a phosphoramidate, a thiophosphoramidate, a phosphonamide, or a mixture thereof, in the presence of a polar promoter, to form a molybdenum complex wherein from 0.01 to 2 atoms of molybdenum are present per basic nitrogen atom, and the promoter is present in the ratio of 0.01 to 50 moles of polar promoter per mole of molybdenum; and (ii) reacting the molybdenum complex with a sulfur-containing compound in an amount sufficient to provide about 1.5 to 4.0 atoms of sulfur per atom of molybdenum, to thereby form a sulfur- and molybdenum-containing composition,

(2) from 0.05 to 20 % by weight of a carboxylic acid amide, and

(3) from 0.05 to 15 % by weight of a succinimide.

Among other factors, the present invention is based upon the unexpected discovery that additive formulations containing a molybdenum/sulfur complex of a basic nitrogen compound, plus a carboxylic acid amide and a succinimide are surprisingly effective agents for deposit control and reduction of piston ring sticking when combined in fuel-lubricating oil mixtures in two-cycle engines.

DETAILED DESCRIPTION OF THE INVENTION

The fuel composition of the present invention will comprise a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising a base oil of lubricating viscosity and an additive formulation containing (1) a sulfurized molybdenum-containing composition, (2) a carboxylic acid amide, and (3) a succinimide.

The sulfurized molybdenum-containing composition employed in the present invention may be generally characterized as a molybdenum/sulfur complex of a basic nitrogen compound. Such molybdenum/sulfur complexes are known in the art and are described, for example, in U.S. Patent No. 4,263,152 to King et al.

The precise molecular formula of the molybdenum compositions employed in this invention is not known with certainty; however, they are believed to be compounds in which molybdenum, whose valences are satisfied with atoms of oxygen or sulfur, is either complexed by, or the salt of, one or more nitrogen atoms of the basic nitrogen containing compound used in the preparation of these compositions.

The molybdenum compounds used to prepare the molybdenum/sulfur complexes employed in this invention are acidic molybdenum compounds. By acidic is meant that the molybdenum compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure. Typically these molybdenum compounds are hexavalent and are represented by the following compositions: molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate and other alkaline metal molybdates and other molybdenum salts such as hydrogen salts, e.g., hydrogen sodium molybdate, MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, molybdenum trioxide or similar acidic molybdenum compounds. Preferred acidic molybdenum compounds are molybdic acid, ammonium molybdate, and alkali metal molybdates. Particularly preferred are molybdic acid and ammonium molybdate.

The basic nitrogen compound used to prepare the molybdenum/sulfur complexes must have a basic nitrogen content as measured by ASTM D-664 or D-2896. It is preferably oil-soluble. Typical of such compositions are succin-

imides, carboxylic acid amides, hydrocarbyl monoamines, hydrocarbon polyamines, Mannich bases, phosphoramides, thiophosphoramides, phosphoramides, and mixtures thereof. These basic nitrogen-containing compounds are described below (keeping in mind the reservation that each must have at least one basic nitrogen). Any of the nitrogen-containing compositions may be after-treated with, e.g., boron, using procedures well known in the art so long as the compositions continue to contain basic nitrogen. These after-treatments are particularly applicable to succinimides and Mannich base compositions.

The mono and polysuccinimides that can be used to prepare the molybdenum/sulfur complexes described herein are disclosed in numerous references and are well known in the art. Certain fundamental types of succinimides and the related materials encompassed by the term of art "succinimide" are taught in U.S. Patent Nos. 3,219,666; 3,172,892; and 3,272,746. The term "succinimide" is understood in the art to include many of the amide, imide, and amidine species which may also be formed. The predominant product however is a succinimide and this term has been generally accepted as meaning the product of a reaction of an alkenyl substituted succinic acid or anhydride with a nitrogen-containing compound. Preferred succinimides, because of their commercial availability, are those succinimides prepared from a hydrocarbyl succinic anhydride, wherein the hydrocarbyl group contains from about 24 to about 350 carbon atoms, and an ethylene amine, said ethylene amines being especially characterized by ethylene diamine, diethylene triamine, triethylene tetramine, and tetraethylene pentamine. Particularly preferred are those succinimides prepared from polyisobutenyl succinic anhydride of 70 to 128 carbon atoms and tetraethylene pentamine or triethylene tetramine or mixtures thereof.

Also included within the term "succinimide" are the cooligomers of a hydrocarbyl succinic acid or anhydride and a poly secondary amine containing at least one tertiary amino nitrogen in addition to two or more secondary amino groups. Ordinarily this composition has between 1,500 and 50,000 average molecular weight. A typical compound would be that prepared by reacting polyisobutenyl succinic anhydride and ethylene dipiperazine.

Carboxylic acid amide compositions are also suitable starting materials for preparing the molybdenum/sulfur complexes employed in this invention. Typical of such compounds are those disclosed in U.S. Patent No. 3,405,064. These compositions are ordinarily prepared by reacting a carboxylic acid or anhydride or ester thereof, having at least 12 to about 350 aliphatic carbon atoms in the principal aliphatic chain and, if desired, having sufficient pendant aliphatic groups to render the molecule oil soluble with an amine or a hydrocarbyl polyamine, such as an ethylene amine, to give a mono or polycarboxylic acid amide. Preferred are those amides prepared from (1) a carboxylic acid of the formula R^2COOH , where R^2 is C_{12-20} alkyl or a mixture of this acid with a polyisobutenyl carboxylic acid in which the polyisobutenyl group contains from 72 to 128 carbon atoms and (2) an ethylene amine, especially triethylene tetramine or tetraethylene pentamine or mixtures thereof.

Another class of compounds which are useful in this invention are hydrocarbyl monoamines and hydrocarbyl polyamines, preferably of the type disclosed in U.S. Patent No. 3,574,576. The hydrocarbyl group, which is preferably alkyl, or olefinic having one or two sites of unsaturation, usually contains from 9 to 350, preferably from 20 to 200 carbon atoms. Particularly preferred hydrocarbyl polyamines are those which are derived, e.g., by reacting polyisobutenyl chloride and a polyalkylene polyamine, such as an ethylene amine, e.g., ethylene diamine, diethylene triamine, tetraethylene pentamine, 2-aminoethylpiperazine, 1,3-propylene diamine, 1,2-propylenediamine, and the like.

Another class of compounds useful for supplying basic nitrogen are the Mannich base compositions. These compositions are prepared from a phenol or C_{9-200} alkylphenol, an aldehyde, such as formaldehyde or formaldehyde precursor such as paraformaldehyde, and an amine compound. The amine may be a mono or polyamine and typical compositions are prepared from an alkylamine, such as methylamine or an ethylene amine, such as, diethylene triamine, or tetraethylene pentamine, and the like. The phenolic material may be sulfurized and preferably is dodecylphenol or a C_{80-100} alkylphenol. Typical Mannich bases which can be used in this invention are disclosed in U.S. Patent No. 4,157,309 and U.S. Patent Nos. 3,649,229; 3,368,972; and 3,539,663. The last referenced patent discloses Mannich bases prepared by reacting an alkylphenol having at least 50 carbon atoms, preferably 50 to 200 carbon atoms with formaldehyde and an alkylene polyamine $HN(ANH)_nH$ where A is a saturated divalent alkyl hydrocarbon of 2 to 6 carbon atoms and n is 1-10 and where the condensation product of said alkylene polyamine may be further reacted with urea or thiourea. The utility of these Mannich bases as starting materials for preparing lubricating oil additives can often be significantly improved by treating the Mannich base using conventional techniques to introduce boron into the composition.

Another class of composition useful for preparing the molybdenum/sulfur complexes employed in this invention are the phosphoramides and phosphoramides such as those disclosed in U.S. Patent Nos. 3,909,430 and 3,968,157. These compositions may be prepared by forming a phosphorus compound having at least one P-N bond. They can be prepared, for example, by reacting phosphorus oxychloride with a hydrocarbyl diol in the presence of a monoamine or by reacting phosphorus oxychloride with a difunctional secondary amine and a mono-functional amine. Thiophosphoramides can be prepared by reacting an unsaturated hydrocarbon compound containing from 2 to 450 or more carbon atoms, such as polyethylene, polyisobutylene, polypropylene, ethylene, 1-hexene, 1,3-hexadiene, isobutylene, 4-methyl-1-pentene, and the like, with phosphorus pentasulfide and a nitrogen-containing compound as defined above,

particularly an alkylamine, alkyldiamine, alkylpolyamine, or an alkyleneamine, such as ethylene diamine, diethylene-triamine, triethylenetetramine, tetraethylenepentamine, and the like.

Another class of nitrogen-containing compositions useful in preparing the molybdenum complexes employed in this invention includes the so-called dispersant viscosity index improvers (VI improvers). These VI improvers are commonly prepared by functionalizing a hydrocarbon polymer, especially a polymer derived from ethylene and/or propylene, optionally containing additional units derived from one or more co-monomers such as alicyclic or aliphatic olefins or diolefins. The functionalization may be carried out by a variety of processes which introduce a reactive site or sites which usually has at least one oxygen atom on the polymer. The polymer is then contacted with a nitrogen-containing source to introduce nitrogen-containing functional groups on the polymer backbone. Commonly used nitrogen sources include any basic nitrogen compound especially those nitrogen-containing compounds and compositions described herein. Preferred nitrogen sources are alkylene amines, such as ethylene amines, alkyl amines, and Mannich bases.

Preferred basic nitrogen compounds for use in this invention are succinimides, carboxylic acid amides, and Mannich bases.

Representative sulfur sources for preparing the molybdenum complexes used in this invention are sulfur, hydrogen sulfide, sulfur monochloride, sulfur dichloride, phosphorus pentasulfide, R_2S_x where R is hydrocarbyl, preferably C_1 - C_{40} alkyl, and x is at least 2, inorganic sulfides and polysulfides such as $(NH_4)_2S_x$, where x is at least 1, thioacetamide, thiourea, and mercaptans of the formula RSH where R is as defined above. Also useful as sulfurizing agents are traditional sulfur-containing antioxidants such as wax sulfides and polysulfides, sulfurized olefins, sulfurized carboxylic and esters and sulfurized ester-olefins, and sulfurized alkylphenols and the metal salts thereof.

The sulfurized fatty acid esters are prepared by reacting sulfur, sulfur monochloride, and/or sulfur dichloride with an unsaturated fatty ester under elevated temperatures. Typical esters include C_1 - C_{20} alkyl esters of C_8 - C_{24} unsaturated fatty acids, such as palmitoleic, oleic, ricinoleic, petroselinic, vaccenic, linoleic, linolenic, oleostearic, licanic, paranaric, tariric, gadoleic, arachidonic, cetoleic, etc. Particularly good results have been obtained with mixed unsaturated fatty acid esters, such as are obtained from animal fats and vegetable oils, such as tall oil, linseed oil, olive oil, castor oil, peanut oil, rape oil, fish oil, sperm oil, and so forth.

Exemplary fatty esters include lauryl tallate, methyl oleate, ethyl oleate, lauryl oleate, cetyl oleate, cetyl linoleate, lauryl ricinoleate, oleyl linoleate, oleyl stearate, and alkyl glycerides.

Cross-sulfurized ester olefins, such as a sulfurized mixture of C_{10} - C_{25} olefins with fatty acid esters of C_{10} - C_{25} fatty acids and C_1 - C_{25} alkyl or alkenyl alcohols, wherein the fatty acid and/or the alcohol is unsaturated may also be used.

Sulfurized olefins are prepared by the reaction of the C_3 - C_6 olefin or a low-molecular-weight polyolefin derived therefrom with a sulfur-containing compound such as sulfur, sulfur monochloride, and/or sulfur dichloride.

Also useful are the aromatic and alkyl sulfides, such as dibenzyl sulfide, dicytyl sulfide, dicetyl sulfide, diparaffin wax sulfide and polysulfide, cracked wax-olefin sulfides and so forth. They can be prepared by treating the starting material, e.g., olefinically unsaturated compounds, with sulfur, sulfur monochloride, and sulfur dichloride. Particularly preferred are the paraffin wax thiomers described in U.S. Patent No. 2,346,156.

Sulfurized alkyl phenols and the metal salts thereof include compositions such as sulfurized dodecylphenol and the calcium salts thereof. The alkyl group ordinarily contains from 9-300 carbon atoms. The metal salt may be preferably, a Group I or Group II salt, especially sodium, calcium, magnesium, or barium.

Preferred sulfur sources are sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is hydrocarbyl, preferably C_1 - C_{10} alkyl, and x is at least 3, mercaptans wherein R is C_1 - C_{10} alkyl, inorganic sulfides and polysulfides, thioacetamide, and thiourea. Most preferred sulfur sources are sulfur, hydrogen sulfide, phosphorus pentasulfide, and inorganic sulfides and polysulfides.

The polar promoter used in the preparation of the molybdenum complexes employed in this invention is one which facilitates the interaction between the acidic molybdenum compound and the basic nitrogen compound. A wide variety of such promoters are well known to those skilled in the art. Typical promoters are 1,3-propanediol, 1,4-butane-diol, diethylene glycol, butyl cellosolve, propylene glycol, 1,4-butyleneglycol, methyl carbitol, ethanolamine, diethanolamine, N-methyl-diethanol-amine, dimethyl formamide, N-methyl acetamide, dimethyl acetamide, methanol, ethylene glycol, dimethyl sulfoxide, hexamethyl phosphoramide, tetrahydrofuran and water. Preferred are water and ethylene glycol. Particularly preferred is water.

While ordinarily the polar promoter is separately added to the reaction mixture, it may also be present, particularly in the case of water, as a component of non-anhydrous starting materials or as waters of hydration in the acidic molybdenum compound, such as $(NH_4)_6Mo_7O_{24} \cdot 4 H_2O$. Water may also be added as ammonium hydroxide.

A method for preparing the molybdenum/sulfur complexes used in this invention is to prepare a solution of the acidic molybdenum precursor and a polar promoter with a basic nitrogen-containing compound with or without diluent. The diluent is used, if necessary, to provide a suitable viscosity for easy stirring. Typical diluents are lubricating oil and liquid compounds containing only carbon and hydrogen. If desired, ammonium hydroxide may also be added to the reaction mixture to provide a solution of ammonium molybdate. This reaction is carried out at a temperature from the melting point of the mixture to reflux temperature. It is ordinarily carried out at atmospheric pressure although higher

or lower pressures may be used if desired. This reaction mixture is treated with a sulfur source as defined above at a suitable pressure and temperature for the sulfur source to react with the acidic molybdenum and basic nitrogen compounds. In some cases, removal of water from the reaction mixture may be desirable prior to completion of reaction with the sulfur source.

In the reaction mixture, the ratio of molybdenum compound to basic nitrogen compound is not critical; however, as the amount of molybdenum with respect to basic nitrogen increases, the filtration of the product becomes more difficult. Since the molybdenum component probably oligomerizes, it is advantageous to add as much molybdenum as can easily be maintained in the composition. Usually, the reaction mixture will have charged to it from 0.01 to 2.00 atoms of molybdenum per basic nitrogen atom. Preferably from 0.4 to 1.0, and most preferably from 0.4 to 0.7, atoms of molybdenum per atom of basic nitrogen is added to the reaction mixture.

The sulfur source is usually charged to the reaction mixture in such a ratio to provide 1.5 to 4.0 atoms of sulfur per atom of molybdenum. Preferably from 2.0 to 4.0 atoms of sulfur per atom of molybdenum is added, and most preferably, 2.5 to 4.0 atoms of sulfur per atom of molybdenum.

The polar promoter, which is preferably water, is ordinarily present in the ratio of 0.1 to 50 moles of promoter per mole of molybdenum. Preferably from 0.5 to 25 and most preferably 1.0 to 15 moles of the promoter is present per mole of molybdenum.

As described above, the additive formulation employed in the present invention contains (1) a sulfurized molybdenum-containing composition, (2) a carboxylic acid amide, and (3) a succinimide.

The carboxylic amide component of the presently employed additive formulation may be any of the carboxylic acid amide compounds described herein as useful in the preparation of the molybdenum/sulfur complex. Preferred carboxylic acid amide components include those amides derived from a carboxylic acid of the formula R^2COOH , wherein R^2 is C_{12} - C_{20} alkyl, and an ethylene amine, such as triethylene tetramine or tetraethylene pentamine.

Similarly, the succinimide component of the presently employed additive formulation may be any of the succinimide compounds described herein as useful in the preparation of the molybdenum/sulfur complex. Preferred succinimide components include those derived from polyisobutenyl succinic anhydride, wherein the polyisobutenyl group contains from about 50 to 250 carbon atoms, and an ethylene amine, such as triethylene tetramine or tetraethylene pentamine.

The additive formulation employed in the present invention may additionally contain a flocculant inhibitor and/or a lubricity agent, such as a polyisobutene. If necessary, a diluent oil may also be included.

Other additives such as viscosity index improvers, antioxidants, dispersants, coupling agents, pour point depressants, extreme pressure agents, color stabilizers, rust inhibitors, anticorrosion agents, and the like, may also be present in the additive formulation.

The lubricant composition employed in the present invention comprises a major amount of a base oil of lubricating viscosity and a minor amount of the additive formulation described above.

The base oil employed may be any of a wide variety of oils of lubricating viscosity. Thus, the base oil can be a refined paraffin type base oil, a refined naphthenic base oil, or a synthetic hydrocarbon or non-hydrocarbon oil of lubricating viscosity. The base oil can also be a mixture of mineral and synthetic oils. For purposes of the present invention, the mineral lubricating oils are preferred, since they are presently in more general use in two-cycle engines.

The presently employed lubricant composition containing the additive formulation described herein can be conveniently prepared using conventional techniques by admixing the appropriate amount of each component of the additive formulation with a lubricating oil.

Generally, the amount of the molybdenum-containing additive will vary from about 0.05 to 15% by weight and preferably from about 0.2 to 10% by weight, based on the total lubricant composition, including base oil. The carboxylic acid amide component will vary from about 0.05 to 20% by weight and preferably from about 0.2 to 15% by weight. The succinimide component will vary from about 0.5 to 15% by weight and preferably from about 0.2 to 10% by weight.

The two-cycle engine fuel composition contemplated by the present invention comprises a major amount of fuel boiling in the gasoline range and minor amount of the lubricant composition disclosed herein.

For purposes of the present invention, the lubricant composition will generally be added directly to the fuel to form a mixture of lubricant and fuel which is then introduced into the two-cycle engine cylinder. Generally, the resulting fuel composition will contain from about 15 to 250 parts fuel per 1 part lubricant, and more typically about 50 to 100 parts fuel per 1 part lubricant. For some two-cycle engine applications, the lubricant may be directly injected into the combustion chamber along with the fuel or into the fuel just prior to the time the fuel enters the combustion chamber.

The fuel employed in the present fuel composition is a hydrocarbon distillate fuel boiling in the gasoline range. In such gasoline fuels, other fuel additives may also be included such as antiknock agents, e.g., methylcyclopentadienyl manganese tricarbonyl, tetramethyl or tetraethyl lead, or other dispersants or detergents such as various substituted amines, etc. Also included may be lead scavengers such as aryl halides, e.g., dichlorobenzene or alkyl halides, e.g., ethylene dibromide. Additionally, antioxidants, metal deactivators, pour point depressants, corrosion inhibitors and demulsifiers may be present.

The following examples are presented to illustrate specific embodiments of this invention and are not to be con-

strued in any way as limiting the scope of the invention.

EXAMPLES

Example 1

To a 5000 ml flask was added 114 grams molybdenum trioxide and 196 grams of water. Stirring was started and 1200 grams of a solution of a 45% concentrate in oil of the polyisobutenyl succinimide prepared from polyisobutenyl succinic anhydride having a number average molecular weight for the polyisobutenyl group of about 950 and tetraethylene pentamine, and 1200 grams of hydrocarbon thinner were added. The mixture was refluxed at 100°C for 3 hours. The temperature was gradually increased over approximately 1 hour to 170°C while distilling water. The temperature was maintained an additional hour after the water was removed. The temperature was lowered to 100°C-120°C and the mixture filtered and returned to the reaction vessel. To the solution was added 51 grams of sulfur. The mixture was heated to 160°C-180°C for 7 hours. The pressure was slowly reduced to about 50 mm of mercury to remove the hydrocarbon thinner. This produced 1244 grams of product containing 1.80% nitrogen, 5.63% molybdenum, and 3.57% sulfur.

Example 2

To a 5000 ml flask was added 52 grams molybdenum trioxide and 111 grams of water. Stirring was started and 1184 grams of a solution of a 45% concentrate in oil of the succinimide described in Example 1 and 1184 grams of hydrocarbon thinner were added. The mixture was refluxed at 100°C for 3 hours. The temperature was gradually increased over approximately 1 hour to 170°C while distilling water. The temperature was maintained an additional hour after the water was removed. The temperature was lowered to 100°C-120°C and the mixture filtered and returned to the reaction vessel. To the solution was added 47 grams of sulfur. The mixture was heated to 160°C-180°C for 7 hours. The pressure was slowly reduced to about 50 mm of mercury to remove the hydrocarbon thinner. This produced 1220 grams of product containing 1.94% nitrogen, 2.78% molybdenum, and 3.64% sulfur.

Example 3

To a 5000 ml flask was added 49 grams molybdenum trioxide and 105 grams of water. Stirring was started and 1133 grams of a solution of a 45% concentrate in oil of the succinimide described in Example 1 and 1133 grams of hydrocarbon thinner were added. The mixture was refluxed at 100°C for 3 hours. The temperature was gradually increased over approximately 1 hour to 170°C while distilling water. The temperature was maintained an additional hour after the water was removed. The temperature was lowered to 100°C-120°C and the mixture filtered and returned to the reaction vessel. To the solution was added 22 grams of sulfur. The mixture was heated to 160°C-180°C for 7 hours. The pressure was slowly reduced to about 50 mm of mercury to remove the hydrocarbon thinner. This produced 1163 grams of product containing 1.83% nitrogen, 2.79% molybdenum, and 1.97% sulfur.

Example 4

To a 5000 ml flask was added 1200 grams of a polyamide prepared from a C₁₈ carboxylic acid and tetraethylene pentamine and containing 6.4% nitrogen, 1200 grams hydrocarbon thinner, 42 grams molybdenum trioxide, and 90 grams water. The mixture was refluxed at 100°C for 3 hours. The temperature was gradually increased over approximately 1 hour to 170°C while distilling water. The temperature was maintained an additional hour after the water was removed. The temperature was lowered to 100°C-120°C and the mixture filtered and returned to the reaction vessel. To the solution was added 21 grams of sulfur. The mixture was heated to 160°C-180°C for 7 hours. The pressure was slowly reduced to about 50 mm of mercury to remove the hydrocarbon thinner. This produced a product containing 5.88% nitrogen, 2.29% molybdenum, and 1.63% sulfur.

Example 5

The molybdenum/sulfur complexes of Examples 1, 2 and 4 were formulated to provide lubricant compositions containing 10% of the carboxylic acid amide reaction product of isostearic acid and tetraethylene pentamine, 2% of a polyisobutenyl succinimide prepared from polyisobutenyl succinic anhydride wherein the polyisobutenyl group has a number average molecular weight of about 950 and tetraethylene pentamine, 2% of the molybdenum/sulfur complex of Examples 1, 2 and 4, respectively, 5% of a polyisobutene having a number average molecular weight of about 950 as a lubricity agent, 0.5% of a flocculant inhibitor, 1% of a diluent oil and about 79.5% of a base oil. The base oil contains

about 10% of a 150 bright stock, about 70% of a mixture of 350N and 650N neutral oils, and about 20% of a petroleum distillate solvent.

Example 6

Two-Cycle Gasoline Engine Test

This test was used to evaluate the detergency and general performance of the fuel composition of this invention in a two-cycle water-cooled outboard engine. Piston varnish, ring sticking and general engine deposits were evaluated.

The test engine used was an Outboard Marine Company Johnson Model No. J70ELEIE outboard engine, which is a 70 horsepower, water-cooled, three-cylinder, two-cycle engine.

The test procedure involved a two-hour break-in period, wherein the engine was run at 3,000 rpm for 1 hour, then at 4,000 rpm for 1 hour, using a fuel:lubricant ratio of 50:1.

The test was then conducted for 98 hours using a 50:1 fuel to lubricant ratio on a 55 minute wide-open throttle, 5 minute idle cycle. The total test time, including break-in, was 100 hours.

At the conclusion of the test, the engine was disassembled and rated. The average piston rating and average second-ring sticking rating for 3 cylinders was measured. In the rating system employed, the higher the numerical rating, the better the cleanliness performance, with 10.0 being the maximum rating. Except for the piston rings, the ratings are for cleanliness. The piston rings are rated for the degree of sticking, with a rating of 10.0 indicating a completely free piston ring.

The second-ring sticking values include a National Marine Manufacturers Association (NMMA) rating, a visual rating, and an adjusted rating, which is an average of the NMMA and visual ratings.

The reference oil employed in this test was NMMA reference oil TCW II, used as an industry standard in two-cycle engine tests to measure engine cleanliness. The TCW II reference oil is a standard mineral lubricating oil containing a commercial ashless dispersant for gasoline two-cycle engines. The reference oil is available from Citgo Petroleum Corporation, Tulsa, Oklahoma.

Engine test runs were performed with a 50:1 fuel to lubricant ratio, using lubricant compositions containing the molybdenum/sulfur complexes of Examples 1, 2 and 4, formulated as described in Example 5. The results of the engine tests are shown in Table 1.

The results shown in Table 1 demonstrate that the fuel composition of the present invention is highly effective in reducing piston deposits and piston ring sticking in two-cycle engines, and generally exceeds the performance of a fuel containing the industry standard reference oil.

TABLE 1

TWO-CYCLE ENGINE TEST RESULTS							
Average Rating for 3 Cylinders							
Additive	Piston Skirt	Crown	2-Ring Land	Under-Crown	Second-Ring Sticking		
					NMMA	Visual	Adj.
TCW II Reference Oil	7.1	2.8	3.7	2.8	6.8	5.7	6.3
Example 1 ^(a)	7.4	3.4	4.4	2.5	7.1	6.1	6.6
Example 4 ^(a)	7.7	3.1	4.8	3.9	7.8	6.8	7.3
Example 2 ^(a)	7.8	3.4	4.4	3.3	8.5	6.5	7.5

^(a) Formulated as in Example 5.

Claims

1. A fuel composition for two-cycle engines comprising a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising:

(A) a major amount of a base oil of lubricating viscosity, and

(B) a minor amount of an additive formulation comprising:

(1) from 0.05 to 15 % by weight of a sulfurized molybdenum-containing composition prepared by (i) reacting an acidic molybdenum compound and a basic nitrogen compound selected from the group consisting of a succinimide, a carboxylic acid amide, a hydrocarbyl monoamine, a hydrocarbyl polyamine, a Mannich base, a phosphoramidate, a thiophosphoramidate, a phosphonamide, or a mixture thereof, in the presence of a polar promoter, to form a molybdenum complex wherein from 0.01 to 2 atoms of molybdenum are present per basic nitrogen atom, and the promoter is present in the ratio of 0.01 to 50 moles of polar promoter per mole of molybdenum; and (ii) reacting the molybdenum complex with a sulfur-containing compound in an amount sufficient to provide about 1.5 to 4.0 atoms of sulfur per atom of molybdenum, to thereby form a sulfur- and molybdenum-containing composition,

(2) from 0.05 to 20 % by weight of a carboxylic acid amide, and

(3) from 0.05 to 15 % by weight of a succinimide.

2. The fuel composition of Claim 1, wherein the sulfur source for component (1) is sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is hydrocarbyl, and x is at least 2, inorganic sulfides or inorganic polysulfides, thioacetamide, thiourea, mercaptans of the formula RSH where R is hydrocarbyl, or a sulfur-containing antioxidant.
3. The fuel composition of Claim 2, wherein the sulfur source for component (1) is sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is C_{1-4} hydrocarbyl, and x is at least 3, inorganic sulfides, or inorganic polysulfides, thioacetamide, thiourea or RSH where R is C_{1-40} alkyl, and the acidic molybdenum compound is molybdic acid, ammonium molybdate, or alkali metal molybdate.
4. The fuel composition of Claim 3, wherein said sulfur source is sulfur, hydrogen sulfide, RSH where R is C_{1-10} alkyl, phosphorus pentasulfide, or $(NH_4)_2S_{x'}$, where x' is at least 1, said acidic molybdenum compound is molybdic acid, or ammonium molybdate, and said basic nitrogen compound is a succinimide, carboxylic acid amide, or Mannich base.
5. The fuel composition of Claim 4, wherein said basic nitrogen compound is a C_{24-350} hydrocarbyl succinimide, carboxylic acid amide, or a Mannich base prepared from a C_{9-200} alkylphenol, formaldehyde, and an amine.
6. The fuel composition of Claim 5, wherein said basic nitrogen compound is a polyisobutenyl succinimide prepared from polyisobutenyl succinic anhydride and tetraethylene pentamine or triethylene tetramine.
7. The fuel composition of Claim 5, wherein said basic nitrogen compound is a carboxylic acid amide prepared from one or more carboxylic acids of the formula R^2COOH , or a derivative thereof which upon reaction with an amine yields a carboxylic acid amide, wherein R^2 is C_{12-350} alkyl or C_{12-350} alkenyl and a hydrocarbyl polyamine.
8. The fuel composition of Claim 7, wherein R^2 is C_{12-20} alkyl or C_{12-20} alkenyl and the hydrocarbyl polyamine is tetraethylene pentamine or triethylene tetramine.
9. The fuel composition of Claim 5, wherein said basic nitrogen compound is a Mannich base prepared from dodecylphenol, formaldehyde, and methylamine.
10. The fuel composition of Claim 5, wherein said basic nitrogen compound is a Mannich base prepared from C_{80-100} alkylphenol, formaldehyde and triethylene tetramine, tetraethylene pentamine, or mixtures thereof.
11. The fuel composition of Claim 1, wherein the polar promoter is water.
12. The fuel composition of Claim 1, wherein the carboxylic acid amide of component (2) is derived from a carboxylic acid of the formula R^2COOH , wherein R^2 is C_{12-20} alkyl, and an ethylene amine.
13. The fuel composition of Claim 1, wherein the succinimide of component (3) is derived from polyisobutenyl succinic anhydride, wherein the polyisobutenyl group contains from 50 to 250 carbon atoms, and an ethylene amine.
14. The fuel composition of Claim 1, wherein the lubricant composition contains 0.05 to 15% by weight of the molybdenum-containing composition of component (1), 0.05 to 20% by weight of the carboxylic acid amide of component (2), and 0.05 to 15% by weight of the succinimide of component (3).

15. The fuel composition of Claim 1, wherein the molybdenum complex is reacted with the sulfur-containing compound in an amount sufficient to provide 2.0 to 4.0 atoms of sulfur per atom of molybdenum.

16. The fuel composition of Claim 15, wherein the molybdenum complex is reacted with the sulfur-containing compound in an amount sufficient to provide 2.5 to 4.0 atoms of sulfur per atom of molybdenum.

17. The fuel composition of Claim 1, wherein the additive formulation further contains a flocculant inhibitor.

18. The fuel composition of Claim 17, wherein the additive formulation further contains a lubricity agent.

19. A method for reducing engine deposits and piston ring sticking in a two-cycle engine which comprises operating the two-cycle engine with a fuel composition comprising a major amount of fuel boiling in the gasoline range and a minor amount of a lubricant composition comprising:

(A) a major amount of a base oil of lubricating viscosity, and

(B) a minor amount effective to reduce engine deposits and piston ring sticking of an additive formulation comprising:

(1) from 0.05 to 15 % by weight of a sulfurized molybdenum-containing composition prepared by (i) reacting an acidic molybdenum compound and a basic nitrogen compound selected from the group consisting of a succinimide, a carboxylic acid amide, a hydrocarbyl monoamine, a hydrocarbyl polyamine, a Mannich base, a phosphoramidate, a thiophosphoramidate, a phosphonamide, or a mixture thereof, in the presence of a polar promoter, to form a molybdenum complex wherein from 0.01 to 2 atoms of molybdenum are present per basic nitrogen atom, and the promoter is present in the ratio of 0.01 to 50 moles of polar promoter per mole of molybdenum; and (ii) reacting the molybdenum complex with a sulfur-containing compound in an amount sufficient to provide 1.5 to 4.0 atoms of sulfur per atom of molybdenum, to thereby form a sulfur- and molybdenum-containing composition;

(2) from 0.05 to 20 % by weight of a carboxylic acid amide; and

(3) from 0.05 to 15 % by weight of a succinimide.

20. The method of Claim 19 wherein the sulfur source for component (1) is sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is hydrocarbyl, and x is at least 2, inorganic sulfides or inorganic polysulfides, thioacetamide, thiourea, mercaptans of the formula RSH where R is hydrocarbyl, or a sulfur-containing antioxidant.

21. The method of Claim 20 wherein the sulfur source for component (1) is sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R is C_{1-4} hydrocarbyl, and x is at least 3, inorganic sulfides, or inorganic polysulfides, thioacetamide, thiourea or RSH where R is C_{1-40} alkyl, and the acidic molybdenum compound is molybdic acid, ammonium molybdate, or alkali metal molybdate.

22. The method of Claim 21 wherein said sulfur source is sulfur, hydrogen sulfide, RSH where R is C_{1-10} alkyl, phosphorus pentasulfide, or $(NH_4)_2S_{x'}$, where x' is at least 1, said acidic molybdenum compound is molybdic acid, or ammonium molybdate, and said basic nitrogen compound is a succinimide, carboxylic acid amide, or Mannich base.

23. The method of Claim 22 wherein said basic nitrogen compound is a C_{24-350} hydrocarbyl succinimide, carboxylic acid amide, or a Mannich base prepared from a C_{9-200} alkylphenol, formaldehyde, and an amine.

24. The method of Claim 23 wherein said basic nitrogen compound is a polyisobutenyl succinimide prepared from polyisobutenyl succinic anhydride and tetraethylene pentamine or triethylene tetramine.

25. The method of Claim 23 wherein said basic nitrogen compound is a carboxylic acid amide prepared from one or more carboxylic acids of the formula R^2COOH , or a derivative thereof which upon reaction with an amine yields a carboxylic acid amide, wherein R^2 is C_{12-350} alkyl or C_{12-350} alkenyl and a hydrocarbyl polyamine.

26. The method of Claim 25 wherein R^2 is C_{12-20} alkyl or C_{12-20} alkenyl and the hydrocarbyl polyamine is tetraethylene

pentamine or triethylene tetramine.

27. The method of Claim 23 wherein said basic nitrogen compound is a Mannich base prepared from dodecylphenol, formaldehyde, and methylamine.

28. The method of Claim 23 wherein said basic nitrogen compound is a Mannich base prepared from C₈₀₋₁₀₀ alkylphenol, formaldehyde and triethylene tetramine, tetraethylene pentamine, or mixtures thereof.

29. The method of Claim 19 wherein the polar promoter is water.

30. The method of Claim 19 wherein the carboxylic acid amide of component (2) is derived from a carboxylic acid of the formula R²COOH, wherein R² is C₁₂₋₂₀ alkyl, and an ethylene amine.

31. The method of Claim 19 wherein the succinimide of component (3) is derived from polyisobutenyl succinic anhydride, wherein the polyisobutenyl group contains from 50 to 250 carbon atoms, and an ethylene amine.

32. The method of Claim 19 wherein the lubricant composition contains 0.05 to 15% by weight of the molybdenum-containing composition of component (1), 0.05 to 20% by weight of the carboxylic acid amide of component (2), and 0.05 to 15% by weight of the succinimide of component (3).

33. The method of Claim 19 wherein the molybdenum complex is reacted with the sulfur-containing compound in an amount sufficient to provide 2.0 to 4.0 atoms of sulfur per atom of molybdenum.

34. The method of Claim 33 wherein the molybdenum complex is reacted with the sulfur-containing compound in an amount sufficient to provide 2.5 to 4.0 atoms of sulfur per atom of molybdenum.

35. The method of Claim 19 wherein the additive formulation further contains a flocculant inhibitor.

36. The method of Claim 35 wherein the additive formulation further contains a lubricity agent.

Patentansprüche

1. Treibstoffzusammensetzung für Zweitaktmotoren, umfassend eine größere Menge eines im Benzinbereich siedenden Treibstoffs und eine geringere Menge einer Schmiermittelzusammensetzung, umfassend:

- (A) eine größere Menge eines Basisöls mit Schmierviskosität, und
- (B) eine kleinere Menge einer Additiv-Formulierung, umfassend:

- (1) 0,05 bis 15 Gew.% einer sulfurierten molybdänhaltigen Zusammensetzung, hergestellt durch (i) Umsetzen einer sauren Molybdänverbindung und einer basischen Stickstoffverbindung, ausgewählt aus der Gruppe Succinimid, Carbonsäureamid, Kohlenwasserstoffmonoamin, Kohlenwasserstoffpolyamin, Mannich-Base, Phosphoramid, Thiophosphoramid, Phosphonamid oder einem Gemisch davon, in Gegenwart eines polaren Aktivators, so dass ein Molybdänkomplex entsteht, wobei 0,01 bis 2 Molybdänatome pro basischem Stickstoffatom zugegen sind, und der Aktivator im Verhältnis von 0,01 bis 50 Mol polarer Aktivator pro Mol Molybdän zugegen ist; und (ii) Umsetzen des Molybdänkomplexes mit einer schwefelhaltigen Verbindung in einer Menge, die ausreicht, dass etwa 1,5 bis 4,0 Schwefelatome pro Molybdänatom bereitgestellt werden, wodurch eine schwefel- und molybdänhaltige Zusammensetzung entsteht,
- (2) 0,05 bis 20 Gew.% eines Carbonsäureamides, und
- (3) 0,05 bis 15 Gew.% eines Succinimides.

2. Treibstoffzusammensetzung nach Anspruch 1, wobei die Schwefelquelle für Komponente (1) ist: Schwefel, Schwefelwasserstoff, Phosphorpentasulfid, R₂S_x, wobei R Kohlenwasserstoff ist, und x mindestens 2 ist, anorganische Sulfide oder anorganische Polysulfide, Thioacetamid, Thioharnstoff, Mercaptane der Formel RSH, wobei R Kohlenwasserstoff ist, oder ein schwefelhaltiges Antioxidans.

3. Treibstoffzusammensetzung nach Anspruch 2, wobei die Schwefelquelle für Komponente (1) ist: Schwefel, Schwefelwasserstoff, Phosphorpentasulfid, R₂S_x, wobei R C₁₋₄-Kohlenwasserstoff ist, und x mindestens 3 ist, anorgani-

sche Sulfide oder anorganische Polysulfide, Thioacetamid, Thioharnstoff, oder RSH, wobei R C₁₋₄₀-Alkyl ist, und die saure Molybdänverbindung Molybdänsäure, Ammoniummolybdat oder Alkalimetallmolybdat ist.

4. Treibstoffzusammensetzung nach Anspruch 3, wobei die Schwefelquelle Schwefel, Schwefelwasserstoff, RSH, wobei R C₁₋₁₀-Alkyl ist, Phosphorpentasulfid oder (NH₄)₂S_x, ist, wobei x' mindestens 1 ist, die saure Molybdänverbindung Molybdänsäure oder Ammoniummolybdat ist, und die Stickstoffverbindung ein Succinimid, Carbonsäureamid oder eine Mannich-Base ist.
5. Treibstoffzusammensetzung nach Anspruch 4, wobei die basische Stickstoffverbindung ein C₂₄₋₃₅₀-Kohlenwasserstoff-Succinimid, ein Carbonsäureamid oder eine Mannich-Base ist, die aus einem C₉₋₂₀₀-Alkylphenol, Formaldehyd und einem Amin hergestellt ist.
6. Treibstoffzusammensetzung nach Anspruch 5, wobei die basische Stickstoff-Verbindung ein Polyisobutenyl-Succinimid ist, das hergestellt ist aus Polyisobutenyl-Bernsteinsäureanhydrid und Tetraethylenpentamin oder Triethylentetramin.
7. Treibstoffzusammensetzung nach Anspruch 5, wobei die basische Stickstoff-Verbindung ist: ein Carbonsäureamid, hergestellt aus einer oder mehr Carbonsäuren der Formel R²COOH, oder einem Derivat davon, das beim Umsetzen mit einem Amin ein Carbonsäureamid ergibt, wobei R² C₁₂₋₃₅₀-Alkyl oder C₁₂₋₃₅₀-Alkenyl ist, und ein Kohlenwasserstoff-Polyamin.
8. Treibstoffzusammensetzung nach Anspruch 7, wobei R² C₁₂₋₂₀-Alkyl oder C₁₂₋₂₀-Alkenyl ist, und das Kohlenwasserstoff-Polyamin Tetraethylenpentamin oder Triethylentetramin ist.
9. Treibstoffzusammensetzung nach Anspruch 5, wobei die basische Stickstoff-Verbindung eine Mannich-Base ist, hergestellt aus Dodecylphenol, Formaldehyd und Methylamin.
10. Treibstoffzusammensetzung nach Anspruch 5, wobei die basische Stickstoff-Verbindung eine Mannich-Base ist, hergestellt aus C₈₀₋₁₀₀-Alkylphenol, Formaldehyd und Triethylentetramin, Tetraethylenpentamin oder Gemischen davon.
11. Treibstoffzusammensetzung nach Anspruch 1, wobei der polare Aktivator Wasser ist.
12. Treibstoffzusammensetzung nach Anspruch 1, wobei das Carbonsäureamid der Komponente (2) hergeleitet ist von einer Carbonsäure der Formel R²COOH, wobei R² C₁₂₋₂₀-Alkyl ist, und einem Ethylenamin.
13. Treibstoffzusammensetzung nach Anspruch 1, wobei das Succinimid der Komponente (3) hergeleitet ist von Polyisobutenyl-Bernsteinsäureanhydrid, wobei der Polyisobutenylrest 50 bis 250 Kohlenstoffatome enthält, und einem Ethylenamin.
14. Treibstoffzusammensetzung nach Anspruch 1, wobei die Schmiermittelzusammensetzung 0,05 bis 15 Gew.% der molybdänhaltigen Zusammensetzung der Komponente (1), 0,05 bis 20 Gew.% des Carbonsäureamids der Komponente (2) und 0,05 bis 15 Gew.% des Succinimides der Komponente (3) enthält.
15. Treibstoffzusammensetzung nach Anspruch 1, wobei der Molybdänkomplex mit der schwefelhaltigen Verbindung in einer Menge umgesetzt wird, die ausreicht, dass 2,0 bis 4,0 Schwefelatome pro Molybdänatom bereitgestellt werden.
16. Treibstoffzusammensetzung nach Anspruch 15, wobei der Molybdänkomplex mit der schwefelhaltigen Verbindung in einer Menge umgesetzt wird, die ausreicht, dass 2,5 bis 4,0 Schwefelatome pro Molybdänatom bereitgestellt werden.
17. Treibstoffzusammensetzung nach Anspruch 1, wobei die Additiv-Formulierung zudem einen Flockungsmittel-Inhibitor enthält.
18. Treibstoffzusammensetzung nach Anspruch 17, wobei die Additiv-Formulierung zudem ein Schmiermittel enthält.
19. Verfahren zur Verringerung von Motorablagerungen und Kolbenringblockierung in einem Zweitaktmotor, umfas-

send den Betrieb des Zweitaktmotors mit einer Treibstoffzusammensetzung, die eine größere Menge eines im Benzinbereich siedenden Treibstoffs und eine geringere Menge einer Schmiermittelzusammensetzung umfasst, umfassend:

- (A) eine größere Menge eines Basisöls mit Schmierviskosität, und
(B) eine kleinere Menge einer Additiv-Formulierung, die die Verringerung von Motorablagerungen und Kolbenringblockierung bewirkt, umfassend:

(1) 0,05 bis 15 Gew.% einer sulfurierten molybdänhaltigen Zusammensetzung, hergestellt durch (i) Umsetzen einer sauren Molybdänverbindung und einer basischen Stickstoffverbindung, ausgewählt aus der Gruppe mit einem Succinimid, einem Carbonsäureamid, einem Kohlenwasserstoffmonoamin, einem Kohlenwasserstoffpolyamin, einer Mannich-Base, einem Phosphoramid, einem Thiophosphoramid, einem Phosphonamid, oder einem Gemisch davon, in Gegenwart eines polaren Aktivators, so dass ein Molybdänkomplex entsteht, wobei 0,01 bis 2 Molybdänatome pro basischem Stickstoffatom zugegen sind, und der Aktivator im Verhältnis von 0,01 bis 50 Mol polarer Aktivator pro Mol Molybdän zugegen ist; und (ii) Umsetzen des Molybdänkomplexes mit einer schwefelhaltigen Verbindung in einer Menge, die ausreicht, dass 1,5 bis 4,0 Schwefelatome pro Molybdänatom bereitgestellt werden, wodurch eine schwefel- und molybdänhaltige Zusammensetzung entsteht,

(2) 0,05 bis 20 Gew.% eines Carbonsäureamides, und

(3) 0,05 bis 15 Gew.% eines Succinimides.

20. Verfahren nach Anspruch 19, wobei die Schwefelquelle für Komponente (1) ist: Schwefel, Schwefelwasserstoff, Phosphorpentasulfid, R_2S_x , wobei R Kohlenwasserstoff ist, und x mindestens 2 ist, anorganische Sulfide oder anorganische Polysulfide, Thioacetamid, Thioharnstoff, Mercaptane der Formel RSH, wobei R Kohlenwasserstoff ist, oder ein schwefelhaltiges Antioxidans.

21. Verfahren nach Anspruch 20, wobei die Schwefelquelle für Komponente (1) ist: Schwefel, Schwefelwasserstoff, Phosphorpentasulfid, R_2S_x , wobei R C_{1-4} -Kohlenwasserstoff ist, und x mindestens 3 ist, anorganische Sulfide oder anorganische Polysulfide, Thioacetamid, Thioharnstoff, oder RSH, wobei R C_{1-40} -Alkyl ist, und die saure Molybdänverbindung Molybdänsäure, Ammoniummolybdat oder Alkalimetallmolybdat ist.

22. Verfahren nach Anspruch 21, wobei die Schwefelquelle Schwefel, Schwefelwasserstoff, RSH, wobei R C_{1-10} -Alkyl ist, Phosphorpentasulfid oder $(NH_4)_2S_x$ ist, wobei x' mindestens 1 ist, die saure Molybdänverbindung Molybdänsäure oder Ammoniummolybdat ist, und die basische Stickstoffverbindung ein Succinimid, Carbonsäureamid oder eine Mannich-Base ist.

23. Verfahren nach Anspruch 22, wobei die basische Stickstoffverbindung ein C_{24-350} -Kohlenwasserstoff-Succinimid, ein Carbonsäureamid oder eine Mannich-Base ist, die aus einem C_{9-200} -Alkylphenol, Formaldehyd und einem Amin hergestellt ist.

24. Verfahren nach Anspruch 23, wobei die basische Stickstoff-Verbindung ein Polyisobutenyl-Succinimid ist, das hergestellt ist aus Polyisobutenyl-Bernsteinsäureanhydrid und Tetraethylenpentamin oder Triethylentetramin.

25. Verfahren nach Anspruch 23, wobei die basische Stickstoff-Verbindung ist: ein Carbonsäureamid, hergestellt aus einer oder mehr Carbonsäuren der Formel R^2COOH , oder einem Derivat davon, das beim Umsetzen mit einem Amin ein Carbonsäureamid ergibt, wobei R^2 C_{12-350} -Alkyl oder C_{12-350} -Alkenyl ist, und ein Kohlenwasserstoff-Polyamin.

26. Verfahren nach Anspruch 25, wobei R^2 C_{12-20} -Alkyl oder C_{12-20} -Alkenyl ist, und das Kohlenwasserstoff-Polyamin Tetraethylenpentamin oder Triethylentetramin ist.

27. Verfahren nach Anspruch 23, wobei die basische Stickstoff-Verbindung eine Mannich-Base ist, hergestellt aus Dodecylphenol, Formaldehyd und Methylamin.

28. Verfahren nach Anspruch 23, wobei die basische Stickstoff-Verbindung eine Mannich-Base ist, hergestellt aus C_{80-100} -Alkylphenol, Formaldehyd und Triethylentetramin, Tetraethylenpentamin oder Gemischen davon.

29. Verfahren nach Anspruch 19, wobei der polare Aktivator Wasser ist.

30. Verfahren nach Anspruch 19, wobei das Carbonsäureamid der Komponente (2) hergeleitet ist von einer Carbonsäure der Formel R^2COOH , wobei R^2 C_{12-20} -Alkyl ist, und einem Ethylenamin.
31. Verfahren nach Anspruch 19, wobei das Succinimid der Komponente (3) hergeleitet ist von Polyisobutenyl-Bernsteinsäureanhydrid, wobei der Polyisobutenylrest 50 bis 250 Kohlenstoffatome enthält, und einem Ethylenamin.
32. Verfahren nach Anspruch 19, wobei die Schmiermittelzusammensetzung 0,05 bis 15 Gew.% der molybdänhaltigen Zusammensetzung der Komponente (1), 0,05 bis 20 Gew.% des Carbonsäureamids der Komponente (2) und 0,05 bis 15 Gew.% des Succinimides der Komponente (3) enthält.
33. Verfahren nach Anspruch 19, wobei der Molybdänkomplex mit der schwefelhaltigen Verbindung in einer Menge umgesetzt wird, die ausreicht, dass 2,0 bis 4,0 Schwefelatome pro Molybdänatom bereitgestellt werden.
34. Verfahren nach Anspruch 33, wobei der Molybdänkomplex mit der schwefelhaltigen Verbindung in einer Menge umgesetzt wird, die ausreicht, dass 2,5 bis 4,0 Schwefelatome pro Molybdänatom bereitgestellt werden.
35. Verfahren nach Anspruch 19, wobei die Additiv-Formulierung zudem einen Flockungsmittel-Inhibitor enthält.
36. Verfahren nach Anspruch 35, wobei die Additiv-Formulierung zudem ein Schmiermittel enthält.

Revendications

1. Composition de carburant pour moteurs deux temps, comprenant une quantité dominante d'un carburant bouillant dans la plage de l'essence et une petite quantité d'une composition de lubrifiant comprenant :
 - (A) une quantité dominante d'une huile de base de viscosité propre à la lubrification, et
 - (B) une petite quantité d'une formulation d'additif comprenant :
 - (1) 0,05 à 15 % en poids d'une composition sulfurée contenant du molybdène préparée (i) en faisant réagir un composé de molybdène acide et un composé azoté basique choisi dans le groupe consistant en succinimide, un amide d'acide carboxylique, une hydrocarbylemono-amine, une hydrocarbylepolyamine, une base de Mannich, un phosphoramidate, un thiophosphoramidate, un phosphonamide et un de leurs mélanges, en présence d'un promoteur polaire, pour former un complexe de molybdène dans lequel 0,01 à 2 atomes de molybdène sont présents par atome d'azote basique, et le promoteur est présent en un rapport de 0,01 à 50 moles de promoteur polaire par mole de molybdène ; et (ii) en faisant réagir un complexe de molybdène avec un composé soufré en une quantité suffisante pour fournir environ 1,5 à 4,0 atomes de soufre par atome de molybdène, pour former ainsi une composition contenant du soufre et du molybdène,
 - (2) 0,05 à 20 % en poids d'un amide d'acide carboxylique, et
 - (3) 0,05 à 15 % en poids d'un succinimide.
2. Composition de carburant suivant la revendication 1, dans laquelle la source de soufre pour le constituant (1) est le soufre, l'hydrogène sulfuré, le pentasulfure de phosphore, un composé de formule R_2S_x dans laquelle R représente un groupe hydrocarbyle et x est au moins égal à 2, des sulfures inorganiques ou polysulfures inorganiques, le thio-acétamide, la thiourée, des mercaptans de formule RSH dans laquelle R représente un groupe hydrocarbyle, ou un anti-oxydant contenant du soufre.
3. Composition de carburant suivant la revendication 2, dans laquelle la source de soufre pour le constituant (1) est le soufre, l'hydrogène sulfuré, le pentasulfure de phosphore, un composé de formule R_2S_x dans laquelle R représente un groupe hydrocarbyle en C_1 à C_4 et x est au moins égal à 3, des sulfures inorganiques ou polysulfures inorganiques, le thio-acétamide, la thiourée ou un composé de formule RSH dans laquelle R représente un groupe alkyle en C_1 à C_{40} , et le composé de molybdène acide est l'acide molybdique, le molybdate d'ammonium ou un molybdate de métal alcalin.
4. Composition de carburant suivant la revendication 3, dans laquelle la source de soufre est le soufre, l'hydrogène sulfuré, un composé de formule RSH dans laquelle R représente un groupe alkyle en C_1 à C_{10} , le pentasulfure de phosphore ou un composé de formule $(NH_4)_2S_x$, dans laquelle x est au moins égal à 1, le composé de molybdène acide est l'acide molybdique ou le molybdate d'ammonium, et le composé azoté basique est un succinimide,

un amide d'acide carboxylique ou une base de Mannich.

- 5 5. Composition de carburant suivant la revendication 4, dans laquelle le composé azoté basique est un hydrocarbyle-succinimide en C₂₄ à C₃₅₀, un amide d'acide carboxylique ou une base de Mannich préparée à partir d'un alkylphénol en C₉ à C₂₀₀, de formaldéhyde et d'une amine.
- 10 6. Composition de carburant suivant la revendication 5, dans laquelle le composé azoté basique est un polyisobuténysuccinimide préparé à partir d'un anhydride polyisobuténysuccinique et de tétraéthylène-pentamine ou de triéthylène-tétramine.
- 15 7. Composition de carburant suivant la revendication 5, dans laquelle le composé azoté basique est un amide d'acide carboxylique préparé à partir d'un ou plusieurs acides carboxyliques de formule R²COOH ou d'un de leurs dérivés qui, par réaction avec une amine, donne un amide d'acide carboxylique, R² représente un groupe alkyle en C₁₂ à C₃₅₀ ou un groupe alcényle en C₁₂ à C₃₅₀, et d'une hydrocarbylepolyamine.
- 20 8. Composition de carburant suivant la revendication 7, dans laquelle R² représente un groupe alkyle en C₁₂ à C₂₀ ou un groupe alcényle en C₁₂ à C₂₀ et l'hydrocarbylepolyamine est la tétraéthylène-pentamine ou la triéthylène-tétramine.
- 25 9. Composition de carburant suivant la revendication 5, dans laquelle le composé azoté basique est une base de Mannich préparée à partir de dodécylphénol, de formaldéhyde et de méthylamine.
- 30 10. Composition de carburant suivant la revendication 5, dans laquelle le composé azoté basique est une base de Mannich préparée à partir d'un alkylphénol en C₈₀ à C₁₀₀, de formaldéhyde et de triéthylène-tétramine, de tétraéthylène-pentamine ou de leurs mélanges.
- 35 11. Composition de carburant suivant la revendication 1, dans laquelle le promoteur polaire est l'eau.
- 40 12. Composition de carburant suivant la revendication 1, dans laquelle l'amide d'acide carboxylique du constituant (2) est dérivé d'un acide carboxylique de formule R²COOH, dans laquelle R² représente un groupe alkyle en C₁₂ à C₂₀ et d'une éthylène-amine.
- 45 13. Composition de carburant suivant la revendication 1, dans laquelle le succinimide du constituant (3) est dérivé d'un anhydride polyisobuténysuccinique, dans lequel le groupe polyisobutényle contient 50 à 250 atomes de carbone, et d'une éthylène-amine.
- 50 14. Composition de carburant suivant la revendication 1, dans laquelle la composition de lubrifiant contient 0,05 à 15 % en poids de la composition contenant du molybdène du constituant (1), 0,05 à 20 % en poids de l'amide d'acide carboxylique du constituant (2), et 0,05 à 15 % en poids du succinimide du constituant (3).
- 55 15. Composition de carburant suivant la revendication 1, dans laquelle le composé de molybdène est amené à réagir avec le composé soufré en une quantité suffisante pour fournir 2,0 à 4,0 atomes de soufre par atome de molybdène.
16. Composition de carburant suivant la revendication 15, dans laquelle le complexe de molybdène est amené à réagir avec le composé soufré en une quantité suffisante pour fournir 2,5 à 4,0 atomes de soufre par atome de molybdène.
17. Composition de carburant suivant la revendication 1, dans laquelle la formulation d'additif contient en outre un inhibiteur de floculation.
18. Composition de carburant suivant la revendication 17, dans laquelle la formulation d'additif contient en outre un agent d'onctuosité.
19. Procédé pour réduire les dépôts dans les moteurs et le gommage des segments de pistons dans un moteur deux temps, qui comprend le fonctionnement du moteur deux temps avec une composition de carburant comprenant une quantité dominante d'un carburant bouillant dans la plage de l'essence et une petite quantité d'une composition de lubrifiant contenant :

(A) une quantité dominante d'une huile de base de viscosité propre à la lubrification, et

(B) une petite quantité efficace pour réduire les dépôts dans les moteurs et le gommage des segments de pistons d'une formulation d'additif comprenant :

(1) 0,05 à 15 % en poids d'une composition sulfurée contenant du molybdène préparée (i) en faisant réagir un composé de molybdène acide et un composé azoté basique choisi dans le groupe consistant en un succinimide, un amide d'acide carboxylique, une hydrocarbylemono-amine, une hydrocarbylepolyamine, une base de Mannich, un phosphoramidate, un thiophosphoramidate, un phosphonamide ou un de leurs mélanges, en présence d'un promoteur polaire, pour former un complexe de molybdène dans lequel 0,01 à 2 atomes de molybdène sont présents par atome d'azote basique, et le promoteur est présent en un rapport de 0,01 à 50 moles de promoteur polaire par mole de molybdène ; et (ii) en faisant réagir le complexe de molybdène avec un composé soufré en une quantité suffisante pour fournir environ 1,5 à 4,0 atomes de soufre par atome de molybdène, pour former ainsi une composition contenant du soufre et du molybdène,

(2) 0,05 à 20 % en poids d'un amide d'acide carboxylique, et

(3) 0,05 à 15 % en poids d'un succinimide.

20. Procédé suivant la revendication 19, dans lequel la source de soufre pour le constituant (1) est le soufre, l'hydrogène sulfuré, le pentasulfure de phosphore, un composé de formule R_2S_x dans laquelle R représente un groupe hydrocarbyle et x est au moins égal à 2, des sulfures inorganiques ou polysulfures inorganiques, le thio-acétamide, la thiourée, des mercaptans de formule RSH dans laquelle R représente un groupe hydrocarbyle, ou un anti-oxydant contenant du soufre.

21. Procédé suivant la revendication 20, dans lequel la source de soufre pour le constituant (1) est le soufre, l'hydrogène sulfuré, le pentasulfure de phosphore, un composé de formule R_2S_x dans laquelle R représente un groupe hydrocarbyle en C_1 à C_4 et x est au moins égal à 3, des sulfures inorganiques ou polysulfures inorganiques, le thioacétamide, la thiourée ou un composé de formule RSH dans laquelle R représente un groupe alkyle en C_1 à C_{40} , et le composé de molybdène acide est l'acide molybdique, le molybdate d'ammonium ou un molybdate de métal alcalin.

22. Procédé suivant la revendication 21, dans lequel la source de soufre est le soufre, l'hydrogène sulfuré, un composé de formule RSH dans laquelle R représente un groupe alkyle en C_1 à C_{10} , le pentasulfure de phosphore ou un composé de formule $(NH_4)_2S_{x'}$, dans laquelle x' est au moins égal à 1, le composé de molybdène acide est l'acide molybdique ou le molybdate d'ammonium, et le composé azoté basique est un succinimide, un amide d'acide carboxylique ou une base de Mannich.

23. Procédé suivant la revendication 22, dans lequel le composé azoté basique est un hydrocarbylesuccinimide en C_{24} à C_{350} , Un amide d'acide carboxylique ou une base de Mannich préparée à partir d'un alkylphénol en C_9 à C_{200} , de formaldéhyde et d'une amine.

24. Procédé suivant la revendication 23, dans lequel le composé azoté basique est un polyisobuténylesuccinimide préparé à partir d'un anhydride polyisobuténylesuccinique et de tétraéthylène-pentamine ou de triéthylène-tétramine.

25. Procédé suivant la revendication 23, dans lequel le composé azoté basique est un amide d'acide carboxylique préparé à partir d'un ou plusieurs acides carboxyliques de formule R^2COOH , ou d'un de leurs dérivés qui, par réaction avec une amine, donne un amide d'acide carboxylique, R^2 représentant un groupe alkyle en C_{12} à C_{350} ou un groupe alcényle en C_{12} à C_{350} , et d'une hydrocarbylepolyamine.

26. Procédé suivant la revendication 25, dans lequel R^2 représente un groupe alkyle en C_{12} à C_{20} ou un groupe alcényle en C_{12} à C_{20} et l'hydrocarbylepolyamine est la tétraéthylène-pentamine ou la triéthylène-tétramine.

27. Procédé suivant la revendication 23, dans lequel le composé azoté basique est une base de Mannich préparée à partir de dodécylphénol, de formaldéhyde et de méthylamine.

28. Procédé suivant la revendication 23, dans lequel le composé azoté basique est une base de Mannich préparée à partir d'un alkylphénol en C_{80} à C_{100} , de formaldéhyde et de triéthylène-tétramine, de tétraéthylène-pentamine ou de leurs mélanges.

29. Procédé suivant la revendication 19, dans lequel le promoteur polaire est l'eau.

30. Procédé suivant la revendication 19, dans lequel l'amide d'acide carboxylique du constituant (2) est dérivé d'un acide carboxylique de formule R^2COOH , dans laquelle R^2 représente un groupe alkyle en C_{12} à C_{20} , et d'une éthylène-amine.

31. Procédé suivant la revendication 19, dans lequel le succinimide du constituant (3) est dérivé d'un anhydride polyisobuténysuccinique, dans lequel le groupe polyisobutényle contient 50 à 250 atomes de carbone, et d'une éthylène-amine.

32. Procédé suivant la revendication 19, dans lequel la composition de lubrifiant contient 0,05 à 15 % en poids de la composition contenant du molybdène du constituant (1), 0,05 à 20 % en poids de l'amide d'acide carboxylique du constituant (2), et 0,05 à 15 % en poids du succinimide du constituant (3).

33. Procédé suivant la revendication 19, dans lequel le complexe de molybdène est amené à réagir avec le composé soufré en une quantité suffisante pour fournir 2,0 à 4,0 atomes de soufre par atome de molybdène.

34. Procédé suivant la revendication 33, dans lequel le complexe de molybdène est amené à réagir avec le composé soufré en une quantité suffisante pour fournir 2,5 à 4,0 atomes de soufre par atome de molybdène.

35. Procédé suivant la revendication 19, dans lequel la formulation d'additif contient en outre un inhibiteur de floculation.

36. Procédé suivant la revendication 35, dans lequel la formulation d'additif contient en outre un agent d'onctuosité.