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FUEL COMPOSITION FOR TWO-CYCLE ENGINES

BACKGROUND OF THE INVENTION

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 mowers and other power-operated garden equipment, power chain saws, pumps, electrical generators, marine outboard 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 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

01 exhausted cylinder. Thus, ring sticking can lead to
02 deterioration in engine performance, and unnecessary
03 consumption of fuel and/or lubricant. Spark plug fouling
04 and engine port plugging problems also occur in two-cycle
05 engines.

06

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

24

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

33

34



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

09

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

18

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

25

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

33

34



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

07

08 For example, U.S. Patent No. 4,263,152 to King et al.
09 discloses an antioxidant additive for lubricating oils which
10 is prepared by combining an acidic molybdenum compound, a
11 polar promoter, a basic nitrogen-containing compound and a
12 sulfur source to form a molybdenum and sulfur-containing
13 complex. Similar molybdenum-containing antioxidant
14 additives are disclosed in U.S. Patent Nos. 4,285,822;
15 4,283,295; 4,272,387; 4,265,773; 4,261,843; 4,259,195; and
16 4,259,194. However, none of these patents teaches or
17 appreciates the use of such antioxidant additives, or
18 lubricating oils containing such additives, in admixture
19 with fuels in two-cycle engines. Furthermore, none of these
20 patents teaches or appreciates that such antioxidant
21 additives would be effective deposit control agents or would
22 reduce piston sticking when utilized in fuel-lubricating oil
23 mixtures in two-cycle engines.

24

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

30

31 Accordingly, the present invention is directed to minimizing
32 the problems of varnish build-up and ring sticking in
33 two-cycle engines through the provision of effective
34 additives for fuel-lubricating oil combinations which



01 eliminate or reduce two-cycle engine varnish deposits and
02 piston ring seal failure.

03

04 SUMMARY OF THE INVENTION

05

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

10

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

13

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

15

16 (1) a sulfurized molybdenum-containing composition
17 prepared by (i) reacting an acidic molybdenum
18 compound and a basic nitrogen compound selected
19 from the group consisting of a succinimide, a
20 carboxylic acid amide, a hydrocarbyl monoamine, a
21 hydrocarbyl polyamine, a Mannich base, a
22 phosphoramidate, a thiophosphoramidate, a
23 phosphonamidate, a dispersant viscosity index
24 improver, or a mixture thereof, in the presence of
25 a polar promoter, to form a molybdenum complex
26 wherein from 0.01 to 2 atoms of molybdenum are
27 present per basic nitrogen atom, and the promoter
28 is present in the ratio of 0.01 to 50 moles of
29 polar promoter per mole of molybdenum; and
30 (ii) reacting the molybdenum complex with a
31 sulfur-containing compound in an amount sufficient
32 to provide about 1.5 to 4.0 atoms of sulfur per
33 atom of molybdenum, to thereby form a sulfur- and
34 molybdenum-containing composition,



01 (2) a carboxylic acid amide, and

02

03 (3) a succinimide.

04

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

12

13 DETAILED DESCRIPTION OF THE INVENTION

14

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

22

23 The sulfurized molybdenum-containing composition employed in
24 the present invention may be generally characterized as a
25 molybdenum/sulfur complex of a basic nitrogen compound.
26 Such molybdenum/sulfur complexes are known in the art and
27 are described, for example, in U.S. Patent No. 4,263,152 to
28 King et al., the disclosure of which is hereby incorporated
29 by reference.

30

31 The precise molecular formula of the molybdenum compositions
32 employed in this invention is not known with certainty;
33 however, they are believed to be compounds in which
34 molybdenum, whose valences are satisfied with atoms of



01 oxygen or sulfur, is either complexed by, or the salt of,
02 one or more nitrogen atoms of the basic nitrogen containing
03 compound used in the preparation of these compositions.

04
05 The molybdenum compounds used to prepare the
06 molybdenum/sulfur complexes employed in this invention are
07 acidic molybdenum compounds. By acidic is meant that the
08 molybdenum compounds will react with a basic nitrogen
09 compound as measured by ASTM test D-664 or D-2896 titration
10 procedure. Typically these molybdenum compounds are
11 hexavalent and are represented by the following
12 compositions: molybdic acid, ammonium molybdate, sodium
13 molybdate, potassium molybdate and other alkaline metal
14 molybdates and other molybdenum salts such as hydrogen
15 salts, e.g., hydrogen sodium molybdate, MoOCl_4 , MoO_2Br_2 ,
16 $\text{Mo}_2\text{O}_3\text{Cl}_6$, molybdenum trioxide or similar acidic molybdenum
17 compounds. Preferred acidic molybdenum compounds are
18 molybdic acid, ammonium molybdate, and alkali metal
19 molybdates. Particularly preferred are molybdic acid and
20 ammonium molybdate.

21
22 The basic nitrogen compound used to prepare the
23 molybdenum/sulfur complexes must have a basic nitrogen
24 content as measured by ASTM D-664 or D-2896. It is
25 preferably oil-soluble. Typical of such compositions are
26 succinimides, carboxylic acid amides, hydrocarbyl
27 monoamines, hydrocarbon polyamines, Mannich bases,
28 phosphoramides, thiophosphoramides, phosphoramides,
29 dispersant viscosity index improvers, and mixtures thereof.
30 These basic nitrogen-containing compounds are described
31 below (keeping in mind the reservation that each must have
32 at least one basic nitrogen). Any of the
33 nitrogen-containing compositions may be after-treated with,
34



01 e.g., boron, using procedures well known in the art so long
02 as the compositions continue to contain basic nitrogen.
03 These after-treatments are particularly applicable to
04 succinimides and Mannich base compositions.

05

06 The mono and polysuccinimides that can be used to prepare
07 the molybdenum/sulfur complexes described herein are
08 disclosed in numerous references and are well known in the
09 art. Certain fundamental types of succinimides and the
10 related materials encompassed by the term of art
11 "succinimide" are taught in U.S. Patent Nos. 3,219,666;
12 3,172,892; and 3,272,746, the disclosures of which are
13 hereby incorporated by reference. The term "succinimide" is
14 understood in the art to include many of the amide, imide,
15 and amidine species which may also be formed. The
16 predominant product however is a succinimide and this term
17 has been generally accepted as meaning the product of a
18 reaction of an alkenyl substituted succinic acid or
19 anhydride with a nitrogen-containing compound. Preferred
20 succinimides, because of their commercial availability, are
21 those succinimides prepared from a hydrocarbyl succinic
22 anhydride, wherein the hydrocarbyl group contains from about
23 24 to about 350 carbon atoms, and an ethylene amine, said
24 ethylene amines being especially characterized by ethylene
25 diamine, diethylene triamine, triethylene tetramine, and
26 tetraethylene pentamine. Particularly preferred are those
27 succinimides prepared from polyisobutenyl succinic anhydride
28 of 70 to 128 carbon atoms and tetraethylene pentamine or
29 triethylene tetramine or mixtures thereof.

30

31 Also included within the term "succinimide" are the
32 cooligomers of a hydrocarbyl succinic acid or anhydride and
33 a poly secondary amine containing at least one tertiary
34 amino nitrogen in addition to two or more secondary amino



01 groups. Ordinarily this composition has between 1,500 and
02 50,000 average molecular weight. A typical compound would
03 be that prepared by reacting polyisobutenyl succinic
04 anhydride and ethylene dipiperazine.

05
06 Carboxylic acid amide compositions are also suitable
07 starting materials for preparing the molybdenum/sulfur
08 complexes employed in this invention. Typical of such
09 compounds are those disclosed in U.S. Patent No. 3,405,064,
10 the disclosure of which is hereby incorporated by reference.
11 These compositions are ordinarily prepared by reacting a
12 carboxylic acid or anhydride or ester thereof, having at
13 least 12 to about 350 aliphatic carbon atoms in the
14 principal aliphatic chain and, if desired, having sufficient
15 pendant aliphatic groups to render the molecule oil soluble
16 with an amine or a hydrocarbyl polyamine, such as an
17 ethylene amine, to give a mono or polycarboxylic acid amide.
18 Preferred are those amides prepared from (1) a carboxylic
19 acid of the formula R^2COOH , where R^2 is C_{12-20} alkyl or a
20 mixture of this acid with a polyisobutenyl carboxylic acid
21 in which the polyisobutenyl group contains from 72 to
22 128 carbon atoms and (2) an ethylene amine, especially
23 triethylene tetramine or tetraethylene pentamine or mixtures
24 thereof.

25
26 Another class of compounds which are useful in this
27 invention are hydrocarbyl monoamines and hydrocarbyl
28 polyamines, preferably of the type disclosed in U.S. Patent
29 No. 3,574,576, the disclosure of which is hereby
30 incorporated by reference. The hydrocarbyl group, which is
31 preferably alkyl, or olefinic having one or two sites of
32 unsaturation, usually contains from 9 to 350, preferably
33 from 20 to 200 carbon atoms. Particularly preferred
34



01 hydrocarbyl polyamines are those which are derived, e.g., by
02 reacting polyisobutenyl chloride and a polyalkylene
03 polyamine, such as an ethylene amine, e.g., ethylene
04 diamine, diethylene triamine, tetraethylene pentamine,
05 2-aminoethylpiperazine, 1,3-propylene diamine,
06 1,2-propylenediamine, and the like.

07

08 Another class of compounds useful for supplying basic
09 nitrogen are the Mannich base compositions. These
10 compositions are prepared from a phenol or C₉₋₂₀₀
11 alkylphenol, an aldehyde, such as formaldehyde or
12 formaldehyde precursor such as paraformaldehyde, and an
13 amine compound. The amine may be a mono or polyamine and
14 typical compositions are prepared from an alkylamine, such
15 as methylamine or an ethylene amine, such as, diethylene
16 triamine, or tetraethylene pentamine, and the like. The
17 phenolic material may be sulfurized and preferably is
18 dodecylphenol or a C₈₀₋₁₀₀ alkylphenol. Typical Mannich
19 bases which can be used in this invention are disclosed in
20 U.S. Patent No. 4,157,309 and U.S. Patent Nos. 3,649,229;
21 3,368,972; and 3,539,663, the disclosures of which are
22 hereby incorporated by reference. The last referenced
23 patent discloses Mannich bases prepared by reacting an
24 alkylphenol having at least 50 carbon atoms, preferably 50
25 to 200 carbon atoms with formaldehyde and an alkylene
26 polyamine $\text{HN}(\text{ANH})_n\text{H}$ where A is a saturated divalent alkyl
27 hydrocarbon of 2 to 6 carbon atoms and n is 1-10 and where
28 the condensation product of said alkylene polyamine may be
29 further reacted with urea or thiourea. The utility of these
30 Mannich bases as starting materials for preparing
31 lubricating oil additives can often be significantly
32 improved by treating the Mannich base using conventional
33 techniques to introduce boron into the composition.

34



01 Another class of composition useful for preparing the
02 molybdenum/sulfur complexes employed in this invention are
03 the phosphoramides and phosphonamides such as those
04 disclosed in U.S. Patent Nos. 3,909,430 and 3,968,157, the
05 disclosures of which are hereby incorporated by reference.
06 These compositions may be prepared by forming a phosphorus
07 compound having at least one P-N bond. They can be
08 prepared, for example, by reacting phosphorus oxychloride
09 with a hydrocarbyl diol in the presence of a monoamine or by
10 reacting phosphorus oxychloride with a difunctional
11 secondary amine and a mono-functional amine.

12 Thiophosphoramides can be prepared by reacting an
13 unsaturated hydrocarbon compound containing from 2 to 450 or
14 more carbon atoms, such as polyethylene, polyisobutylene,
15 polypropylene, ethylene, 1-hexene, 1,3-hexadiene,
16 isobutylene, 4-methyl-1-pentene, and the like, with
17 phosphorus pentasulfide and a nitrogen-containing compound
18 as defined above, particularly an alkylamine, alkyldiamine,
19 alkylpolyamine, or an alkyleneamine, such as ethylene
20 diamine, diethylenetriamine, triethylenetetramine,
21 tetraethylenepentamine, and the like.

22

23 Another class of nitrogen-containing compositions useful in
24 preparing the molybdenum complexes employed in this
25 invention includes the so-called dispersant viscosity index
26 improvers (VI improvers). These VI improvers are commonly
27 prepared by functionalizing a hydrocarbon polymer,
28 especially a polymer derived from ethylene and/or propylene,
29 optionally containing additional units derived from one or
30 more co-monomers such as alicyclic or aliphatic olefins or
31 diolefins. The functionalization may be carried out by a
32 variety of processes which introduce a reactive site or
33 sites which usually has at least one oxygen atom on the
34 polymer. The polymer is then contacted with a



01 nitrogen-containing source to introduce nitrogen-containing
02 functional groups on the polymer backbone. Commonly used
03 nitrogen sources include any basic nitrogen compound
04 especially those nitrogen-containing compounds and
05 compositions described herein. Preferred nitrogen sources
06 are alkylene amines, such as ethylene amines, alkyl amines,
07 and Mannich bases.

08

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

11

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

25

26 The sulfurized fatty acid esters are prepared by reacting
27 sulfur, sulfur monochloride, and/or sulfur dichloride with
28 an unsaturated fatty ester under elevated temperatures.
29 Typical esters include C_1-C_{20} alkyl esters of C_8-C_{24}
30 unsaturated fatty acids, such as palmitoleic, oleic,
31 ricinoleic, petroselinic, vaccenic, linoleic, linolenic,
32 oleostearic, licanic, paranaric, tariric, gadoleic,
33 arachidonic, cetoleic, etc. Particularly good results have
34



01 been obtained with mixed unsaturated fatty acid esters, such
02 as are obtained from animal fats and vegetable oils, such as
03 tall oil, linseed oil, olive oil, castor oil, peanut oil,
04 rape oil, fish oil, sperm oil, and so forth.

05

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

10

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

16

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

21

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

30

31 Sulfurized alkyl phenols and the metal salts thereof include
32 compositions such as sulfurized dodecylphenol and the
33 calcium salts thereof. The alkyl group ordinarily contains
34



01 from 9-300 carbon atoms. The metal salt may be preferably,
02 a Group I or Group II salt, especially sodium, calcium,
03 magnesium, or barium.

04

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

12

13 The polar promoter used in the preparation of the molybdenum
14 complexes employed in this invention is one which
15 facilitates the interaction between the acidic molybdenum
16 compound and the basic nitrogen compound. A wide variety of
17 such promoters are well known to those skilled in the art.
18 Typical promoters are 1,3-propanediol, 1,4-butane-diol,
19 diethylene glycol, butyl cellosolve, propylene glycol,
20 1,4-butyleneglycol, methyl carbitol, ethanolamine,
21 diethanolamine, N-methyl-diethanol-amine, dimethyl
22 formamide, N-methyl acetamide, dimethyl acetamide, methanol,
23 ethylene glycol, dimethyl sulfoxide, hexamethyl
24 phosphoramide, tetrahydrofuran and water. Preferred are
25 water and ethylene glycol. Particularly preferred is water.

26

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

33

34

This Sheet Has Been Replaced



01 A method for preparing the molybdenum/sulfur complexes used
02 in this invention is to prepare a solution of the acidic
03 molybdenum precursor and a polar promoter with a basic
04 nitrogen-containing compound with or without diluent. The
05 diluent is used, if necessary, to provide a suitable
06 viscosity for easy stirring. Typical diluents are
07 lubricating oil and liquid compounds containing only carbon
08 and hydrogen. If desired, ammonium hydroxide may also be
09 added to the reaction mixture to provide a solution of
10 ammonium molybdate. This reaction is carried out at a
11 temperature from the melting point of the mixture to reflux
12 temperature. It is ordinarily carried out at atmospheric
13 pressure although higher or lower pressures may be used if
14 desired. This reaction mixture is treated with a sulfur
15 source as defined above at a suitable pressure and
16 temperature for the sulfur source to react with the acidic
17 molybdenum and basic nitrogen compounds. In some cases,
18 removal of water from the reaction mixture may be desirable
19 prior to completion of reaction with the sulfur source.
20
21 In the reaction mixture, the ratio of molybdenum compound to
22 basic nitrogen compound is not critical; however, as the
23 amount of molybdenum with respect to basic nitrogen
24 increases, the filtration of the product becomes more
25 difficult. Since the molybdenum component probably
26 oligomerizes, it is advantageous to add as much molybdenum
27 as can easily be maintained in the composition. Usually,
28 the reaction mixture will have charged to it from 0.01 to
29 2.00 atoms of molybdenum per basic nitrogen atom.
30 Preferably from 0.4 to 1.0, and most preferably from 0.4 to
31 0.7, atoms of molybdenum per atom of basic nitrogen is added
32 to the reaction mixture.
33
34



01 The sulfur source is usually charged to the reaction mixture
02 in such a ratio to provide 1.5 to 4.0 atoms of sulfur per
03 atom of molybdenum. Preferably from 2.0 to 4.0 atoms of
04 sulfur per atom of molybdenum is added, and most preferably,
05 2.5 to 4.0 atoms of sulfur per atom of molybdenum.

06

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

12

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

17

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

26

27 Similarly, the succinimide component of the presently
28 employed additive formulation may be any of the succinimide
29 compounds described herein as useful in the preparation of
30 the molybdenum/sulfur complex. Preferred succinimide
31 components include those derived from polyisobutenyl
32 succinic anhydride, wherein the polyisobutenyl group
33 contains from about 50 to 250 carbon atoms, and an ethylene
34



01 amine, such as triethylene tetramine or tetraethylene
02 pentamine.

03

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

08

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

14

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

19

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

28

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

34



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

09

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

14

15 For purposes of the present invention, the lubricant
16 composition will generally be added directly to the fuel to
17 form a mixture of lubricant and fuel which is then
18 introduced into the two-cycle engine cylinder. Generally,
19 the resulting fuel composition will contain from about 15 to
20 250 parts fuel per 1 part lubricant, and more typically
21 about 50 to 100 parts fuel per 1 part lubricant. For some
22 two-cycle engine applications, the lubricant may be directly
23 injected into the combustion chamber along with the fuel or
24 into the fuel just prior to the time the fuel enters the
25 combustion chamber.

26

27 The fuel employed in the present fuel composition is a
28 hydrocarbon distillate fuel boiling in the gasoline range.
29 In such gasoline fuels, other fuel additives may also be
30 included such as antiknock agents, e.g.,
31 methylcyclopentadienyl manganese tricarbonyl, tetramethyl or
32 tetraethyl lead, or other dispersants or detergents such as
33 various substituted amines, etc. Also included may be lead
34 scavengers such as aryl halides, e.g., dichlorobenzene or



01 alkyl halides, e.g., ethylene dibromide. Additionally,
02 antioxidants, metal deactivators, pour point depressants,
03 corrosion inhibitors and demulsifiers may be present.
04

05 The following examples are presented to illustrate specific
06 embodiments of this invention and are not to be construed in
07 any way as limiting the scope of the invention.
08

09 EXAMPLES

10
11 Example 1
12

13 To a 5000 ml flask was added 114 grams molybdenum trioxide
14 and 196 grams of water. Stirring was started and 1200 grams
15 of a solution of a 45% concentrate in oil of the
16 polyisobutenyl succinimide prepared from polyisobutenyl
17 succinic anhydride having a number average molecular weight
18 for the polyisobutenyl group of about 950 and tetraethylene
19 pentamine, and 1200 grams of hydrocarbon thinner were added.
20 The mixture was refluxed at 100°C for 3 hours. The
21 temperature was gradually increased over approximately
22 1 hour to 170°C while distilling water. The temperature was
23 maintained an additional hour after the water was removed.
24 The temperature was lowered to 100°C-120°C and the mixture
25 filtered and returned to the reaction vessel. To the
26 solution was added 51 grams of sulfur. The mixture was
27 heated to 160°C-180°C for 7 hours. The pressure was slowly
28 reduced to about 50 mm of mercury to remove the hydrocarbon
29 thinner. This produced 1244 grams of product containing
30 1.80% nitrogen, 5.63% molybdenum, and 3.57% sulfur.
31
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01

Example 2

02

03 To a 5000 ml flask was added 52 grams molybdenum trioxide
04 and 111 grams of water. Stirring was started and 1184 grams
05 of a solution of a 45% concentrate in oil of the succinimide
06 described in Example 1 and 1184 grams of hydrocarbon thinner
07 were added. The mixture was refluxed at 100°C for 3 hours.
08 The temperature was gradually increased over approximately
09 1 hour to 170°C while distilling water. The temperature was
10 maintained an additional hour after the water was removed.
11 The temperature was lowered to 100°C-120°C and the mixture
12 filtered and returned to the reaction vessel. To the
13 solution was added 47 grams of sulfur. The mixture was
14 heated to 160°C-180°C for 7 hours. The pressure was slowly
15 reduced to about 50 mm of mercury to remove the hydrocarbon
16 thinner. This produced 1220 grams of product containing
17 1.94% nitrogen, 2.78% molybdenum, and 3.64% sulfur.

18

19

Example 3

20

21 To a 5000 ml flask was added 49 grams molybdenum trioxide
22 and 105 grams of water. Stirring was started and 1133 grams
23 of a solution of a 45% concentrate in oil of the succinimide
24 described in Example 1 and 1133 grams of hydrocarbon thinner
25 were added. The mixture was refluxed at 100°C for 3 hours.
26 The temperature was gradually increased over approximately
27 1 hour to 170°C while distilling water. The temperature was
28 maintained an additional hour after the water was removed.
29 The temperature was lowered to 100°C-120°C and the mixture
30 filtered and returned to the reaction vessel. To the
31 solution was added 22 grams of sulfur. The mixture was
32 heated to 160°C-180°C for 7 hours. The pressure was slowly
33 reduced to about 50 mm of mercury to remove the hydrocarbon

34



01 thinner. This produced 1163 grams of product containing
02 1.83% nitrogen, 2.79% molybdenum, and 1.97% sulfur.

03

04 Example 4

05

06 To a 5000 ml flask was added 1200 grams of a polyamide
07 prepared from a C₁₈ carboxylic acid and tetraethylene
08 pentamine and containing 6.4% nitrogen, 1200 grams
09 hydrocarbon thinner, 42 grams molybdenum trioxide, and
10 90 grams water. The mixture was refluxed at 100°C for
11 3 hours. The temperature was gradually increased over
12 approximately 1 hour to 170°C while distilling water. The
13 temperature was maintained an additional hour after the
14 water was removed. The temperature was lowered to
15 100°C-120°C and the mixture filtered and returned to the
16 reaction vessel. To the solution was added 21 grams of
17 sulfur. The mixture was heated to 160°C-180°C for 7 hours.
18 The pressure was slowly reduced to about 50 mm of mercury to
19 remove the hydrocarbon thinner. This produced a product
20 containing 5.88% nitrogen, 2.29% molybdenum, and 1.63%
21 sulfur.

22

23 Example 5

24

25 The molybdenum/sulfur complexes of Examples 1, 2 and 4 were
26 formulated to provide lubricant compositions containing 10%
27 of the carboxylic acid amide reaction product of isostearic
28 acid and tetraethylene pentamine, 2% of a polyisobutenyl
29 succinimide prepared from polyisobutenyl succinic anhydride
30 wherein the polyisobutenyl group has a number average
31 molecular weight of about 950 and tetraethylene pentamine,
32 2% of the molybdenum/sulfur complex of Examples 1, 2 and 4,
33 respectively, 5% of a polyisobutene having a number average

34



01 molecular weight of about 950 as a lubricity agent, 0.5% of
02 a flocculant inhibitor, 1% of a diluent oil and about 79.5%
03 of a base oil. The base oil contains about 10% of a
04 150 bright stock, about 70% of a mixture of 350N and 650N
05 neutral oils, and about 20% of a petroleum distillate
06 solvent.

07

08

Example 6

09

Two-Cycle Gasoline Engine Test

10

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

15

16 The test engine used was an Outboard Marine Company Johnson
17 Model No. J70ELEIE outboard engine, which is a
18 70 horsepower, water-cooled, three-cylinder, two-cycle
19 engine.

20

21 The test procedure involved a two-hour break-in period,
22 wherein the engine was run at 3,000 rpm for 1 hour, then at
23 4,000 rpm for 1 hour, using a fuel:lubricant ratio of 50:1.

24

25 The test was then conducted for 98 hours using a 50:1 fuel
26 to lubricant ratio on a 55 minute wide-open throttle,
27 5 minute idle cycle. The total test time, including
28 break-in, was 100 hours.

29

30 At the conclusion of the test, the engine was disassembled
31 and rated. The average piston rating and average
32 second-ring sticking rating for 3 cylinders was measured.
33 In the rating system employed, the higher the numerical
34 rating, the better the cleanliness performance, with 10.0



01 being the maximum rating. Except for the piston rings, the
02 ratings are for cleanliness. The piston rings are rated for
03 the degree of sticking, with a rating of 10.0 indicating a
04 completely free piston ring.

05

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

10

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

18

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

24

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

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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.

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01 WHAT IS CLAIMED IS:

02

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

06

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

09

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

12

13 (1) a sulfurized molybdenum-containing
14 composition prepared by (i) reacting an
15 acidic molybdenum compound and a basic
16 nitrogen compound selected from the group
17 consisting of a succinimide, a carboxylic
18 acid amide, a hydrocarbyl monoamine, a
19 hydrocarbyl polyamine, a Mannich base, a
20 phosphoramidate, a thiophosphoramidate, a
21 phosphonamidate, a dispersant viscosity index
22 improver, or a mixture thereof, in the
23 presence of a polar promoter, to form a
24 molybdenum complex wherein from 0.01 to
25 2 atoms of molybdenum are present per basic
26 nitrogen atom, and the promoter is present in
27 the ratio of 0.01 to 50 moles of polar
28 promoter per mole of molybdenum; and
29 (ii) reacting the molybdenum complex with a
30 sulfur-containing compound in an amount
31 sufficient to provide about 1.5 to 4.0 atoms
32 of sulfur per atom of molybdenum, to thereby
33 form a sulfur- and molybdenum-containing
34 composition,





- 01 (2) a carboxylic acid amide, and
02
03 (3) a succinimide.
04
- 05 2. The fuel composition of Claim 1, wherein the sulfur
06 source for component (1) is sulfur, hydrogen sulfide,
07 phosphorus pentasulfide, R_2S_x where R is hydrocarbyl,
08 and x is at least 2, inorganic sulfides or inorganic
09 polysulfides, thioacetamide, thiourea, mercaptans of
10 the formula RSH where R is hydrocarbyl, or a
11 sulfur-containing antioxidant.
12
- 13 3. The fuel composition of Claim 2, wherein the sulfur
14 source for component (1) is sulfur, hydrogen sulfide,
15 phosphorus pentasulfide, R_2S_x where R is C_{1-4}
16 hydrocarbyl, and x is at least 3, inorganic sulfides,
17 or inorganic polysulfides, thioacetamide, thiourea or
18 RSH where R is C_{1-40} alkyl, and the acidic molybdenum
19 compound is molybdic acid, ammonium molybdate, or
20 alkali metal molybdate.
21
- 22 4. The fuel composition of Claim 3, wherein said sulfur
23 source is sulfur, hydrogen sulfide, RSH where R is C_{1-10}
24 alkyl, phosphorus pentasulfide, or $(NH_4)_2S_{x'}$, where x'
25 is at least 1, said acidic molybdenum compound is
26 molybdic acid, or ammonium molybdate, and said basic
27 nitrogen compound is a succinimide, carboxylic acid
28 amide, or Mannich base.
29
- 30 5. The fuel composition of Claim 4, wherein said basic
31 nitrogen compound is a C_{24-350} hydrocarbyl succinimide,
32 carboxylic acid amide, or a Mannich base prepared from
33 a C_{9-200} alkylphenol, formaldehyde, and an amine.
34





- 01 6. The fuel composition of Claim 5, wherein said basic
02 nitrogen compound is a polyisobutenyl succinimide
03 prepared from polyisobutenyl succinic anhydride and
04 tetraethylene pentamine or triethylene tetramine.
05
- 06 7. The fuel composition of Claim 5, wherein said basic
07 nitrogen compound is a carboxylic acid amide prepared
08 from one or more carboxylic acids of the formula
09 $R^2\text{COOH}$, or a derivative thereof which upon reaction
10 with an amine yields a carboxylic acid amide, wherein
11 R^2 is C_{12-350} alkyl or C_{12-350} alkenyl and a hydrocarbyl
12 polyamine.
13
- 14 8. The fuel composition of Claim 7, wherein R^2 is C_{12-20}
15 alkyl or C_{12-20} alkenyl and the hydrocarbyl polyamine is
16 tetraethylene pentamine or triethylene tetramine.
17
- 18 9. The fuel composition of Claim 5, wherein said basic
19 nitrogen compound is a Mannich base prepared from
20 dodecylphenol, formaldehyde, and methylamine.
21
- 22 10. The fuel composition of Claim 5, wherein said basic
23 nitrogen compound is a Mannich base prepared from
24 C_{80-100} alkylphenol, formaldehyde and triethylene
25 tetramine, tetraethylene pentamine, or mixtures
26 thereof.
27
- 28 11. The fuel composition of Claim 1, wherein the polar
29 promoter is water.
30
- 31 12. The fuel composition of Claim 1, wherein the carboxylic
32 acid amide of component (2) is derived from a
33
34





- 01 carboxylic acid of the formula $R^2\text{COOH}$, wherein R^2 is
02 C_{12-20} alkyl, and an ethylene amine.
03
- 04 13. The fuel composition of Claim 1, wherein the
05 succinimide of component (3) is derived from
06 polyisobutenyl succinic anhydride, wherein the
07 polyisobutenyl group contains from about 50 to
08 250 carbon atoms, and an ethylene amine.
09
- 10 14. The fuel composition of Claim 1, wherein the lubricant
11 composition contains about 0.05 to 15% by weight of the
12 molybdenum-containing composition of component (1),
13 about 0.05 to 20% by weight of the carboxylic acid
14 amide of component (2), and about 0.05 to 15% by weight
15 of the succinimide of component (3).
16
- 17 15. The fuel composition of Claim 1, wherein the molybdenum
18 complex is reacted with the sulfur-containing compound
19 in an amount sufficient to provide about 2.0 to
20 4.0 atoms of sulfur per atom of molybdenum.
21
- 22 16. The fuel composition of Claim 15, wherein the
23 molybdenum complex is reacted with the
24 sulfur-containing compound in an amount sufficient to
25 provide about 2.5 to 4.0 atoms of sulfur per atom of
26 molybdenum.
27
- 28 17. The fuel composition of Claim 1, wherein the additive
29 formulation further contains a flocculant inhibitor.
30
- 31 18. The fuel composition of Claim 17, wherein the additive
32 formulation further contains a lubricity agent.
33
34





- 01 19. A method for reducing engine deposits and piston ring
02 sticking in a two-cycle engine which comprises
03 operating the two-cycle engine with a fuel composition
04 comprising a major amount of fuel boiling in the
05 gasoline range and a minor amount of a lubricant
06 composition comprising:
07
08 (A) a major amount of a base oil of lubricating
09 viscosity, and
10
11 (B) a minor amount effective to reduce engine deposits
12 and piston ring sticking of an additive
13 formulation comprising:
14
15 (1) a sulfurized molybdenum-containing
16 composition prepared by (i) reacting an
17 acidic molybdenum compound and a basic
18 nitrogen compound selected from the group
19 consisting of a succinimide, a carboxylic
20 acid amide, a hydrocarbyl monoamine, a
21 hydrocarbyl polyamine, a Mannich base, a
22 phosphoramidate, a thiophosphoramidate, a
23 phosphonamidate, a dispersant viscosity index
24 improver, or a mixture thereof, in the
25 presence of a polar promoter, to form a
26 molybdenum complex wherein from 0.01 to
27 2 atoms of molybdenum are present per basic
28 nitrogen atom, and the promoter is present in
29 the ratio of 0.01 to 50 moles of polar
30 promoter per mole of molybdenum; and
31 (ii) reacting the molybdenum complex with a
32 sulfur-containing compound in an amount
33 sufficient to provide about 1.5 to 4.0 atoms
34 of sulfur per atom of molybdenum, to thereby





01 form a sulfur- and molybdenum-containing
02 composition;

03

04 (2) a carboxylic acid amide; and

05

06 (3) a succinimide.

07

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

15

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

24

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

32

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- 01 23. The method of Claim 22 wherein said basic nitrogen
02 compound is a C_{24-350} hydrocarbyl succinimide,
03 carboxylic acid amide, or a Mannich base prepared from
04 a C_{9-200} alkylphenol, formaldehyde, and an amine.
05
- 06 24. The method of Claim 23 wherein said basic nitrogen
07 compound is a polyisobutenyl succinimide prepared from
08 polyisobutenyl succinic anhydride and tetraethylene
09 pentamine or triethylene tetramine.
10
- 11 25. The method of Claim 23 wherein said basic nitrogen
12 compound is a carboxylic acid amide prepared from one
13 or more carboxylic acids of the formula R^2COOH , or a
14 derivative thereof which upon reaction with an amine
15 yields a carboxylic acid amide, wherein R^2 is C_{12-350}
16 alkyl or C_{12-350} alkenyl and a hydrocarbyl polyamine.
17
- 18 26. The method of Claim 25 wherein R^2 is C_{12-20} alkyl or
19 C_{12-20} alkenyl and the hydrocarbyl polyamine is
20 tetraethylene pentamine or triethylene tetramine.
21
- 22 27. The method of Claim 23 wherein said basic nitrogen
23 compound is a Mannich base prepared from dodecylphenol,
24 formaldehyde, and methylamine.
25
- 26 28. The method of Claim 23 wherein said basic nitrogen
27 compound is a Mannich base prepared from C_{80-100}
28 alkylphenol, formaldehyde and triethylene tetramine,
29 tetraethylene pentamine, or mixtures thereof.
30
- 31 29. The method of Claim 19 wherein the polar promoter is
32 water.
33
34





- 01 30. The method of Claim 19 wherein the carboxylic acid
02 amide of component (2) is derived from a carboxylic
03 acid of the formula $R^2\text{COOH}$, wherein R^2 is C_{12-20} alkyl,
04 and an ethylene amine.
05
- 06 31. The method of Claim 19 wherein the succinimide of
07 component (3) is derived from polyisobutenyl succinic
08 anhydride, wherein the polyisobutenyl group contains
09 from about 50 to 250 carbon atoms, and an ethylene
10 amine.
11
- 12 32. The method of Claim 19 wherein the lubricant
13 composition contains about 0.05 to 15% by weight of the
14 molybdenum-containing composition of component (1),
15 about 0.05 to 20% by weight of the carboxylic acid
16 amide of component (2), and about 0.05 to 15% by weight
17 of the succinimide of component (3).
18
- 19 33. The method of Claim 19 wherein the molybdenum complex
20 is reacted with the sulfur-containing compound in an
21 amount sufficient to provide about 2.0 to 4.0 atoms of
22 sulfur per atom of molybdenum.
23
- 24 34. The method of Claim 33 wherein the molybdenum complex
25 is reacted with the sulfur-containing compound in an
26 amount sufficient to provide about 2.5 to 4.0 atoms of
27 sulfur per atom of molybdenum.
28
- 29 35. The method of Claim 19 wherein the additive formulation
30 further contains a flocculant inhibitor.
31
- 32 36. The method of Claim 35 wherein the additive formulation
33 further contains a lubricity agent.
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ABSTRACT OF THE DISCLOSURE

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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 base oil of lubricating viscosity and an additive formulation comprising (1) a molybdenum/sulfur complex of a basic nitrogen compound, (2) a carboxylic acid amide, and (3) a succinimide.

PR3534

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REPLACEMENT SHEET	
✓ Description: page 1. to page 28.	
✓ (Index) : page 28. to page 32.	
✓ Drawing(s) : page 32. to page 33.	
✓ Abstract : page 33. to page 34.	
DATE OF RECEIPT 15/11/98	

FUEL COMPOSITION FOR TWO-CYCLE ENGINES

BACKGROUND OF THE INVENTION

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 mowers and other power-operated garden equipment, power chain saws, pumps, electrical generators, marine outboard 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 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

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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 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 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.

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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.

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.

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.

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.

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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.

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 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

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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) 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 phosphonamidate, a dispersant viscosity index improver, 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,

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(2) a carboxylic acid amide, and

(3) 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 disclosure of which is hereby incorporated by reference.

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

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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 succinimides, carboxylic acid amides, hydrocarbyl monoamines, hydrocarbon polyamines, Mannich bases, phosphoramides, thiophosphoramides, phosphonamides, dispersant viscosity index improvers, 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,

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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 disclosures of which are hereby incorporated by reference. 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

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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, the disclosure of which is hereby incorporated by reference. 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 disclosure of which is hereby incorporated by reference. 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

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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 C₉₋₂₀₀ 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 C₈₀₋₁₀₀ 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 disclosures of which are hereby incorporated by reference. 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 $\text{HN}(\text{ANH})_n\text{H}$ 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.

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Another class of composition useful for preparing the molybdenum/sulfur complexes employed in this invention are the phosphoramides and phosphonamides such as those disclosed in U.S. Patent Nos. 3,909,430 and 3,968,157, the disclosures of which are hereby incorporated by reference. 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, diethylenetriamine, 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

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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_{1-40} 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

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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, dixylyl 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

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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.

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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.

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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 $R^2\text{COOH}$, 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

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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.

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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

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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 construed 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.

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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

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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 C_{18} 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

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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

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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.

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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.

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WHAT IS CLAIMED IS:

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) 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, a dispersant viscosity index improver, 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,

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- (2) a carboxylic acid amide, and
 - (3) 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.

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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

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carboxylic acid of the formula $R^2\text{COOH}$, 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 about 50 to 250 carbon atoms, and an ethylene amine.
14. The fuel composition of Claim 1, wherein the lubricant composition contains about 0.05 to 15% by weight of the molybdenum-containing composition of component (1), about 0.05 to 20% by weight of the carboxylic acid amide of component (2), and about 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 about 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 about 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.

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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) 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, a dispersant viscosity index improver, 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

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form a sulfur- and molybdenum-containing composition;

(2) a carboxylic acid amide; and

(3) 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.

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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 C_{80-100} alkylphenol, formaldehyde and triethylene tetramine, tetraethylene pentamine, or mixtures thereof.
29. The method of Claim 19 wherein the polar promoter is water.

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30. The method of Claim 19 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.
31. The method of Claim 19 wherein the succinimide of component (3) is derived from polyisobutenyl succinic anhydride, wherein the polyisobutenyl group contains from about 50 to 250 carbon atoms, and an ethylene amine.
32. The method of Claim 19 wherein the lubricant composition contains about 0.05 to 15% by weight of the molybdenum-containing composition of component (1), about 0.05 to 20% by weight of the carboxylic acid amide of component (2), and about 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 about 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 about 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.

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FUEL COMPOSITION FOR TWO-CYCLE ENGINES

ABSTRACT OF THE DISCLOSURE

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 base oil of lubricating viscosity and an additive formulation comprising (1) a molybdenum/sulfur complex of a basic nitrogen compound, (2) a carboxylic acid amide, and (3) a succinimide.

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