

5 **PREPARATION OF A MOLYBDENUM IMIDE ADDITIVE COMPOSITION AND
LUBRICATING OIL COMPOSITIONS CONTAINING SAME**

FIELD OF THE INVENTION

10 This invention relates to new lubricating oil additives and lubricating oil compositions. More specifically, it relates to new lubricating oil compositions containing a friction reducing component comprising the salt or complex of a molybdenum oxide, sulfide, or oxysulfide and an imide.

15 BACKGROUND OF THE INVENTION

Molybdenum disulfide has long been known as a desirable additive for use in lubricating oil compositions. Molybdenum disulfide is ordinarily finely ground and then dispersed in the lubricating oil composition to impart friction modifying and antiwear properties. However,
20 one of the major detriments to using finely ground molybdenum disulfide is its lack of solubility.

As an alternative to using finely ground molybdenum disulfide as a friction modifier, a number of other approaches involving various salts of molybdenum compounds have been
25 employed. Molybdenum dithiocarbamates (MoDTC) and molybdenum dithiophosphates (MoDTP) are well known in the art to impart friction modifying properties. Representative compositions of MoDTC are described in Larson et al., U.S. Pat. No. 3,419,589, which teaches molybdenum (VI) dioxide dialkyldithiocarbamates; Farmer et al., U.S. Pat. No. 3,509,051, which teaches sulfurized oxymolybdenum dithiocarbamates; and Sakurai et al.,
30 U.S. Pat. No. 4,098,705, which teaches sulfur containing molybdenum dihydrocarbyl dithiocarbamate compositions.

Representative compounds of MoDTP are the compositions described in Rowan et al., U.S. Pat. No. 3,494,866, such as oxymolybdenum diisopropylphosphorodithioate.

35 Another method of incorporating molybdenum compounds in oil is to prepare a colloidal complex of molybdenum disulfide or oxysulfides dispersed using known dispersants. Known dispersants include basic nitrogen containing compounds including succinimides, carboxylic

5 acid amides, phosphonoamides, thiophosphonoamides, Mannich bases, and hydrocarbonpolyamines.

King et al., U.S. Pat. No. 4,263,152; King et al., U.S. Pat. No. 4,261,843; and King et al., U.S. Pat. No. 4,259,195 teach molybdenum compounds used as anti-oxidant and anti-wear additives comprising an acidic molybdenum compound and a basic nitrogen compound
10 which acts as a dispersant.

DeVries et al., U.S. Pat. No. 4,259,194 discloses a sulfur containing additive comprising the reaction product of ammonium tetrathiomolybdate and a basic nitrogen compound for use as an anti-oxidant, anti-wear agent, and friction modifier.

15

Nemo, U.S. Pat. No. 4,705,643 teaches the preparation of carboxylic acid amides as detergent additives in lubricating oils.

Udding et al., U.S. Pat. No. 5,468,891 describes antifriction additives for lubricating oils
20 comprising a molybdenum-containing complex prepared by reacting an alkaline earth metal salt of a carboxylic acid, an amine and a source of cationic molybdenum, wherein the ratio of the number of equivalents of acid groups to the number of moles of molybdenum (eq:mol) is in the range from 1:10 to 10:1, and the ratio of the number of equivalents of acid groups to the number of moles of amine (eq:mol) is in the range from 20:1 to 1:10.

25

Ruhe, Jr. et al., U.S. Pat. No. 6,962,896 describes antioxidant additives for lubricating oils comprising low color molybdenum compounds.

Gatto et al., U.S. Pat No. 6,174,842 discloses a lubricating oil composition comprising a
30 lubricating oil, an oil-soluble molybdenum compound substantially free of reactive sulfur, an oil-soluble diarylamine and a calcium phenate as an anti-wear and anti-oxidant additive.

SUMMARY OF THE INVENTION

35 In one embodiment, the invention is directed to an oil soluble additive composition comprising a salt or complex of (i) a molybdenum component which comprises a molybdenum oxide, sulfide, or oxysulfide of the general formula MoO_xS_y wherein $x \geq 0$, $y \geq 0$, and $12 \geq (x+y) \geq 2$; and (ii) an imide wherein said imide comprises the reaction product of at

- 5 least one dicarboxylic acid component having from about 8 to about 22 carbon atoms, and at least one nitrogen compound selected from ammonia and a polyamine.

In one embodiment, the invention is directed to a lubricating oil composition comprising an oil of lubricating viscosity and an oil soluble additive composition comprising a salt or
10 complex of: (i) a molybdenum component which comprises a molybdenum oxide, sulfide, or oxysulfide of the general formula MoO_xS_y wherein $x \geq 0$, $y \geq 0$, and $12 \geq (x+y) \geq 2$; and (ii) an imide wherein said imide comprises the reaction product of at least one dicarboxylic acid component, having from about 8 to about 22 carbon atoms, and at least one nitrogen compound selected from ammonia and a polyamine.

15

In one embodiment, the invention is directed to a process for preparing an oil soluble additive composition which comprises reacting (i) a molybdenum component which is, or is capable of forming, a molybdenum oxide, sulfide, or oxysulfide of the general formula MoO_xS_y wherein $x \geq 0$, $y \geq 0$, and $12 \geq (x+y) \geq 2$; (ii) an imide which comprises the reaction product of a
20 at least one dicarboxylic acid component having from about 8 to about 22 carbon atoms, and at least one nitrogen compound selected from ammonia and a polyamine component.

DETAILED DESCRIPTION OF THE INVENTION

25 While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof and are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by
30 the appended claims.

Definitions

The following terms will be used throughout the specification and will have the following meanings unless otherwise indicated.

35

The term "polyamines" refers to organic compounds containing more than one basic nitrogen. The organic portion of the compound may contain aliphatic, cyclic, or aromatic carbon atoms.

5

The term “polyalkyleneamines” or “polyalkylenepolyamines” refers to compounds represented by the general formula



10

wherein R is an alkylene group of preferably 2-3 carbon atoms and n is an integer of from about 1 to 11.

15

The term “imide” or “polyimide” typically refers to the reaction product of a dicarboxylic acid, dicarboxylate, anhydride of a dicarboxylic acid, or ester of a dicarboxylic acid and primary amines or ammonia. Typically, imides are compounds that have two carbonyl groups bound to nitrogen and contain five- or six-membered rings. Examples include succinimide, phthalimide, and the like.

20

The terms “molybdenum oxide,” “molybdenum sulfide,” and “molybdenum oxysulfide” refer to compounds of the general formula MoO_xS_y wherein $x \geq 0$, $y \geq 0$, and $12 \geq (x+y) \geq 2$.

25

The term “dicarboxylic acid component” refers to dicarboxylic acids, dicarboxylates, dicarboxylic anhydrides, and the esters of dicarboxylic acids. Preferred species of dicarboxylic acid components are dicarboxylic acids and dicarboxylic acid anhydrides.

30

It is believed that the precise molecular formula of the oil soluble additive composition of the invention comprises the salt or complex of (1) a molybdenum component comprising a molybdenum oxide, sulfide, or oxysulfide and (2) a low molecular weight succinimide, prepared from a hydrocarbyl succinic anhydride and wherein the hydrocarbyl group contains from about 8 to about 22 carbon atoms. Although the precise formulas are not known with certainty, they are believed to be compounds in which molybdenum, whose valences are satisfied with atoms of oxygen and sulfur, is either complexed by or is the salt of one or more basic nitrogens of the imide used in the preparation of these additives.

35

Molybdenum Component

The molybdenum component used to prepare the oil soluble additive composition of the present invention is a molybdenum containing compound which is a molybdenum oxide, sulfide, or oxysulfide having the general formula of MoO_xS_y wherein $x \geq 0$, $y \geq 0$ and $12 \geq$

5 $(x+y) \geq 2$. The molybdenum component can include molybdenum in any oxidation state. The molybdenum component useful in the preparation of the oil-soluble additive composition of the invention may be derived from molybdenum compounds including, but not limited to, molybdenum hexacarbonyl, molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, other alkali metal molybdates, alkaline earth metal molybdates,
10 MoOCl_4 , MoO_2Br_2 , and $\text{Mo}_2\text{O}_3\text{Cl}_6$. Other molybdenum components include molybdenum trioxide, ammonium tetrathiomolybdate, and molybdenum disulfide. In one embodiment, the molybdenum components are molybdenum trioxide and those components derived from molybdic acid and ammonium molybdate. In one embodiment, the molybdenum component is molybdenum trioxide.

15

Imide component

The dicarboxylic acid component used in the preparation of the oil soluble additive composition of the invention includes aliphatic and aromatic dicarboxylic acids, dicarboxylic
20 acid salts, dicarboxylic acid anhydrides, or dicarboxylic acid esters having from at least 4 to 40 carbon atoms, preferably from 4 to 30 carbon atoms, more preferred from 4 to 22 carbon atoms, and even more preferred from 8 to 22 carbon atoms. Examples of dicarboxylic acids include the following: succinic acid, maleic acid, fumaric acid, phthalic acid, glutaric acid, traumatic acid, muconic acid, sebacic acid, azeloic acid, suberic acid, glutaric acid, adipic
25 acid, pimelic acid, and the like. Alkylated anhydride of a carboxylic acid can also be used, for example, dodecenyl succinic anhydride, hexadecenyl succinic anhydride, and octadecenylsuccinic anhydride, and the like. Mixtures of dicarboxylic acids, dicarboxylic acid salts, dicarboxylic anhydrides, and dicarboxylic acid esters can be used in the preparation of the invention. Preferably, the dicarboxylic acid component is an aliphatic dicarboxylic acid.
30 Particularly preferred anhydrides of dicarboxylic acid components are hexadecenyl succinic anhydride and octadecenyl succinic anhydride.

In one embodiment, dicarboxylic anhydrides are used to prepare the lubricating oil additive composition of the present invention. In one embodiment, succinimides and
35 polysuccinimides, which are derived from dicarboxylic anhydrides, may be used to prepare the lubricating oil additive composition described herein. Preparation of the succinimides and polysuccinimides is 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. Pat. 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 8 to about 22 carbon atoms, and an ethylene amine, said ethylene amines being especially characterized by ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, and higher molecular weight polyethylene amines. Particularly preferred are those succinimides prepared from hydrocarbyl succinic anhydride having 8 to 22 carbon atoms and a polyamine component having from about 2 and 10 nitrogens. Preferably, the hydrocarbyl group contains from about 12 to 18 carbon atoms. More preferably, the hydrocarbyl group contains from about 16 to 18 carbon atoms.

In one embodiment, the nitrogen compound may be ammonia or a polyamine component. The polyamine component used in the preparation of the oil soluble additive composition of the present invention includes aromatic, cyclic, and aliphatic (linear and branched) polyamines and mixtures thereof. Examples of aromatic polyamines include, but are not limited to, phenylenediamine, 2,2'-diaminodiphenylmethane, 2,4- and 2,6-diaminotoluene, 2,6-diamino-p-xylene, multi-nuclear and condensed aromatic polyamines such as naphthylene-1,4-diamine, benzidine, 2,2'-dichloro-4,4'-diphenyl diamine and 4,4'-diaminoazobenzene. In another embodiment the polyamine component comprises polyamines of from about 5 to 32 ring members and having from about 2 to 8 amine nitrogen atoms. Such polyamine compounds include such compounds as piperazine, 2-methylpiperazine, N-(2-aminoethyl)piperazine, N-(2-hydroxyethyl)piperazine, 1,2-bis-(N-piperazinyl)ethane, 3-aminopyrrolidine, N-(2-aminoethyl)pyrrolidine, and aza crown compounds such as triazacyclononane, tetraazacyclododecane, and the like.

In a preferred embodiment, the polyamine component used in the preparation of this invention are polyalkylenepolyamines and can be represented by the general formula



- 5 wherein R is an alkylene group of preferably 2-3 carbon atoms and n is an integer of from 1 to 11.

Specific examples of polyalkylenepolyamines include, but are not limited to,
 diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine,
 10 hexaethyleneheptamine, heptaethyleneoctamine, octaethylenenonamine,
 nonaethylenedecamine, decaethyleneundecamine, undecaethylenedodecamine,
 dipropylenetriamine, tripropylenetetramine, tetrapropylenepentamine,
 pentapropylenehexamine, hexapropyleneheptamine, heptapropyleneoctamine,
 octapropylenenonamine, nonapropylenedecamine, decapropyleneundecamine,
 15 undecapropylenedodecamine, di(trimethylene)triamine, tri(trimethylene)tetramine,
 tetra(trimethylene)pentamine, penta(triethylene)hexamine, hexa(trimethylene)heptamine,
 hepta(trimethylene)octamine, octa(trimethylene)nonamine, nona(trimethylene)decamine,
 deca(trimethylene)undecamine and undeca(trimethylene)dodecamine.

- 20 Succinic acid or anhydride component and an amine component are reacted to form the imide, the charge mole ratio of the succinic acid or anhydride component to amine component is about 6:1 to 1:1. Preferably the charge mole ratio of the succinic acid or anhydride component to amine component is about 4:1 to 1:1. More preferred, the charge mole ratio of the succinic acid or anhydride component to amine component is about 2:1 to
 25 1:1. In another embodiment, the charge mole ratio of the succinic acid or anhydride component to amine component is about 1.5:1 to 1:1. In a further embodiment, the charge mole ratio is from about 1.7:1 to about 1.3:1.

Promoter

30

In one embodiment of the present invention, at least one polar promoter is added during the reaction process. The at least one promoter may comprise a protic polar solvent. In one embodiment, the protic polar solvent comprises water, methanol and the like.

- 35 The protic polar solvent facilitates the interaction between the molybdenum component and the basic nitrogen of the polyamine or imide component. A wide variety of such promoters may be used. Typical promoters are alcohols, 1,3-propanediol, 1,4-butanediol, diethylene glycol, butyl cellosolve, propylene glycol, 1,4-butyleneglycol, methyl carbitol, ethanolamine,

5 diethanolamine, N-methyl-diethanol-amine, dimethyl formamide, N-methyl acetamide, dimethyl acetamide, ammonium hydroxides, tetra-alkyl ammonium hydroxides, alkali metal hydroxides, methanol, ethylene glycol, dimethyl sulfoxide, hexamethyl phosphoramide, tetrahydrofuran, acetic acid, inorganic acids, and water. Preferred are water and ethylene glycol. Particularly preferred is water.

10 While ordinarily the protic polar solvent 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 molybdenum component, such as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. Water may also be added as ammonium hydroxide.

15 Sulfur Source

In one embodiment, a source of sulfur is added to the reaction process to prepare the additive composition. Representative sulfur sources for preparing the oil soluble additive
20 compositions of this invention include, but are not limited to sulfur, hydrogen sulfide, sulfur monochloride, sulfur dichloride, phosphorus pentasulfide, R_2S_x where R is hydrocarbyl, preferably $\text{C}_1\text{-C}_{40}$ alkyl, and x is at least 2, inorganic sulfides and polysulfides such as $(\text{NH}_4)_2\text{S}_x$, 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-
25 containing antioxidants such as wax sulfides and polysulfides, sulfurized olefins, sulfurized carboxylic acid esters and sulfurized ester-olefins, and sulfurized alkylphenols and the metal salts thereof.

Preferred sulfur sources are sulfur, hydrogen sulfide, phosphorus pentasulfide, R_2S_x where R
30 is hydrocarbyl, preferably $\text{C}_1\text{-C}_{10}$ alkyl, and x is at least 3, mercaptans wherein R is $\text{C}_1\text{-C}_{10}$ alkyl, inorganic sulfides and polysulfides, thioacetamide, and thiourea. Most preferred sulfur sources are sulfur, hydrogen sulfide, phosphorus pentasulfide, and inorganic sulfides and polysulfides.

35 Method for Making the Oil Soluble Additive Composition

In one embodiment, the preparation of this invention may be carried out by reacting the molybdenum component with the imide component to form a salt or complex of a

5 molybdenum oxide, sulfide or oxysulfide and an imide followed by sulfurization with a sulfur component to form the salt or complex of a molybdenum oxide, sulfide or oxysulfide and an imide.

10 A diluent may be used to enable the reaction mixture to be efficiently stirred. Typical diluents are lubricating oil and liquid compounds containing only carbon and hydrogen. If the mixture is sufficiently fluid to permit satisfactory mixing, no diluent is necessary. A diluent which does not react with the molybdenum component is desirable.

15 A general method for preparing the oil soluble additive compositions of this invention comprises reacting (1) a molybdenum component and (2) an imide of a succinic acid or anhydride and an amine in which the succinic acid or anhydride and amine have a charge mole ratio (CMR) of between about 2:1 to 1:1, (3) a protic polar solvent and, optionally, (4) a diluent, to form a salt or complex. The diluent is used, if necessary, to provide a suitable viscosity to facilitate mixing and handling. Typical diluents are lubricating oil and liquid
20 compounds containing only carbon and hydrogen. Optionally, ammonium hydroxide may also be added to the reaction mixture to provide a solution of ammonium molybdate. The molybdenum component, imide, protic polar solvent and diluent, if used, are charged to a reactor and heated at a temperature less than or equal to about 200°C, and greater than about 120°C. The temperature is maintained at a temperature less than or equal to about 200°C,
25 and greater than about 120°C, until the molybdenum component is sufficiently reacted. The reaction time for this step is typically in the range of from about 1 to about 30 hours and preferably from about 1 to about 10 hours.

Typically excess water and any volatile diluents are removed from the reaction mixture.
30 Removal methods include, but are not limited to, vacuum distillation or nitrogen stripping while maintaining the temperature of the reactor at a temperature less than or equal to about 200°C, and greater than about 120°C. The removal of water and volatile diluents is ordinarily carried out under reduced pressure. The pressure may be reduced incrementally to avoid problems with foaming. After the desired pressure is reached, the stripping step is typically
35 carried out for a period of about 0.5 to about 5 hours and preferably from about 0.5 to about 2 hours.

The reaction mixture may be further reacted with a sulfur component as defined above, at a

5 suitable pressure and temperature not to exceed 200°C. The sulfurization step is typically carried out for a period of from about 0.5 to about 5 hours and preferably from about 0.5 to about 2 hours. In some cases, removal of the polar promoter from the reaction mixture may be desirable prior to completion of reaction with the sulfur component.

10 The sulfur component is usually charged to the reaction mixture in such a ratio to provide up to 12 atoms of sulfur per atom of molybdenum. In one embodiment, the oil soluble composition of the invention will have a mole ratio of molybdenum to sulfur of 1:0 to 1:8. In another embodiment the ratio of molybdenum to sulfur is from about 1:0 to 1:4. In a further embodiment, the ratio of molybdenum to sulfur is from about 1:1 to 1:4.

15

In the reaction mixture the ratio of molybdenum atoms to basic nitrogen atoms provided by the imide can range from about 0.01 to 4.0 atoms of molybdenum per basic nitrogen atom. Usually the reaction mixture is charged from 0.01 to 2.00 atoms of molybdenum per basic nitrogen atom provided by the imide. Preferably from 0.4 to 1.0, and most preferably from

20 0.4 to 0.7, atoms of molybdenum per atom of basic nitrogen is added to the reaction mixture.

The polar promoter, which is preferably water, is ordinarily present in the ratio of 0.1 to 50 moles of water per mol 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.

25

The charge mole ratio of the succinic acid or anhydride component to amine is critical and can range from about 6:1 to 1:1. In one embodiment the charge mole ratio is from about 4:1 to 1:1. In one embodiment the charge mole ratio is from about 2:1 to 1:1. In another embodiment the charge mole ratio is from about 1.5:1 to 1:1. In a further embodiment the

30 charge mole ratio is from about 1.7:1 to 1.3:1. The amide formed from the reaction of the succinic acid or anhydride component and the amine may occur prior to, during, or after the introduction of the molybdenum component to the reaction mixture.

Specifically, the preparation of the additive composition may be prepared by combining the

35 molybdenum component and the imide component. Furthermore, at least one source of polar promoter is added to the reaction mixture. In one embodiment, at least one source of polar promoter is added along with the molybdenum, after the imide component has been prepared, thereby producing a first reaction product. The imide component can be formed prior to

5 reaction with the molybdenum component or in situ from a succinic acid or anhydride component and an amine component. The first reaction product—the product of the imide and the molybdenum reaction -- is heated, in a first heating step, to at least 80°C. The first reaction product of the molybdenum component and the imide component is sulfurized by reacting with a sulfur component and heating, in a second heating step to drive off any excess
10 polar promoter, the mixture at a temperature of greater than 120°C, thereby producing a second reaction product, which is a salt or complex of a molybdenum oxide, sulfide, or oxysulfide and an imide. In one embodiment the temperature of the second heating step is at least 140°C.

15 In one embodiment, the additive composition of the present invention is prepared by mixing and stirring an imide component, base oil and a polar promoter, such as 2-ethylhexanol, in a first heating step, at a temperature of at least 70°C, thereby producing a reaction mixture. A molybdenum component and at least one source of water are added to the reaction mixture and heated, in a second heating step, to at least 85°C, thereby producing a first reaction
20 product. The first reaction product is further heated, in a third heating step, to at least 170°C to remove 2-ethylhexanol. The temperature is decreased, in a fourth heating step, to no more than 100°C. A source of sulfur is added to the first reaction product, thereby producing a second reaction product which is then heated, in a fifth heating step, to at least 120°C. In one embodiment the temperature of the fifth heating step is at least 140°C.

25

Additive Concentrates

In many instances, it may be advantageous to form concentrates of the oil soluble additive composition of the present invention within a carrier liquid. These additive concentrates
30 provide a convenient method of handling, transporting, and ultimately blending into lubricant base oils to provide a finished lubricant. Generally, the oil soluble additive concentrates of the invention are not useable or suitable as finished lubricants on their own. Rather, the oil soluble additive concentrates are blended with lubricant base oil stocks to provide a finished lubricant. It is desired that the carrier liquid readily solubilizes the oil soluble additive of the
35 invention and provides an oil additive concentrate that is readily soluble in the lubricant base oil stocks. In addition, it is desired that the carrier liquid not introduce any undesirable characteristics, including, for example, high volatility, high viscosity, and impurities such as heteroatoms, to the lubricant base oil stocks and thus, ultimately to the finished lubricant. The

5 present invention therefore further provides an oil soluble additive concentrate composition comprising an inert carrier fluid and from 2.0 % to 90% by weight, based on the total concentrate, of an oil soluble additive composition according to the invention. The inert carrier fluid may be a lubricating oil.

10 These concentrates usually contain from about 2.0% to about 90% by weight, preferably 10% to 50% by weight of the oil soluble additive composition of this invention and may contain, in addition, one or more other additives known in the art and described below. The remainder of the concentrate is the substantially inert carrier liquid.

15 Lubricating Oil Compositions

In one embodiment of the invention, the oil soluble additive composition of the present invention can be mixed with a base oil of lubricating viscosity to form a lubricating oil composition. The lubricating oil composition comprises a major amount of a base oil of
20 lubricating viscosity and a minor amount of the oil soluble additive composition of the present invention described above.

The lubricating oil which may be used in this invention includes a wide variety of hydrocarbon oils, such as naphthenic bases, paraffin bases and mixed base oils as well as
25 synthetic oils such as esters and the like. The lubricating oils which may be used in this invention also include oils from biomass such as plant and animal derived oils. The lubricating oils may be used individually or in combination and generally have a viscosity which ranges from 7 to 3,300 cSt and usually from 20 to 2000 cSt at 40°C. Thus, the base oil can be a refined paraffin type base oil, a refined naphthenic base oil, or a synthetic
30 hydrocarbon or non-hydrocarbon oil of lubricating viscosity. The base oil can also be a mixture of mineral and synthetic oils. Mineral oils for use as the base oil in this invention include, for example, paraffinic, naphthenic and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include, for example, both hydrocarbon synthetic oils and synthetic esters and mixtures thereof having the desired viscosity. Hydrocarbon
35 synthetic oils may include, for example, oils prepared from the polymerization of ethylene, i.e., polyalphaolefin or PAO, or from hydrocarbon synthesis procedures using carbon monoxide and hydrogen gases such as in a Fisher-Tropsch process. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity.

5 Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of monocarboxylic acids and polycarboxylic acids, as well as mono-hydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaproate, di-2-ethylhexyl adipate, dilaurylsebacate, and the like. Complex esters prepared from mixtures of mono and dicarboxylic acids and mono and
10 dihydroxy alkanols can also be used. Blends of mineral oils with synthetic oils are also useful.

The lubricating oil compositions containing the oil soluble additives of this invention can be prepared by admixing, by conventional techniques, the appropriate amount of the oil soluble
15 additives of the invention with a lubricating oil. The selection of the particular base oil depends on the contemplated application of the lubricant and the presence of other additives. Generally, the amount of the oil soluble additive composition of the invention in the lubricating oil composition of the invention will vary from 0.05 to 15% by weight and preferably from 0.2 to 1% by weight, based on the total weight of the lubricating oil
20 composition. In one embodiment, the molybdenum content of the lubricating oil composition will be between about 50 parts per million (ppm) and 5000 ppm, preferably between about 90 ppm to 1500 ppm. In another embodiment the molybdenum content of the lubricating oil composition will be between about 500 ppm and 700 ppm.

25 Additional Additives

If desired, other additives may be included in the lubricating oil and lubricating oil concentrate compositions of this invention. These additives include antioxidants or oxidation inhibitors, dispersants, rust inhibitors, anticorrosion agents and so forth. Also, anti-foam
30 agents, stabilizers, anti-stain agents, tackiness agents, anti-chatter agents, dropping point improvers, anti-squawk agents, extreme pressure agents, odor control agents and the like may be included.

The following additive components are examples of some of the components that can be
35 favorably employed in the lubricating oil compositions of the present invention. These examples of additional additives are provided to illustrate the present invention, but they are not intended to limit it:

5 Metal Detergents

Detergents which may be employed in the present invention include alkyl or alkenyl aromatic sulfonates, calcium phenate, borated sulfonates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanoic
10 acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof.

Anti-Wear Agents

As their name implies, these agents reduce wear of moving metallic parts. Examples of such
15 agents include, but are not limited to, zinc dithiophosphates, carbarmates, esters, and molybdenum complexes.

Rust Inhibitors (Anti-Rust Agents)

Anti-rust agents reduce corrosion on materials normally subject to corrosion. Examples of
20 anti-rust agents include, but are not limited to, nonionic polyoxyethylene surface active agents such as polyoxyethylene lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol mono-oleate, and polyethylene glycol mono-oleate. Other
25 compounds useful as anti-rust agents include, but are not limited to, stearic acid and other fatty acids, dicarboxylic acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and phosphoric ester.

Demulsifiers

Demulsifiers are used to aid the separation of an emulsion. Examples of demulsifiers
30 include, but are not limited to, block copolymers of polyethylene glycol and polypropylene glycol, polyethoxylated alkylphenols, polyesteramides, ethoxylated alkylphenol-formaldehyde resins, polyvinylalcohol derivatives and cationic or anionic polyelectrolytes. Mixtures of different types of polymers may also be used.

35 Friction Modifiers

Additional friction modifiers may be added to the lubricating oil of the present invention. Examples of friction modifiers include, but are not limited to, fatty alcohols, fatty acids,

5 amines, ethoxylated amines, borated esters, other esters, phosphates, phosphites and phosphonates.

Multifunctional Additives

Additives with multiple properties such as anti-oxidant and anti-wear properties may also be
10 added to the lubricating oil of the present invention. Examples of multi-functional additives include, but are not limited to, sulfurized oxymolybdenum dithiocarbamate, sulfurized oxymolybdenum organo phosphorodithioate, oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-molybdenum complexes, and sulfur-containing molybdenum complexes.

15

Viscosity Index Improvers

Viscosity index improvers, also known as viscosity modifiers, comprise a class of additives that improve the viscosity-temperature characteristics of the lubricating oil, making the oil's viscosity more stable as its temperature changes. Viscosity index improvers may be added to
20 the lubricating oil composition of the present invention. Examples of viscosity index improvers include, but are not limited to, polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, alkaline earth metal salts of phosphosulfurized polyisobutylene, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

25

Pour Point Depressants

Pour point depressants are polymers that are designed to control wax crystal formation in lubricating oils resulting in lower pour point and improved low temperature flow performance. Examples of pour point depressants include, but are not limited to,
30 polymethyl methacrylate, ethylene vinyl acetate copolymers, polyethylene polymers, and alkylated polystyrenes.

Foam Inhibitors

Foam inhibitors are used to reduce the foaming tendencies of the lubricating oil. Examples of
35 foam inhibitors include, but are not limited to, alkyl methacrylate polymers, alkylacrylate copolymers, and polymeric organosiloxanes such as dimethylsiloxane polymers.

Metal Deactivators

- 5 Metal deactivators create a film on metal surfaces to prevent the metal from causing the oil to be oxidized. Examples of metal deactivators include, but are not limited to, disalicylidene propylenediamine, triazole derivatives, thiadiazole derivatives, bis-imidazole ethers, and mercaptobenzimidazoles.

Dispersants

- 10 Dispersants diffuse sludge, carbon, soot, oxidation products, and other deposit precursors to prevent them from coagulating resulting in reduced deposit formation, less oil oxidation, and less viscosity increase. Examples of dispersants include, but are not limited to, alkenyl succinimides, alkenyl succinimides modified with other organic compounds, alkenyl succinimides modified by post-treatment with ethylene carbonate or boric acid, alkali metal
15 or mixed alkali metal, alkaline earth metal borates, dispersions of hydrated alkali metal borates, dispersions of alkaline-earth metal borates, polyamide ashless dispersants and the like or mixtures of such dispersants.

Anti-Oxidants

- 20 Anti-oxidants reduce the tendency of mineral oils to deteriorate by inhibiting the formation of oxidation products such as sludge and varnish-like deposits on the metal surfaces. Examples of anti-oxidants useful in the present invention include, but are not limited to, phenol type (phenolic) oxidation inhibitors, such as 4,4'-methylene-bis(2,6-di-tert-butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol), 2,2'-methylene-bis(4-
25 methyl-6-tert-butylphenol), 4,4'-butylidene-bis(3-methyl-6-tert-butylphenol), 4,4'-isopropylidene-bis(2,6-di-tert-butylphenol), 2,2'-methylene-bis(4-methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol), 2,2'-5-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol,
30 2,6-di-tert-1-dimethylamino-p-cresol, 2,6-di-tert-4-(N,N'-dimethylaminomethylphenol), 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-10-butylbenzyl)-sulfide, and bis(3,5-di-tert-butyl-4-hydroxybenzyl). Diphenylamine-type oxidation inhibitors include, but are not limited to, alkylated diphenylamine, phenyl-alpha-naphthylamine, and
35 alkylated-alpha-naphthylamine. Other types of oxidation inhibitors include metal dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis(dibutyldithiocarbamate).

5 Applications

Lubricating oil compositions containing the oil soluble additive compositions disclosed herein are effective as either fluid and grease compositions for modifying the friction properties of the lubricating oil which may, when used as a crankcase lubricant, lead to
10 improved mileage for the vehicle being lubricated with a lubricating oil of this invention.

The lubricating oil compositions of this invention may be used in marine cylinder lubricants as in crosshead diesel engines, crankcase lubricants as in automobiles and railroads, lubricants for heavy machinery such as steel mills and the like, or as greases for bearings and
15 the like. Whether the lubricant is fluid or solid will ordinarily depend on whether a thickening agent is present. Typical thickening agents include polyurea acetates, lithium stearate and the like. The oil soluble additive composition of the invention may also find utility as an anti-oxidant, anti-wear additive in explosive emulsion formulations.

20 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

25

Example 1

In a 3-neck 500 mL glass reactor equipped with a temperature controller, mechanical stirrer, and water cooled condenser, 27.1 g of a succinimide, prepared from a hexadecenyl succinic anhydride (HDSA) and triethylene tetramine (TETA) at a molar ratio of TETA to HDSA of
30 0.67 to 1, was charged. Additionally, 12.3 g of 100 neutral oil, and 70 mL of xylene were charged to the glass reactor. The mixture was heated to a temperature of 85 °C where upon, 2.98 g of molybdenum oxide and 3.0 g of water were charged to the reactor. The reactor was then held at a reaction temperature of 85 °C for 2.5 hrs. Subsequently 1.33 g of elemental sulfur was charged to the reactor. The sulfurization reaction was carried out at 140 °C for 3
35 hrs, and xylene and water were removed continuously with nitrogen sweep.

The product contained 4.50% by weight of molybdenum, 3.06% by weight of sulfur, and 5.1% by weight of nitrogen.

5

Example 2

A lubricating oil composition was prepared by adding 1.11% by weight (equivalent to 500 ppm of molybdenum) of the lubricating oil additive of Example 1 to the lubricating oil formulation in Comparative Example A.

10

Example 3

To a glass reactor equipped with temperature controller, and water cooled condenser, 8.2 g of succinimide as prepared in Example 1, 22.8 g of 2-ethylhexanol, and 3.7 g of 100 neutral oil were charged. The mixture was heated to a temperature of 85 °C where upon 0.90 g of molybdenum oxide and 1.0 g of water were charged to the reactor. The reactor was then held at a reaction temperature of 85 °C for 2 hrs. Upon completion of the molybdatation reaction, water and 2-ethylhexanol were removed by distillation at 170 °C and a pressure of 50 millimeters of mercury (absolute) or less for approximately 30 minutes. The reaction mixture was cooled to 90 °C, where upon 0.40 g of elemental sulfur was charged to the reactor. The sulfurization reaction was carried out at 140 °C for 3 hrs.

20

The product contained 4.57% by weight of molybdenum, 3.06% by weight of sulfur, and 5.3% by weight of nitrogen.

25 **Example 4**

A lubricating oil composition was formed by adding 1.09% by weight (equivalent to 500 ppm of molybdenum) of the lubricating oil additive of Example 3 to lubricating oil formulation in Comparative Example A.

30 **Comparative Example A**

A baseline lubricating oil formulation was formed containing 4 % by weight of an ashless dispersant, 3.01 % by weight of alkaline earth metal carboxylate detergent, 0.62 % by weight of a zinc dialkyldithiophosphate, 1.2 % by weight of an antioxidant, 4.3 % by weight of a non-dispersant type viscosity index improver, 5 ppm of a foam inhibitor in a Group II base oil.

35

Comparative Example B

5 A lubricating oil composition was prepared by adding 500 ppm of molybdenum oxysulfide succinimide complex, derived from a polyisobutenyl (having an average molecular weight of 1000) succinimide, as described in Ruhe et al, U.S. Pat No. 6,962,896 to lubricating oil formulation in Comparative Example A.

10 **Comparative Example C**

A lubricating oil composition was prepared by adding 500 ppm of molybdenum oxysulfide succinimide complex, derived from a polyisobutenyl (having an average molecular weight of 1000) succinimide, as described in King et al, U.S. Pat No. 4,263,152 to lubricating oil formulation in Comparative Example A.

15

Comparative Example D

A lubricating oil composition was prepared by adding 0.82% by weight (equivalent to 500 ppm of molybdenum) of molybdenum dithiocarbamate (MoDTC, available from AdekaUSA Corporation, Saddle River, New Jersey) to lubricating oil formulation in Comparative

20 Example A.

Example 5

To a glass reactor equipped with a temperature controller, and water cooled condenser, 8.0 g of a succinimide, prepared from a octadecenyl succinic anhydride (ODSA) and tetraethylene
25 pentamine (TEPA) at a molar ratio of amine to ODSA of 1.0 to 1.0, 2.0 g of neutral oil, and 25.0 g of toluene were charged The mixture was heated to 85 °C where upon 1.10 g of molybdenum oxide and 2.0 g of water were charged to the reactor. The reactor was then held at a reaction temperature of 85 °C for 1.5 hrs. Upon completion of the molybdation reaction, 0.49 g of elemental sulfur was charged to the reactor. The sulfurization reaction was carried
30 out at 105 °C for 3 hrs. The reaction mixture was then filtered through filter aid and toluene and water were removed using rotory evaporator.

The product contained 2.06% by weight of molybdenum and 2.34% by weight of sulfur.

Example 6

35 A lubricating oil composition was prepared by adding 500 ppm of molybdenum of the lubricating oil additive of Example 5 to lubricating oil formulation in Comparative Example A.

5 Comparative Example E

A lubricating oil composition was prepared by adding 500 ppm of molybdenum dialkyldithiophosphate (MoDTP, available as “Molyvan L” from R.T. Vanderbilt Company, Norwalk, CT) to lubricating oil formulation in Comparative Example A.

- 10 The compositions described above were tested for friction performance in a Mini-Traction Machine (MTM) bench test. The MTM is manufactured by PCS Instruments and operates in pin-on-disk configuration in which a stainless steel ball (6mm) is loaded against a rotating disk (32100 steel). The condition employs a load of 10 Newtons, a speed of 500mm/s, temperature of 120°C, and has a run-time of 60 minutes. The results are averaged for the last
- 15 10 minutes and are summarized in the Table 1.

Table 1 – Comparison of Coefficients of Friction (COF) for Various Examples:

Examples	Description	Mo ppm in finished oil	Coefficient of Friction (avg. of last 10 mins)
2	C16 succinimide	500	0.054
4	C16 succinimide	500	0.053
6	C18 succinimide	500	0.067
Comp. A	(baseline)	0	0.128
Comp. B	1000MW PIB succinimide	500	0.115
Comp. C	1000MW PIB succinimide	500	0.120
Comp. D	MoDTC	500	0.050
Comp. E	MoDTP	500	0.047

- 20 Examples 2, 4, and 6 in Table 1 show that the coefficients of friction (wherein the lower the COF, the better the friction reducing properties) of the lubricating oil composition of the present invention is comparable to that of molybdenum dithiocarbamate (Comp. D) and molybdenum dithiophosphate (Comp. E), both are well know friction reducers. Examples 2, 4, and 6 also show superior friction reducing properties as compared to a molybdenum
- 25 succinimide complex synthesized from a polyisobutenyl succinimide wherein the polyisobutenyl group has around 1000 molecular weight equivalent of carbon atoms (Comp. B and C). As evidenced by the data in Table 1, friction reducing properties are improved

- 5 when a lower molecular weight hydrocarbyl succinimide (e.g., about 16 to 18 carbon atoms) is employed.

5 WHAT IS CLAIMED IS:

1. An oil soluble additive composition comprising a salt or complex of
 - (i) a molybdenum component which comprises a molybdenum oxide, sulfide, or
10 oxysulfide of the general formula MoO_xS_y wherein $x \geq 0$, $y \geq 0$, and $12 \geq (x+y) \geq 2$; and
 - (ii) an imide wherein said imide comprises the reaction product of at least one dicarboxylic acid component having from about 8 to about 22 carbon atoms, and at least one nitrogen compound selected from ammonia and a polyamine.
15
2. The oil soluble additive composition of claim 1, wherein the molybdenum component is a molybdenum sulfide.
3. The oil soluble additive composition of claim 1, wherein the imide contains at least
20 one basic nitrogen.
4. The oil soluble additive composition of claim 1, wherein the imide is a phthalamide.
5. The oil soluble additive composition of claim 1, wherein the imide is a hydrocarbyl
25 succinimide.
6. The oil soluble additive composition of claim 5 wherein the hydrocarbyl succinimide is prepared from a hydrocarbyl succinic anhydride and wherein the hydrocarbyl group contains from about 8 to about 22 carbon atoms.
30
7. The oil soluble additive composition of claim 1, wherein the dicarboxylic acid component is a dicarboxylic acid, dicarboxylic acid salt, dicarboxylic acid anhydride, dicarboxylic acid ester, or mixtures thereof.
35
8. The oil soluble additive composition of claim 1, wherein the dicarboxylic acid component is a hydrocarbyl dicarboxylic acid wherein the hydrocarbyl group contains from about 8 to about 22 carbon atoms.

5

9. The oil soluble additive composition of claim 1, wherein the charge mole ratio of the dicarboxylic acid component to the nitrogen compound is about 6:1 to 1:1.

10. The oil soluble additive composition of claim 1, wherein the polyamine is a polyalkylenepolyamine of the general formula



and wherein R is an alkylene group of 2-3 carbon atoms and n is an integer of from 1 to 11.

11. The oil soluble composition of claim 1, wherein the polyamine is tetraethylenepentamine (TEPA), diethylenetriamine (DETA), ethylenediamine (EDA), or mixtures thereof.

12. The oil soluble additive composition of claim 1, wherein the molybdenum component is sulfurized.

13. The oil soluble additive composition of claim 1, wherein the mole ratio of molybdenum to sulfur in the oil soluble additive composition is about 1:0 to 1:8.

14. A lubricating oil composition comprising:

(1) an oil of lubricating viscosity and

(2) an oil soluble additive composition comprising a salt or complex of:

(i) a molybdenum component which comprises a molybdenum oxide, sulfide, or oxysulfide of the general formula MoO_xS_y wherein $x \geq 0$, $y \geq 0$, and $12 \geq (x+y) \geq 2$;

and

(ii) an imide wherein said imide comprises the reaction product of at least one dicarboxylic acid component, having from about 8 to about 22 carbon atoms, and at least one nitrogen compound selected from ammonia and a polyamine.

15. The lubricating oil composition of claim 14, wherein the molybdenum content of the lubricating oil composition is between about 50 ppm and 5000 ppm.

- 5 16. The lubricating oil composition of claim 14, wherein the oil soluble additive composition content is between 0.05 to 15% by weight.
- 10 17. A process for preparing an oil soluble additive composition which comprises reacting:
- (i) a molybdenum component which is, or is capable of forming, a molybdenum oxide, sulfide, or oxysulfide of the general formula MoO_xS_y wherein $x \geq 0$, $y \geq 0$, and $12 \geq (x+y) \geq 2$;
 - (ii) an imide which comprises the reaction product of a at least one dicarboxylic acid component having from about 8 to about 22 carbon atoms, and at least one nitrogen compound selected from ammonia and a polyamine component.
- 15
18. The process of claim 17, wherein the product obtained from the reaction of step (i) and step (ii) is sulfurized in an amount sufficient to provide 0.01 to 12 atoms of sulfur per atom of molybdenum.
- 20
19. The process of claim 17, wherein the reaction of the molybdenum component and the imide is in the presence of a polar promoter.
- 25 20. The process of claim 19, wherein the polar promoter is selected from the group consisting of 1,3-propanediol, 1,4-butanediol, diethylene glycol, butyl cellosolve, propylene glycol, 1,4-butyleneglycol, methyl carbitol, ethanolamine, ammonium hydroxide, alkyl ammonium hydroxide, metal hydroxide, N-methyl-diethanol-amine, dimethyl formamide, N-methyl acetamide, dimethyl acetamide, methanol, ethylene glycol, dimethyl sulfoxide, hexamethyl phosphoramide, tetrahydrofuran, water,
- 30 inorganic acid, and mixtures thereof.
21. The process of claim 20, wherein the polar promoter is water.
- 35 22. The process of claim 18, wherein the sulfurization is carried out with a sulfur source selected from 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.

5

23. The process of claim 17, wherein the molybdenum component is selected from the group consisting of molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, metal molybdates, MoOC_{14} , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{C}_{16}$, molybdenum trioxide, and mixtures thereof.

10

24. The process of claim 17, wherein the molybdenum component is molybdenum trioxide.

15

25. The process of claim 17, wherein the dicarboxylic acid component comprises at least one hydrocarbyl succinic acid or anhydride.

26. The process of claim 17, wherein the polyamine component comprises a polyalkylenepolyamine represented by the general formula



20

and wherein R is an alkylene group of 2-3 carbon atoms and n is an integer of from 1 to 11.

27. The process of claim 17, wherein the polyamine component is tetraethylenepentamine (TEPA), diethylenetriamine (DETA), ethylenediamine (EDA), or mixtures thereof.

25

30

35