

5 **A POST-TREATED MOLYBDENUM IMIDE ADDITIVE COMPOSITION,
METHODS OF MAKING SAME AND LUBRICATING OIL COMPOSITIONS
CONTAINING SAME**

 This application claims priority to United States Provisional Patent Application
10 number 61/740,668 which was filed on December 21, 2012.

FIELD OF THE INVENTION

 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
15 component comprising the post-treated salt of a molybdenum oxide, sulfide, or oxysulfide
and an alkenyl succinimide.

BACKGROUND OF THE INVENTION

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

25 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
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
30 teaches molybdenum (VI) dioxide dialkyldithiocarbamates; Farmer et al., U.S. Pat. No.
3,509,051, which teaches sulfurized oxymolybdenum dithiocarbamates; and Sakurai et al.,
U.S. Pat. No. 4,098,705, which teaches sulfur containing molybdenum dihydrocarbyl
dithiocarbamate compositions.

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

- 5 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 acid amides, phosphonoamides, thiophosphonoamides, Mannich bases, and hydrocarbonpolyamines.
- 10 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 which acts as a dispersant.
- 15 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.
- 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 and polyamide dispersants including molybdenum oxysulfide polyamides.
- 30 Gatto et al., U.S. Pat No. 6,174,842 discloses a lubricating oil composition comprising a 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.
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SUMMARY OF THE INVENTION

An embodiment of the present invention is directed to an oil soluble additive composition prepared by a process comprising: reacting, (a) a molybdenum component; (b) an imide
10 derived from the reaction product of a hydrocarbyl dicarboxylic acid component and a polyamine wherein said reaction product is prepared by first charging a polyamine to a reaction vessel and then charging a hydrocarbyl dicarboxylic acid component to the reaction vessel, wherein the charge mole ratio of the the hydrocarbyl dicarboxylic acid component to the polyamine is from about 1:1 to about 1:0.5; and (c) a post-treating agent, thereby
15 producing a post-treated moblydated succinimide additive composition.

An embodiment of the present invention is directed to a lubricating oil composition comprising: (a) an oil of lubricating viscosity; and (b) the reaction product of (i) a molybdenum component; (ii) an imide derived from the reaction product of a hydrocarbyl
20 dicarboxylic acid component and a polyamine component wherein said imide comprises the reaction product prepared by first charging a polyamine to a reaction vessel and then charging a dicarboxylic acid component to the reaction vessel, wherein the charge mole ratio of the hydrocarbyl dicarboxylic acid component to the polyamine component is from about 1:1 to about 1:0.5; and (iii) a post-treating agent, thereby producing a post-treated moblydated
25 succinimide additive composition.

An embodiment of the present invention is directed to a process for preparing an oil soluble additive composition which comprises reacting: (a) a molybdenum component; (b) an imide derived from the reaction product of a hydrocarbyl dicarboxylic acid component and a
30 polyamine wherein said reaction product is prepared by first charging a polyamine to a reaction vessel and then charging a dicarboxylic acid component to the reaction vessel, wherein the charge mole ratio of the dicarboxylic acid component to the polyamine component is from about 1:1 to about 1:0.5; and (c) a post-treating agent, thereby producing a post-treated moblydated succinimide additive composition.

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DETAILED DESCRIPTION OF THE INVENTION

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 the appended claims.

Definitions

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

The term “amide” or “polyamide” refers to the reaction product of a carboxylic acid, carboxylate, anhydride of a carboxylic acid, or ester of a carboxylic acid and a polyamine.

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The term “carrier fluid” refers to a liquid that readily solubilizes an oil soluble additive, thereby providing an additive concentrate that is readily soluble in lubricant base oil stocks.

The term “dicarboxylic acid component” refers to dicarboxylic acids, salts of dicarboxylic acid, anhydrides of dicarboxylic acids, and the esters of dicarboxylic acids.

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The term “fatty acid” refers to a carboxylic acid component derived from or contained in an animal or vegetable fat or oil comprising an alkyl chain of from 4 to 22 carbon atoms with a terminal carboxyl group.

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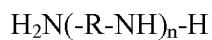
The term “imide” or “polyimide” refers to the reaction product of a dicarboxylic acid, carboxylate, anhydride of a dicarboxylic acid, or ester of a dicarboxylic acid and a polyamine.

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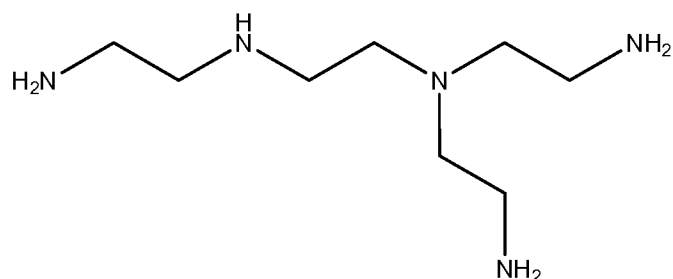
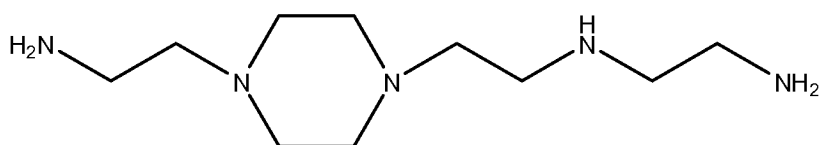
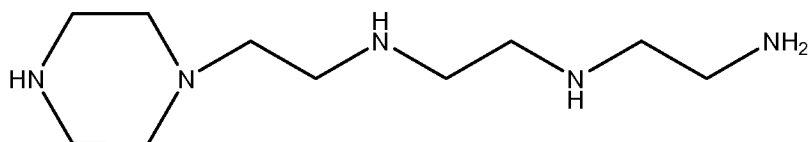
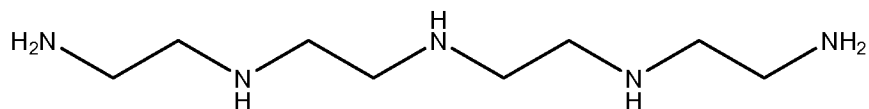
The terms “molybdenum oxide,” “molybdenum sulfide,” and “molybdenum oxysulfide” refer to compounds of the general formula MoO_xS_y wherein $x \geq 0$, $y \geq 0$, and $12 \geq (x+y) \geq 2$.

- 5 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.

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



- wherein R is an alkylene group of preferably 2-3 carbon atoms and n is an integer of from about 1 to 11. Branching may occur on the internal nitrogen atom(s). Also, the structure may contain cyclic nitrogen-containing structures. The cyclic structures typically occur between
15 the nitrogen atoms of consecutive repeating units. The following are examples of such structures:



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The term “polar promoter” refers to compounds that facilitate the reaction between non-polar organic compounds and polar or insoluble organic or inorganic reactants.

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The present invention is directed to an oil soluble lubricating oil additive. The additive is prepared by reacting a molybdenum component and an imide component thereby producing a molybdated imide which is reacted with a post-treating agent. It has been further discovered

5 that controlling the addition sequence of reactants results in an improved product that has a higher TBN and molybdenum content.

Molybdenum Component

The molybdenum component used to prepare the oil soluble additive composition of the
10 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 $12 \geq (x+y) \geq 2$. 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
15 molybdate, potassium molybdate, other alkali metal molybdates, alkaline earth metal molybdates, 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. Preferred molybdenum components are molybdenum trioxide and those components derived from molybdic acid and ammonium molybdate. A more preferred molybdenum
20 component is molybdenum trioxide.

Imide component

Amides and imides used in the preparation of the oil soluble additive composition of the
25 present invention are the reaction product of a hydrocarbyl dicarboxylic acid component and a polyamine component. The hydrocarbyl dicarboxylic acid component is the reaction product of a dicarboxylic acid component and a hydrocarbyl component.

The dicarboxylic acid components are substituted (i.e., hydrocarbyl) acylating agents,
30 preferably dicarboxylic acids or anhydrides of the dicarboxylic acid components, more preferably anhydrides of succinic acid components.

The hydrocarbyl component may have a molecular weight of up to 5000 daltons. Preferably, the molecular weight of the hydrocarbyl component is from about 110 to about 5000. More
35 preferred, the molecular weight of the hydrocarbyl component is from about 110 to 2300. Most preferred, the molecular weight of the hydrocarbyl component is from about 110 to about 1300. In one embodiment, the molecular weight of the hydrocarbyl component is from about 180 to about 5000. More preferred, the molecular weight of the hydrocarbyl

5 component is from about 200 to about 5000. The hydrocarbyl component generally contains an average number of carbon atoms from about 8 to about 400, preferably from about 12 to about 93, more preferably from about 16 to about 72.

10 Preferably, the hydrocarbyl component is an alkyl group or an alkenyl group. The alkenyl group may be derived from one or more of the olefins.

Examples of the olefins are derived from polymers of ethylene, propylene, butylene and isobutylene include butene, isobutene, 1-octene, octene, 1-nonene, 1-decene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-15 nonadecene, 1-eicosene, 1-henicosene, 1-docosene, 1-tetracosene, etc. Commercially available alpha-olefin fractions that can be used include the C₁₅₋₁₈ alpha-olefins, C₁₂₋₁₆ alpha-olefins, C₁₄₋₁₆ alpha-olefins, C₁₄₋₁₈ alpha-olefins, C₁₆₋₁₈ alpha-olefins, C₁₆₋₂₀ alpha-olefins, C₂₂₋₂₈ alpha-olefins, etc. The C₁₆ and C₁₆₋₁₈ alpha-olefins and polyisobutene are particularly preferred.

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The succinic acylating agents are prepared by reacting the above-described olefins or isomerized olefins with unsaturated dicarboxylic acids such as fumaric acids or maleic acid or anhydrides of the dicarboxylic acids at a temperature of about 160°C to about 240°C, preferably about 185°C to about 210°C. Free radical inhibitors (e.g., t-butyl catechol) may be 25 used to reduce or prevent the formation of polymeric byproducts. The procedures for preparing the acylating agents are well known to those skilled in the art and have been described for example in U.S. Pat. No. 3,412,111; and Ben et al, "The Ene Reaction of Maleic Anhydride With Alkenes", J. C. S. Perkin II (1977), pages 535-537. These references are incorporated by reference for their disclosure of procedures for making the above 30 acylating agents.

The hydrocarbyl-substituted succinic acylating agents are available commercially and may be purchased from Dixie Chemical Company, Inc., Pasadena, Texas or from Chevron Oronite Company LLC, Houston, Texas.

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In the reaction of the hydrocarbyl dicarboxylic acid component and the amine component to form an imide, the charge mole ratio of the hydrocarbyl dicarboxylic acid component to

5 amine component is about 1:1 to 1:0.5. Preferably from about 1:1 to 1:0.7. More preferred about 1:0.9.

In one embodiment, the imide is derived from 1) an aliphatic dicarboxylic acid component having from about 8 and 400 carbons and 2) a polyamine component having from about 2
10 and 10 nitrogen atoms. In a preferred embodiment the aliphatic dicarboxylic acid component is a hydrocarbyl, such as hexadecenyl, succinic anhydride and the polyamine component is selected from the group consisting of tetraethylenepentamine, diethylenetriamine, ethylenediamine, and mixtures thereof. In a preferred embodiment the hydrocarbyl dicarboxylic acid component is polyisobutenyl succinic anhydride (PIBSA) and the
15 polyamine component is selected from the group consisting of tetraethylenepentamine, diethylenetriamine, ethylenediamine and mixtures thereof.

The hydrocarbyl dicarboxylic acid component and polyamine component described herein below can be reacted to form imides prior to or during reaction with the molybdenum
20 component. Imide compositions useful in the invention include those disclosed in U.S. Pat. Nos. 8,076,275; 6,962,896; 6,156,850 and 5,821,205 and the like, the disclosures of which is hereby incorporated by reference. These compositions are ordinarily prepared by reacting a dicarboxylic acid, dicarboxylic acid salt, dicarboxylic acid anhydride, or dicarboxylic acid ester having at least 8 to about 400 carbon atoms and, if desired, having pendant aliphatic
25 groups to render the molecule oil soluble, with a polyamine, such as an ethylene diamine, to give an imide. Preferred are those imides prepared from (1) an aliphatic dicarboxylic anhydride, such as succinic anhydride and (2) an ethylene polyamine, such as tetraethylenepentamine, diethylenetriamine, ethylene diamine or mixtures thereof. Preferably, the imides useful in this invention will have at least two basic nitrogens.

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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
35 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

5 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 N-(2-aminoethyl)piperazine, 3-aminopyrrolidine, N-(2-aminoethyl)pyrrolidine, and the like.

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



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

15 Specific examples of polyalkylenepolyamines include, but are not limited to, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine, hexaethylenheptamine, heptaethylenoctamine, octaethylenenonamine, nonaethylenedecamine, decaethylenundecamine, undecaethylenedodecamine, dipropylenetriamine, tripropylenetetramine, tetrapropylenepentamine,
 20 pentapropylenhexamine, hexapropylenheptamine, heptapropylenoctamine, octapropylenenonamine, nonapropylenedecamine, decapropylenundecamine, 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,
 25 deca(trimethylene)undecamine and undeca(trimethylene)dodecamine.

Post-Treating Agent

In one embodiment, a post-treating agent is employed to post-treat the product of the reaction
 30 of the molybdenum component and the hydrocarbyl succinimide. Typical post-treating agents are cyclic carbonates and epoxides. Examples of post-treating agents are disclosed in Wollenberg et al., U.S. Patent No. 4,612,132, Wollenberg et al., U.S. Patent No. 4,746,446; Wollenberg et al., U.S. Patent No. 4,713,188 and the like as well as other post-treatment processes each of which are incorporated herein by reference in its entirety. Examples of
 35 other post-treating agents are disclosed in LeSeur et al., U.S. Patent No. 3,373,111 and Efner, U.S. Patent No. 4,737,160 and the like as well other post-treatment processes each of which are incorporated herein by reference in its entirety. In one embodiment, the post-treating agent may be ethylene carbonate or glycerine carbonate.

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Method for Making the Oil Soluble Composition of the Present Invention

In an embodiment of the presently claimed invention, the preparation of this invention may be carried out by reacting a dicarboxylic acid component, such as alkenyl succinic anhydride, with a polyamine component under reaction conditions thereby producing a reaction product that includes an imide component, such as succinimide. The imide reaction product may also contain amide components. The polyamine component is first charged to a reaction vessel. After the polyamine has been charged, a dicarboxylic acid component, such as alkenyl succinic anhydride, is charged to the reaction vessel. A post-treating agent is then added to the reaction mixture under reaction conditions thereby resulting in a post-treated imide reaction product. The post-treated imide reaction product is then reacted with a source of molybdenum, optionally employing a polar promoter, thereby resulting in a molybdated post-treated imide product.

In one embodiment, a polyamine component is charged to a reaction vessel. After the polyamine has been charged, a dicarboxylic acid component, such as alkenyl succinic anhydride, is charged to the reaction vessel under reaction conditions thereby producing a reaction product that includes an imide component, such as succinimide. The imide reaction product may also contain amide components. A source of molybdenum is reacted with the imide product, optionally employing a polar promoter, to form a molybdated imide product. Following removal of any polar promoter, the molybdated imide product is then reacted with a post-treating agent thereby resulting in a molybdated post-treated imide product.

The reaction is ordinarily carried out at atmospheric pressure; however, higher or lower pressures may be used, if desired, using methods that are well-known to those skilled in the art. 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.

5 As mentioned hereinabove, optionally, a polar promoter may be employed in the preparation of the present invention. The polar promoter facilitates the interaction between the molybdenum component and the basic nitrogen of the polyamine or amide component. A wide variety of such promoters may be used. Typical promoters are 1,3-propanediol, 1,4-butanediol, diethylene glycol, butyl cellosolve, propylene glycol, 1,4-butyleneglycol, methyl
10 carbitol, ethanolamine, 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.

15 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 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.

20 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 dicarboxylic acid and a polyamine in which the dicarboxylic acid and polyamine have a charge mole ratio (CMR) of between about 2:1 to 1:1. Optionally, (3) a polar promoter or (4) a diluent, to form a salt
25 or (5) both a polar promoter and a diluent may be added. The diluent is used, if necessary, to provide a suitable viscosity to facilitate mixing and handling. Typical diluents are lubricating oil and liquid 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, polar promoter, if used, and diluent, if used,
30 are charged to a reactor and heated at a temperature less than or equal to about 200°C, preferably from about 70°C to about 120°C. The temperature is maintained at a temperature less than or equal to about 200°C, preferably at about 70°C to about 90°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.

35 Typically excess water and any volatile diluents are removed from the reaction mixture. 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

5 200°C, preferably between about 70°C to about 90°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 carried out for a period of about 0.5 to about 5 hours and preferably from about 0.5 to about 2 hours.

10

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 amide. Preferably from 0.4 to 1.0, and most preferably from
15 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.

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The charge mole ratio of the dicarboxylic acid component to polyamine is critical and can range from about 1:1 to 1:0.5. In one embodiment the charge mole ratio is from about 1:1 to 1:0.7. In another embodiment the preferred charge mole ratio is about 1:0.9. The imide formed from the reaction of the hydrocarbyl dicarboxylic acid component and the polyamine
25 may occur prior to, during, or after the introduction of the molybdenum component to the reaction mixture.

The reaction mixture (i.e., the reaction of the molybdenum component, the imide component and the optional steps described hereinabove) be further reacted with a post-treating agents
30 including, but not limited to, cyclic carbonates (i.e., ethylene carbonate), acrylic acid and glycerine carbonate.

Additive Concentrates

In many instances, it may be advantageous to form concentrates of the oil soluble additive
35 composition of the present invention within a carrier fluid. These additive concentrates 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

5 soluble additive concentrates are blended with lubricant base oil stocks to provide a finished lubricant. It is desired that the carrier fluid readily solubilizes the oil soluble additive of the 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 fluid not introduce any undesirable characteristics, including, for example, high volatility, high viscosity, and impurities such as
10 heteroatoms, to the lubricant base oil stocks and thus, ultimately to the finished lubricant. The 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.

15 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 fluid.

20 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
25 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
30 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 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
35 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

5 oils and synthetic esters and mixtures thereof having the desired viscosity. Hydrocarbon 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.

10 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

15 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

20 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 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 composition. In one

25 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.

30 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 agents, stabilizers, anti-stain agents, anti-chatter agents, dropping point improvers, anti-

35 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 favorably employed in the lubricating oil compositions of the present invention. These

- 5 examples of additional additives are provided to illustrate the present invention, but they are not intended to limit it:

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
- 10 multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl naphthenates, metal salts of alkanoic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof.

15 Anti-Wear Agents

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

20

Rust Inhibitors (Anti-Rust Agents)

- Anti-rust agents reduce corrosion on materials normally subject to corrosion. Examples of anti-rust agents include, but are not limited to, nonionic polyoxyethylene surface active
- 25 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 compounds useful as anti-rust agents include, but are not limited to, stearic acid and other
- 30 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 include, but are not limited to, block copolymers of polyethylene glycol and polypropylene
- 35 glycol, polyethoxylated alkylphenols, polyesteramides, ethoxylated alkylphenol-

- 5 formaldehyde resins, polyvinylalcohol derivatives and cationic or anionic polyelectrolytes. Mixtures of different types of polymers may also be used.

Friction Modifiers

Additional friction modifiers may be added to the lubricating oil of the present invention.

- 10 Examples of friction modifiers include, but are not limited to, fatty alcohols, fatty acids, amines, ethoxylated amines, borated esters, other esters, phosphates, phosphites and phosphonates.

Multifunctional Additives

- 15 Additives with multiple properties such as anti-oxidant and anti-wear properties may also be 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
20 molybdenum complexes.

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
25 viscosity more stable as its temperature changes. Viscosity index improvers may include functionalized viscosity index improvers, such as dispersant viscosity index improvers, that may provide an additional benefit. Viscosity index improvers may be added to the lubricating oil composition of the present invention. Examples of viscosity index improvers include, but are not limited to, polymethacrylate type polymers, ethylene-propylene
30 copolymers, styrene-isoprene copolymers, alkaline earth metal salts of phosphosulfurized polyisobutylene, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.

Pour Point Depressants

- 35 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,

- 5 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
10 foam inhibitors include, but are not limited to, alkyl methacrylate polymers, alkylacrylate copolymers, and polymeric organosiloxanes such as dimethylsiloxane polymers.

Metal Deactivators

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

Dispersants

- 20 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, polyamide
25 ashless dispersants and the like or mixtures of such dispersants.

Anti-Oxidants

- 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
30 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-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),
35 2,2'-5-methylene-bis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol,

5 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-tert-butyl-phenol,
2,6-di-tert-butyl-4-dimethylamino-p-cresol, 2,6-di-tert-butyl-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-butylbenzyl)-sulfide, and
bis(3,5-di-tert-butyl-4-hydroxybenzyl). Diphenylamine-type oxidation inhibitors include, but
10 are not limited to, alkylated diphenylamine, phenyl-alpha-naphthylamine, and
alkylated-alpha-naphthylamine. Other types of oxidation inhibitors include metal
dithiocarbamate (e.g., zinc dithiocarbamate), and methylenebis(dibutyldithiocarbamate).

Applications

15 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
improved mileage for the vehicle being lubricated with a lubricating oil of this invention.

20 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
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
25 like.

Additional Applications

The oil soluble additive compositions of the invention can be envisioned as hydrotreating
catalyst precursors in addition to their use as lubricating oil additives. The oil soluble
30 additive compositions of the invention can act as a catalyst precursor and can be contacted
with hydrocarbons and decomposed, in the presence of hydrogen and sulfur or sulfur-bearing
compounds to form an active catalyst for hydrotreating a hydrocarbonaceous feedstock. The
oil soluble additive compositions of the invention can be heated to the decomposition
temperature and decomposed in the presence of hydrogen a hydrocarbon, and sulfur or sulfur-
35 bearing compounds, e.g., at "on-oil" conditions, to form the active catalyst species for
hydrotreating.

5 The nature of the hydrocarbon is not critical, and can generally include any hydrocarbon compound, acyclic or cyclic, saturated or unsaturated, unsubstituted or inertly substituted. The preferred hydrocarbons are those which are liquid at ordinary temperatures, exemplary of which are such straight chain saturated acyclic hydrocarbons as octane, tridecane, eicosane, nonacosane, or the like; straight chain unsaturated acyclic hydrocarbons as 2-hexene, 1,4-
10 hexadiene, and the like; branched chain saturated acyclic hydrocarbons as 3-methylpentane, neopentane, isohexane, 2,7,8-triethyldecane, and the like; branched chain unsaturated acyclic hydrocarbons such as 3,4-dipropyl-1,3-hexadiene-5-yne, 5,5-dimethyl-1-hexene, and the like; cyclic hydrocarbons, saturated or unsaturated, such as cyclohexane, 1,3-cyclohexadiene, and the like; and including such aromatics as cumene, mesitylene, styrene, toluene, o-xylene, or
15 the like. The more preferred hydrocarbons are those derived from petroleum, including especially admixtures of petroleum hydrocarbons characterized as virgin naphthas, cracked naphthas, Fischer-Tropsch naphtha, light cycle oil, medium cycle oil, heavy cycle oil, and the like, typically those containing from about 5 to about 30 carbon atoms, preferably from about 5 to about 20 carbon atoms and boiling within a range of from about 30°C to about 450°C,
20 preferably from about 150°C to about 300°C. In decomposing the oil soluble additive compositions of the invention to form a hydrotreating catalyst, a packed bed containing the oil soluble additive compositions of the invention is contacted in a hydrogen atmosphere with both the hydrocarbon and sulfur or sulfur-bearing compound and heated at conditions which decompose said oil soluble additive compositions of the invention.

25 The sulfur or sulfur-bearing compound is characterized as an organo-sulfur or hydrocarbyl-sulfur compound, which contains one or more carbon-sulfur bonds within the total molecule, and generally includes acyclic or cyclic, saturated or unsaturated, substituted or inertly substituted compounds. Exemplary of acyclic compounds of this character are ethyl sulfide,
30 n-butyl sulfide, n-hexylthiol, diethylsulfone, allyl isothiocyanate, dimethyl disulfide, ethylmethylsulfone, ethylmethylsulfoxide, and the like; cyclic compounds of such character are methylthiophenol, dimethylthiophene, 4-mercaptobenzoic acid, benzenesulfonic acid, 5-formamido-benzothiazole, 1-naphthalenesulfonic acid, dibenzylthiophene, and the like. The sulfur must be present in at least an amount sufficient to provide the desired stoichiometry
35 required for the catalyst, and preferably is employed in excess of this amount. Suitably, both the hydrocarbon and sulfur for the reaction can be supplied by the use of a sulfur-containing hydrocarbon compound, e.g., a heterocyclic sulfur compound, or compounds. Exemplary of heterocyclic sulfur compounds suitable for such purpose are thiophene, dibenzothiophene,

5 tetraphenylthiophene, tetramethyldibenzothiophene, tetrahydrodibenzothiophene, thianthrene, tetramethylthianthrene, and the like. The hydrogen required for forming the catalysts of this invention may be pure hydrogen, an admixture of gases rich in hydrogen or a compound which will generate in situ hydrogen, e.g., a hydrogen-generating gas such as carbon monoxide mixtures with water, or a hydrogen donor solvent.

10

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.

15 EXAMPLES

Comparative Example

To a 1000 mL 5-neck round bottom flask equipped with a mechanical stirrer, dean stark trap,
20 reflux condenser, heat mantle, thermocouple, temperature controller, addition funnel and nitrogen inlet was added 200.09 g of octadecenyl succinic anhydride (ODSA) and 100 g of a 100 neutral oil. To the stirred mixture 53.3 g of diethylene triamine (DETA) was added, dropwise, starting at 85°C. During the addition the temperature increased exothermically to 110 °C. The temperature was increased to 160 °C and was maintained overnight with
25 removal of water to form a succinimide reaction product with a TBN of 119 mgKOH/g. The succinimide product was heated to 165 °C in the same reactor and 63.4 g of molten ethylene carbonate (EC) was added. The reaction was maintained at 165 °C overnight to form an EC treated succinimide product with a TBN of 49 mgKOH/g.

30 130.15 g of the EC treated succinimide product was added to a 500 mL 4-neck round bottom flask equipped with a mechanical stirrer, dean stark trap, reflux condenser, heat mantle, thermocouple, temperature controller, addition funnel and nitrogen inlet. The succinimide was dissolved in xylene at 65 °C then 7.3 g of molybdenum trioxide, 4.9 g of deionized water, and a drop of defoamer were added. The reactants were stirred at 90 °C for 3 hours,
35 then xylenes and water were removed en vacuo at 120 °C. After filtration through diatomaceous earth in xylene and removal of solvent, a molybdated product with 3% molybdenum content was obtained.

5 *Example 1*

To a 5L 3 neck round bottom reactor flask equipped with a mechanical stirrer, dean stark trap, reflux condenser, heat mantle, thermocouple, temperature controller, addition funnel and nitrogen inlet was added 504.5 grams of diethylene triamine (DETA). The DETA was heated to 80 °C and 1901.5 grams of octadecylsuccinic anhydride (ODSA) was added to the round
 10 bottom flask via the addition funnel. The temperature increased exothermically to 120 °C during the addition of ODSA and was then increased to 160- 165 °C and held for several hours to remove water. The succinimide formed had a TBN of 174 mgKOH/g.

The succinimide was treated with ethylene carbonate (EC) in the same manner as the
 15 comparative example to form an EC treated succinimide product with a TBN of 58.4 mgKOH/g.

The EC treated succinimide was treated with molybdenum trioxide in the same manner as the comparative example to form a molybdated product with 4.55% molybdenum content.

20 The improved reaction process advantageously results in intermediate reaction products with higher TBN and a final product with a greater molybdenum content.

Examples 2-5 were prepared according to the process in Example 1. The succinimide was
 25 post-treated with ethylene carbonate or acrylic acid. When acrylic acid is the post-treating agent, then the post-treating temperature was about 70-110°C.

Table 1.

Example	Post-treatment	Dicarboxylic acid component: polyamine CMR	%Mo
2	EC	0.5	4.54
3	EC	1	5.36
4	AA	0.5	sediment
5	AA	1	4.27

5 WHAT IS CLAIMED IS:

1. An oil soluble additive composition prepared by a process comprising:
reacting,

- 10 (a) a molybdenum component;
(b) an imide derived from the reaction product of a hydrocarbyl
dicarboxylic acid component and a polyamine wherein said reaction
product is prepared by first charging a polyamine to a reaction vessel
and then charging a hydrocarbyl dicarboxylic acid component to the
15 reaction vessel, wherein the charge mole ratio of the hydrocarbyl
dicarboxylic acid component to the polyamine is from about 1:1 to
about 1:0.5; and
(c) a post-treating agent, thereby producing a post-treated molybdated
succinimide additive composition.

- 20 2. The oil soluble additive composition of claim 1, wherein the molybdenum
component is selected from the group consisting of molybdic acid, ammonium
molybdate, sodium molybdate, potassium molybdate, metal molybdates, MoOCl_4 ,
 MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{Cl}_6$, molybdenum trioxide, and mixtures thereof.

- 25 3. The oil soluble additive composition of claim 1, the hydrocarbyl dicarboxylic acid
component is a dicarboxylic acid, salt of a dicarboxylic acid, anhydride of a
dicarboxylic acid, ester of a dicarboxylic acid ester, or mixtures thereof.

- 30 4. The oil soluble additive composition of claim 3, wherein the wherein the
hydrocarbyl dicarboxylic acid component is an alkyl or alkenyl succinic
anhydride.

5. 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.

- 5 6. The oil soluble composition of claim 5, wherein the polyamine is
tetraethylenepentamine (TEPA), diethylenetriamine (DETA), ethylenediamine
(EDA), or mixtures thereof.
- 10 7. The oil soluble additive composition of claim 1 wherein the post-treating agent is
a cyclic carbonate.
- 15 8. A lubricating oil composition comprising:
a. an oil of lubricating viscosity; and
b. the reaction product of
15 i. a molybdenum component;
ii. an imide derived from the reaction product of a hydrocarbyl dicarboxylic acid
component and a polyamine component wherein said imide comprises the
reaction product prepared by first charging a polyamine to a reaction vessel
and then charging a dicarboxylic acid component to the reaction vessel,
20 wherein the charge mole ratio of the hydrocarbyl dicarboxylic acid
component to the polyamine component is from about 1:1 to about 1:0.5; and
iii. a post-treating agent, thereby producing a post-treated molybdated
succinimide additive composition.
- 25 9. The lubricating oil composition of claim 8, wherein the molybdenum content of
the lubricating oil composition is between about 50 ppm and 5000 ppm.
- 30 10. The lubricating oil composition of claim 8, wherein the oil soluble additive
composition content is between 0.05 to 15% by weight.
- 35 11. The oil soluble additive composition of claim 8, wherein the post-treating agent is
a cyclic carbonate.
12. A process for preparing an oil soluble additive composition which comprises
reacting:
 (a) a molybdenum component;
 (b) an imide derived from the reaction product of a hydrocarbyl
dicarboxylic acid component and a polyamine wherein said reaction

5 product is prepared by first charging a polyamine to a reaction vessel
and then charging a dicarboxylic acid component to the reaction vessel,
wherein the charge mole ratio of the dicarboxylic acid component to
the polyamine component is from about 1:1 to about 1:0.5; and
(c) a post-treating agent, thereby producing a post-treated molybdated
10 succinimide additive composition.

13. The process of claim 12, wherein the hydrocarbyl dicarboxylic acid component is
a dicarboxylic acid, salt of a dicarboxylic acid, anhydride of a dicarboxylic acid,
ester of a dicarboxylic acid ester, or mixtures thereof.

15

14. The process of claim 13, wherein the hydrocarbyl dicarboxylic acid component is
an alkyl or alkenyl succinic anhydride.

20

15. The process of claim 12, wherein said reaction of said molybdenum component
and said imide is in the presence of a polar promoter.

25

16. The process of claim 15, 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, inorganic acid, and mixtures thereof.

30

17. The process of claim 12, wherein the molybdenum component is selected from the
group consisting of molybdic acid, ammonium molybdate, sodium molybdate,
potassium molybdate, metal molybdates, MoOCl_4 , MoO_2Br_2 , $\text{Mo}_2\text{O}_3\text{C}_{16}$,
molybdenum trioxide, and mixtures thereof.

35

18. The process of claim 12, wherein the polyamine component comprises a
polyalkylenepolyamine represented by the general formula



- 5 and wherein R is an alkylene group of 2-3 carbon atoms and n is an integer of from 1 to 11.
19. The process of claim 18, wherein the polyamine component is
10 tetraethylenepentamine (TEPA), diethylenetriamine (DETA), ethylenediamine (EDA), or mixtures thereof.
20. The oil soluble additive composition of claim 19, wherein the post-treating agent is a cyclic carbonate.