(12) STANDARD PATENT (11) Application No. **AU 2017202845 B2**
(19) AUSTRALIAN PATENT OFFICE

(54) Title
AROMATIC IMIDES AND ESTERS AS LUBRICANT ADDITIVES

(51) International Patent Classification(s)
C10M 129/72 (2006.01) *C10N 30/12* (2006.01)
C10M 133/16 (2006.01) *C10N 40/04* (2006.01)
C10N 30/06 (2006.01) *C10N 40/25* (2006.01)

(21) Application No: **2017202845** (22) Date of Filing: **2017.04.28**

(43) Publication Date: **2017.05.18**
(43) Publication Journal Date: **2017.05.18**
(44) Accepted Journal Date: **2019.01.17**

(62) Divisional of:
2012253694

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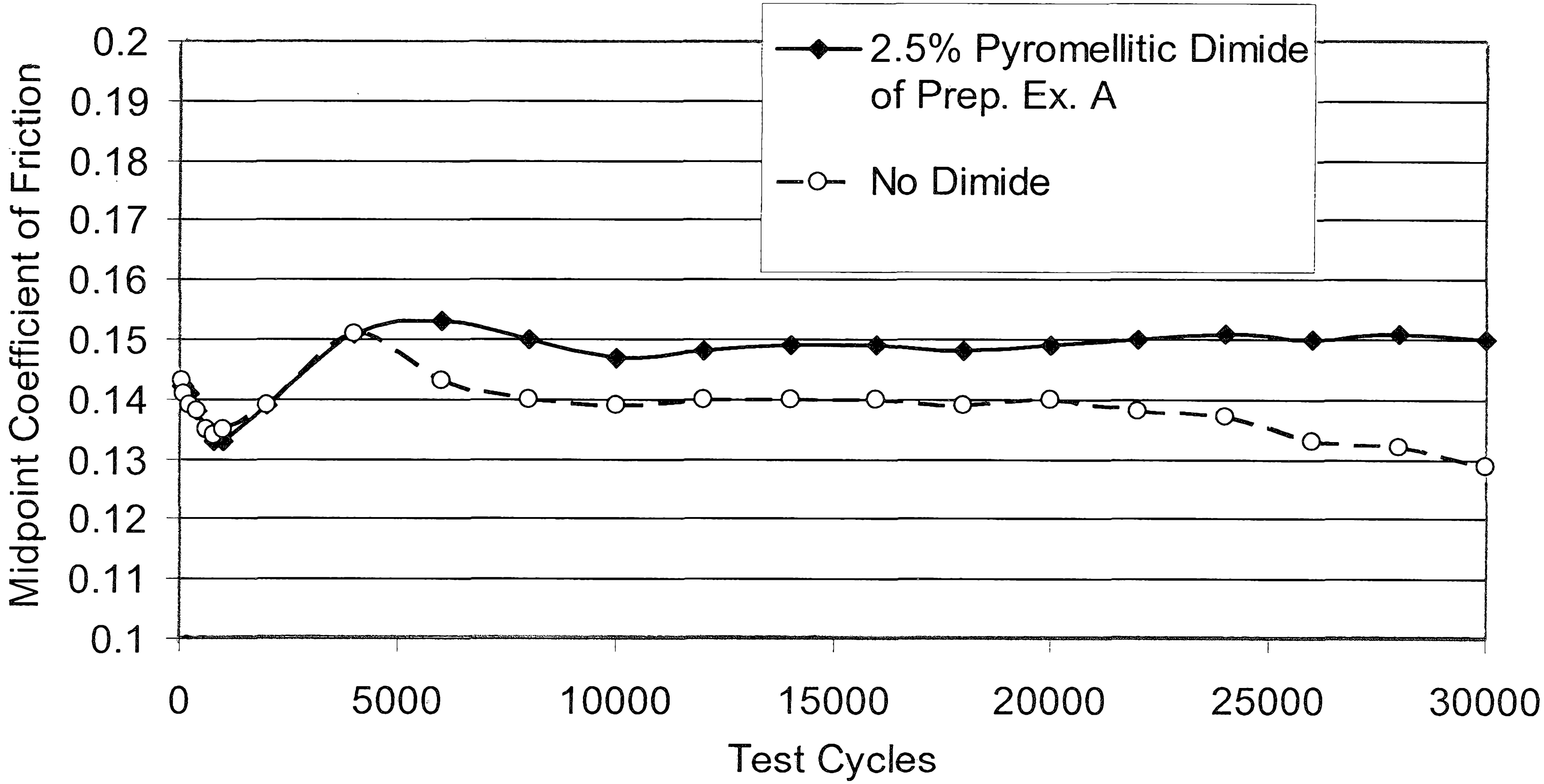
(56) Related Art
US 3078228 A
US 20100009876 A1
US 4661277 A

ABSTRACT OF THE DISCLOSURE

A composition useful as a lubricant for an automatic transmission comprises an oil of lubricating viscosity and a condensation product of an aromatic polycarboxylic acid or mixtures thereof or a reactive equivalent thereof, having at least two carboxylic groups situated so as to permit formation of a cyclic imide having 5 or 6 atoms in said cyclic structure; with an aliphatic primary amine or alcohol, containing 6 to 60 carbon atoms.

Fig. 1


2.5% Pyromellitic Dimide of Prep. Ex. A
No Dimide
Midpoint Coefficient of Friction
0.2
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.1
0
5000
10000
15000
20000
25000
30000
Test Cycles

2017202845 28 Apr 2017

P/00/011
Regulation 3.2

AUSTRALIA

Patents Act 1990

COMPLETE SPECIFICATION

FOR A DIVISIONAL PATENT

ORIGINAL

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Invention Title: AROMATIC IMIDES AND ESTERS AS LUBRICANT ADDITIVES

The following statement is a full description of this invention, including the best method of performing it known to the Applicant:-

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TITLE

Aromatic Imides and Esters as Lubricant Additives

[0001] The present Application is a Divisional Application from Australian Patent Application No. 2012253694. The entire disclosures of Australian Patent Application No. 2012253694 and its corresponding International Patent Application No. PCT/US2012/036867, are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] The present technology relates to the field of additives for fluids such as automatic transmission fluids, traction fluids, fluids for continuously variable transmission fluids (CVTs), dual clutch automatic transmission fluids, farm tractor fluids, engine lubricants, industrial gear lubricants, greases, and hydraulic fluids, as well as for lubricants such as engine oils.

[0003] In the automatic transmission marketplace, where there is rapid engineering change driven by the desire to reduce weight and increase transmission capacity, there is a desire for automatic transmission fluids that exhibit a high static coefficient of friction for improved clutch holding capacity. Continuously slipping torque converter clutches, for instance, impose exacting friction requirements on automatic transmission fluids (ATFs). The fluid must have a good friction versus sliding speed relationship, or an objectionable phenomenon called shudder will occur in the vehicle. Transmission shudder is a self-excited vibrational state also called "stick-slip" or "dynamic frictional vibration," generally occurring in slipping torque converter clutches. The friction characteristics of the fluid and material system, combined with the mechanical design and controls of the transmission, determine the susceptibility of the transmission to shudder. A plot of the measured coefficient of friction (μ) versus sliding speed (V), commonly called a μ-V curve, has been shown to correlate to transmission shudder. Both theory and experiments support the region of positive to slightly negative slope of this μ-V curve to correlate to good anti-shudder performance of transmission fluids. A fluid which allows the vehicle to operate without vibration or shudder is said to have good anti-shudder performance. The fluid should maintain those characteristics over its service lifetime. The longevity of the anti-shudder performance in the vehicle is commonly referred to as "anti-shudder durability." The variable speed friction tester (VSFT) measures the coefficient of friction with respect to sliding speed simulating the speeds, loads, and friction materials found in transmission clutches and correlates to the performance found in actual use. The procedures are well documented in the literature; see for example Society of Automotive Engineers publication #941883.

[0004] The combined requirements of high static coefficient of friction and durable positive slope are often incompatible with traditional ATF friction modifier technology, which is extremely well described in the patent literature. Many of the commonly used friction modifiers result in a low static coefficient of friction and do not have sufficient positive slope durability to be of practical use.

[0005] PCT Publication WO2010/132318, November 18, 2010, discloses a condensation product of a hydroxy-polycarboxylic acid with an N,N-di(hydrocarbyl) alkylenediamine, where each hydrocarbyl group independently comprises 1 to about 22 carbon atoms. The product may be an amide or an imide.

[0006] U.S. Patent Application 2008/0051307, Li, February 28, 2008, discloses a lubricating composition containing (a) a major amount of an ester of a polycarboxylic acylating agent; and (b) at least one compound from (i) a metal hydrocarbyl dithiophosphate, or (ii) a viscosity modifier. The composition is suitable for high temperature engines. The polycarboxylic acylating agent may be, among others, pyromellitic acid.

[0007] U.S. Patent 4,237,022, Barrer, December 2, 1980, discloses tartarimides and lubricants and fuels containing the same. In an example (IX), an automatic transmission fluid is reported containing the reaction product of tartaric acid with Armeen O (essentially oleylamine).

[0008] U.S. Patent Application 2006/0183647, Kocsis et al., August 16, 2006, discloses tartrates, tartrimides, tartramides or combinations thereof useful as additives for lubricants. Various compositions including automatic transmission fluids are said to benefit therefrom. Among the materials disclosed are oleyl tartrimide and tridecylpropoxyamine tartrimide. The alkyl groups of the amines may be linear or branched.

[0009] U.S. Patent 4,789,493, Horodysky, December 6, 1988, discloses lubricants containing N-alkylalkylenediamine amides. Disclosed is $R^2–N(R^3)–R^1–NH–R^3$ wherein R^1 is a C_2 to C_4 alkylene group, R^2 must be a C_{12} to C_{30} hydrocarbyl group, and R^3 is

H, a C_1-C_3 aliphatic group, or R^4-C(=O)-; at least one of the R^3s must be R^4-C(=O)-. R^4 is H or C_{1-4}. An example is Coco-NH-$(CH_2)_3$–NH–C(=O)H .

[0010] U.S. Patent 3,251,853, Hoke, May 17, 1966, discloses an oil-soluble acylated amine. In examples, reactants can xylyl-stearic acid or heptylphenyl-heptanoic acid, with tetraethylene pentamine or dodecylamine or N-2-aminoethyloctadecylamine. An example is the condensation product of N-2-aminoethyloctadecylamine with xylyl-stearic acid.

[0011] U.S. Patent publication 2009/0005277, Watts et al., January 1, 2009, discloses lubricating oil compositions said to have excellent friction stability, comprising, among other components, a polyalkylene polyamine-based friction modifier that has been reacted with an acylating agent to convert at least one secondary amine group into an amide.

[0012] The disclosed technology, therefore, in certain embodiments, provides a friction modifier suitable for providing a transmission fluid, such as an automatic transmission fluid, with a high coefficient of friction or a durable positive slope in a μ-V curve, or both.

[0013] There is also a need for lubricants that exhibit antiwear performance and corrosion inhibition when used to lubricate a mechanical device such as an internal combustion engine, particularly in formulations characterized by low sulfated ash, phosphorus, and sulfur levels. In certain embodiments, the disclosed technology provides one or more of antiwear performance and corrosion inhibition when used to lubricate a mechanical device.

SUMMARY OF THE INVENTION

[0014] The disclosed technology provides a composition comprising (a) an oil of lubricating viscosity and (b) a condensation product of (i) an aromatic polycarboxylic acid or mixtures thereof or a reactive equivalent thereof, having at least two carboxylic groups situated so as to permit formation of a cyclic imide having 5 or 6 atoms in said cyclic structure; with (ii) an aliphatic primary amine or alcohol, containing 6 to 80 carbon atoms.

[0015] In certain embodiments, the aliphatic primary amine or alcohol comprises a primary amine containing 12 to 60 carbon atoms and further containing a secondary or tertiary amino group or an ether group.

[0015a] The disclosed technology further provides a composition comprising (a) an oil of lubricating viscosity and (b) about 0.0001 to about 10 weight percent of a condensation product of (i) an aromatic polycarboxylic acid or mixtures thereof or a reactive equivalent thereof, having at least two carboxylic groups attached to two adjacent carbon atoms, or attached to two carbon atoms which are separated by one atom, but not attached in positions meta to each other on an aromatic ring, the aromatic polycarboxylic acid or reactive equivalent thereof comprising an aromatic ring substituted by at least one succinic acid group or reactive equivalent thereof; with (ii) an aliphatic primary amine comprising N,N-dialkyl-1,3-propanediamine containing 12 to 60 carbon atoms, said condensation product comprising an imide or an amide.

[0016] The disclosed technology further provides a method for lubricating a mechanical device, comprising supplying thereto any of the above-described compositions. In certain embodiments the mechanical device comprises an automatic transmission. In certain embodiments the composition imparts useful frictional properties when lubricating an automatic transmission.

BRIEF DESCRIPTION OF THE FIGURE

[0017] Figure 1 shows the coefficient of friction over 30,000 test cycles provided by a lubricant containing a pyromellitic diimide of the disclosed technology.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Various features and embodiments will be described below by way of non-limiting illustration.

[0019] One component which is used in certain embodiments of the disclosed technology is an oil of lubricating viscosity, which can be present in a major amount, for a lubricant composition, or in a concentrate forming amount, for a concentrate. Suitable oils include natural and synthetic lubricating oils and mixtures thereof. In a fully formulated lubricant, the oil of lubricating viscosity is generally present in a major amount (i.e. an amount greater than 50 percent by weight). Typically, the oil of lubricating viscosity is present in an amount of 75 to 95 percent by weight, and often greater than 80 percent by weight of the composition.

[0020] Natural oils useful in making the inventive lubricants and functional fluids include animal oils and vegetable oils as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic/naphthenic types which may be further refined by hydrocracking and hydrofinishing processes.

[0021] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins, also known as polyalphaolefins; polyphenyls; alkylated diphenyl ethers; alkyl- or dialkylbenzenes; and alkylated diphenyl sulfides; and the derivatives, analogs and homologues thereof. Also included are alkylene oxide polymers and interpolymers and derivatives thereof, in which the terminal hydroxyl groups may have been modified by esterification or etherification. Also included are esters of dicarboxylic acids with a variety of alcohols, or esters made from C5 to C12 monocarboxylic acids and polyols or polyol ethers.

Other synthetic oils include silicon-based oils, liquid esters of phosphorus-containing acids, and polymeric tetrahydrofurans.

[0022] Unrefined, refined and rerefined oils, either natural or synthetic, can be used in the lubricants of the present technology (that is, of the presently disclosed technology). Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Refined oils have been further treated in one or more purification steps to improve one or more properties. They can, for example, be hydrogenated, resulting in oils of improved stability against oxidation.

[0023] In one embodiment, the oil of lubricating viscosity is an API Group I, Group II, Group III, Group IV, or Group V oil, including a synthetic oil, or mixtures thereof. In another embodiment, the oil is Groups II, III, IV, or V. These are classifications established by the API Base Oil Interchangeability Guidelines. Group III oils contain $\leq$0.03 percent sulfur and $\geq$90 percent saturates and have a viscosity index of $\geq$120. Group II oils have a viscosity index of 80 to 120 and contain $\leq$0.03 percent sulfur and $\geq$90 percent saturates. Polyalphaolefins are categorized as Group IV. The oil can also be an oil derived from hydroisomerization of wax such as slack wax or a Fischer-Tropsch synthesized wax. Such “Gas-to-Liquid” oils are typically characterized as Group III. Group V is encompasses “all others” (except for Group I, which contains >0.03% S and/or <90% saturates and has a viscosity index of 80 to 120).

[0024] In one embodiment, at least 50% by weight of the oil of lubricating viscosity is a polyalphaolefin (PAO). Typically, the polyalphaolefins are derived from monomers having from 4 to 30, or from 4 to 20, or from 6 to 16 carbon atoms. Examples of useful PAOs include those derived from 1-decene. These PAOs may have a viscosity of 1.5 to 150 mm^2/s (cSt) at 100°C. PAOs are typically hydrogenated materials.

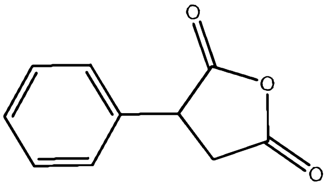
[0025] The oils of the present technology can encompass oils of a single viscosity range or a mixture of high viscosity and low viscosity range oils. In one embodiment, the oil exhibits a 100°C kinematic viscosity of 1 or 2 to 8 or to 10 mm^2/sec (cSt). The overall lubricant composition may be formulated using oil and other components such that the viscosity at 100°C is 1 or 1.5 to 10 or to 15 or to 20 mm^2/sec and the Brookfield viscosity (ASTM-D-2983) at –40°C is less than 20 or 15 Pa-s (20,000 cP or 15,000 cP), such as less than 10 Pa-s, even 5 or less.

[0026] The present technology provides, as one component, a condensation product of an aromatic polycarboxylic acid or mixtures thereof or a reactive equivalent thereof, having at least two carboxylic groups situated so as to permit formation of a cyclic imide having 5 or 6 atoms in said cyclic structure; with an aliphatic primary amine or alcohol, containing 6 to 60 carbon atoms. As used herein, the term "aliphatic" may, in some embodiments, include both cyclic and non-cyclic groups (i.e., "alicyclic"), and in other embodiments, it may be limited to non-cyclic groups. In certain embodiments, these materials are useful as friction modifiers, particularly for lubricating automatic transmissions. In other embodiments, these materials are useful as antiwear agents or corrosion inhibitors, particularly for lubricating internal combustion engines.

[0027] The aromatic polycarboxylic acid or reactive equivalent thereof may be a diacid, a triacid, a tetraacid, or a higher acid (or reactive equivalents). If the reaction product is a monoimide, the polycarboxylic acid will contain at least two acid (or equivalent) groups. If the reaction product is a diimide, the polycarboxylic acid will contain at least four acid (or equivalent) groups. The acid groups are situated so as to permit formation of a 5-membered or 6-membered cyclic imide, which means that they may be, for instance, in positions *ortho* to each other on an aromatic ring, or having other relationships as described in greater detail below (e.g., two carbonyl groups may be attached to two adjacent carbon atoms, or to two carbon atoms which in turn are separated by one atom, but not generally attached in positions *meta* to each other on an aromatic ring). However, this language should not be interpreted to require that that a cyclic imide is necessarily formed in each instance. For instance, amides or esters would not form a cyclic imide structure, but the same geometric relationship of the precursor acid groups would be applicable.

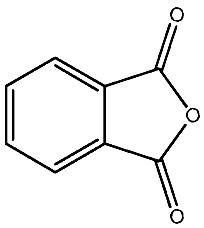
[0028] Reactive equivalents of carboxylic acids include acids, esters, acid halides such as acid chlorides, and anhydrides. The term "carboxylic acid" may be used in this document for simplicity to refer designate a carboxylic acid or a reactive equivalent thereof. For their ready availability and ease of reaction, anhydrides, especially cyclic anhydrides, are often used. Cyclic anhydrides would typically have their carboxylic groups situated so as to permit formation of a cyclic imide having 5 or 6 carbon atoms in a cyclic structure, since cyclic anhydrides themselves would normally constitute a cyclic structure of 5 or 6 atoms. The condensation products of the present technology may have, but will not necessarily have, a cyclic imide structure: they may comprise, for instance, an ester or an amide group or an imidazoline group. The reaction product of an anhydride with an amine or alcohol is usually termed a condensation product, even though a small molecule such as water may not be generated by reaction under all circumstances.

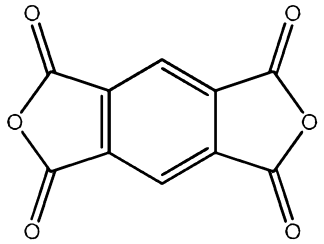
[0029] The carboxylic acid groups may be attached directly to an aromatic group, or they may be indirectly attached through intervening carbon atoms. An example of a material of the latter sort would be an aromatic ring substituted by at least one succinic acid (or anhydride) group, with other ring substituents also optionally present, such as phenylsuccinic acid or anhydride:

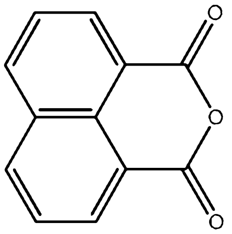


This material has two carboxylic groups situated so as to permit formation of a cyclic imide having 5 carbon atoms in the cyclic structure.

[0030] In other embodiments the aromatic polycarboxylic acid may comprise an aromatic group with at least two carboxylic groups bonded directly to at least two aromatic carbon atoms. The aromatic groups may be simple (one ring) or condensed rings. The carboxylic acid groups may be on adjacent positions on an aromatic ring (e.g., ortho to each other) or they may be appropriately situated on different aromatic rings. Examples include phthalic anhydride, pyromellitic anhydride, and naphthalene-1,8-dioic anhydride. The former have groups on a benzene ring; the latter has groups on a naphthalene (i.e., condensed) ring. The latter is an example of a material having two carboxylic acid groups located on positions 1 and 8 and capable of forming a cyclic imide with 6 atoms in the ring:







[0031] There may be additional substituents on any of the aromatic rings, including additional carboxylic acid groups, hydrocarbyl groups, hydroxy groups, ether groups, and additional aromatic groups (including fused or non-fused rings). Additionally, one carboxylic group may be directly attached to an aromatic ring and a second may be joined through one or more carbon atoms, e.g., 2-carboxymethylbenzoic anhydride.

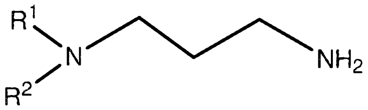
[0032] The aromatic polycarboxylic acid will be condensed with a primary amine or alcohol containing 6 to 60 carbon atoms. The type of condensation product obtained will depend on the reactants. If the reactant is an alcohol, the product will be an ester, either a monoester (i.e., partial esters) or a polyester (that is, a diester, triester, or tetraester, depending on the identity of the aromatic polycarboxylic acid. Polymeric products are not intended by the term "polyester," although polymeric materials would not necessarily be precluded). The type of ester would depend the number of equivalents of the alcohol that are reacted. If the reactant is a primary amine, the product may be an amide or an imide, depending, again, on the number of equivalents of amine reacted and the reaction conditions, as will be evident to the person skilled in the art. More severe conditions are typically required to form the cyclic imide. In certain embodiments the condensation product comprises an imide, and in certain cases a diimide. In certain embodiments the condensation product comprises a pyromellitic diimide.

[0033] The reaction product may be a condensation product with an aliphatic primary amine or an aliphatic alcohol. The product may comprise an ester, amide, or imide, and the imide may be a cyclic imide. The primary amine or alcohol may contain 6 to 80 carbon atoms, or 8 to 70 carbon atoms, or 12 to 60 carbon atoms, or 16 to 50 carbon atoms, or 18 to 40 carbon atoms. The primary amine or the alcohol, having any of the foregoing carbon numbers, may further contain a secondary or a tertiary amino group or an ether group, which may disrupt the carbon chain. In some instances, the carbon atom that would normally be at position 3, 4, 5, 6, or 7 in the carbon chain of the amine or alcohol is replaced by an oxygen or nitrogen atom. In some embodiments this replacement atom is at position 4.

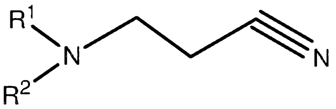
[0034] In certain embodiments, the product is a condensation product with an aliphatic primary amine represented by the formula $H_2N\text{-}(C_nH_{2n})\text{–}X\text{–}R^1$, wherein n is 2 to 6, X is O or N–R^2, R^1 is an alkyl group of at least 8 or at least 10 carbon atoms, and R^2 is H or an alkyl group. Groups R^1 and R^2 may be alkyl groups containing at least 4 carbon atoms, for instance, 6 to 40 or 8 to 30 or 10 to 24 or 12 to 20 or 16 to 18 carbon atoms, and mixtures of such groups. In certain embodiments, the aliphatic primary amine of the above structure comprises an N,N-dialkyl-1,3-propanediamine, which may comprise, for instance, N,N-di-hydrogenatedtallow-1,3-propanediamine, N,N-dicoco-1,3-propanediamine, or N,N-diisostearyl-1,3-propanediamine.

[0035] The hydrocarbyl group or groups within the amine or alcohol may comprise a mixture of individual groups on the same or different molecules having a variety of carbon numbers falling generally within the range of carbon numbers set forth above, although molecules with hydrocarbyl groups falling outside this range may also be present. If a mixture of hydrocarbyl groups is present, they may be primarily of even carbon number (e.g., 12, 14, 16, 18, 20, or 22) as is characteristic of groups derived from many naturally-occurring materials, or they may be a mixture of even and odd carbon numbers or, alternatively, an odd carbon number or a mixture of odd numbers. They may be branched, linear, or cyclic and may be saturated or unsaturated, or combinations thereof. In certain embodiments the hydrocarbyl groups may contain 16 to 18 carbon atoms, and sometimes predominantly 16 or predominantly 18. Specific examples include mixed "coco" groups from cocoamine (predominantly C12 and C14 amines) and mixed "tallow" groups from tallowamine (predominantly C16 and C18 groups), "isostearyl" groups (e.g., isooctadecyl or 16-methylheptadecyl groups), and 2-ethylhexyl groups.

[0036] Diamines suitable for preparing such products include those in the Duomeen™ series, available from AkzoNobel, having a general structure such as

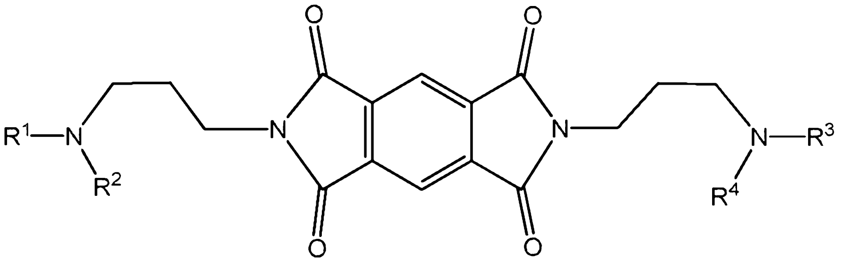


Such polyamines may be prepared by the addition of the monoamine R^1R^2NH to acrylonitrile, to prepare the alkyl nitrile amine (cyanoalkyl amine),



followed by catalytic reduction of the nitrile group using, e.g., H_2 over Pd/C catalyst, to give the diamine.

[0037] Some specific examples of the materials of the disclosed technology include those represented by the following structure (I):



(I)

In this representation, each of R^1 and R^3 may be independently an alkyl group of 10 to 22 carbon atoms and each of R^2 and R^4 may be independently hydrogen or an alkyl group of 1 to 22 carbon atoms, provided that the total number of carbon atoms in R^1 and R^2 is at least 13 and the total number of carbon atoms in R^3 and R^4 is at least about 13. In certain embodiments, R^1, R^2, R^3, and R^4 are independently alkyl groups characteristic of tallowamine (including hydrogenated "tallow" groups) or cocoamine.

[0038] The amount of the condensation product in a fully formulated lubricant may broadly be 0.0001 to 10 percent by weight. When it is employed to lubricate a transmission, suitable amounts include 0.05 to 10 percent by weight, or 0.1 to 10 percent, or 0.3 to 5 percent, or 0.5 to 6 percent or 0.5 to 2.5 percent, or 0.8 to 4 percent, or 1 to 2.5 percent, or 0.8 to 2 percent When it is used to lubricate an internal combustion engine, suitable amounts include 0.0001 to 0.1 percent by weight, or 0.001 to 0.05 percent or 0.002 to 0.03 percent.

[0039] Other components may be present. One such component is a dispersant. It may be described as "other than a condensation product as described above" in the event that some of the products described above may exhibit dispersant characteristics. Examples of dispersants are described in many U.S. Patents including the following: 3,219,666, 3,316,177, 3,340,281, 3,351,552, 3,381,022, 3,433,744, 3,444,170, 3,467,668, 3,501,405, 3,542,680, 3,576,743, 3,632,511, 4,234,435, Re 26,433, and 6,165,235.

[0040] Succinimide dispersants, a species of carboxylic dispersants, are prepared by the reaction of a hydrocarbyl-substituted succinic anhydride (or reactive equivalent thereof, such as an acid, acid halide, or ester) with an amine, as described above. The hydrocarbyl substituent group generally contains an average of at least 8, or 20, or 30, or 35 up to 350, or to 200, or to 100 carbon atoms. In one embodiment, the hydrocarbyl group is derived from a polyalkene. Such a polyalkene can be characterized by an $\overline{M}_n$ (number average molecular weight) of at least 500. Generally, the polyalkene is characterized by an $\overline{M}_n$ of 500, or 700, or 800, or 900 up to 5000, or to 2500, or to 2000, or to 1500. In another embodiment $\overline{M}_n$ varies from 500, or 700, or 800, to 1200 or to 1300. In one embodiment the polydispersity ($\overline{M}_w / \overline{M}_n$) is at least 1.5.

[0041] The polyalkenes include homopolymers and inter-polymers of polymerizable olefin monomers of 2 to 16 or to 6, or to 4 carbon atoms. The olefins may be monoolefins such as ethylene, propylene, 1-butene, isobutene, and 1-octene; or a polyolefinic monomer, such as diolefinic monomer, such 1,3-butadiene and isoprene. In one embodiment, the inter-polymer is a homo-polymer. An example of a polymer is a polybutene. In one instance about 50% or at least 50% of the polybutene is derived from isobutylene. The polyalkenes can be prepared by conventional procedures.

[0042] In one embodiment, the succinic acylating agents are prepared by reacting a polyalkene with an excess of maleic anhydride to provide substituted succinic acylating agents wherein the number of succinic groups for each equivalent weight of substituent group is at least 1.3, e.g., 1.5, or 1.7, or 1.8. The maximum number of succinic groups per substituent group generally will not exceed 4.5, or 2.5, or 2.1, or 2.0. The preparation and use of substituted succinic acylating agents wherein the substituent is derived from such polyolefins are described in U.S. Patent 4,234,435.

[0043] The substituted succinic acylating agent can be reacted with an amine, including those amines described above and heavy amine products known as amine still bottoms. The amount of amine reacted with the acylating agent is typically an amount to provide a mole ratio of CO:N of 1:2 to 1:0.25, or 1:2 to 1:0.75. If the amine is a primary amine, complete condensation to the imide can occur. Varying amounts of amide product, such as the amidic acid, may also be present. If the reaction is, rather, with an alcohol, the resulting dispersant will be an ester dispersant. If both amine and alcohol functionality are present, whether in separate molecules or in the same molecule (as in the above-described condensed amines), mixtures of amide, ester, and possibly imide functionality can be present. These are the so-called ester-amide dispersants.

[0044] "Amine dispersants" are reaction products of relatively high molecular weight aliphatic or alicyclic halides and amines, such as polyalkylene polyamines. Examples thereof are described in the following U.S. Patents: 3,275,554, 3,438,757, 3,454,555, and 3,565,804.

[0045] "Mannich dispersants" are the reaction products of alkyl phenols in which the alkyl group contains at least 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). The materials described in the following U.S. Patents are illustrative: 3,036,003, 3,236,770, 3,414,347, 3,448,047, 3,461,172, 3,539,633, 3,586,629, 3,591,598, 3,634,515, 3,725,480, 3,726,882, and 3,980,569.

[0046] Post-treated dispersants are also part of the present technology. They are generally obtained by reacting carboxylic, amine or Mannich dispersants with reagents such as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds such as boric acid (to give "borated dispersants"), phosphorus compounds such as phosphorus acids or anhydrides, or 2,5-dimercaptothiadiazole (DMTD). Exemplary materials of this kind are described in the following U.S. Patents: 3,200,107, 3,282,955, 3,367,943, 3,513,093, 3,639,242, 3,649,659, 3,442,808, 3,455,832, 3,579,450, 3,600,372, 3,702,757, and 3,708,422.

[0047] Mixtures of dispersants can also be used. The amount of dispersant or dispersants, if present in formulations of the present technology, is generally 0.3 to 10 percent by weight. In other embodiments, the amount of dispersant is 0.5 to 7 percent or 1 to 10 percent or 1 to 5 percent or 1.5 to 9 percent or 2 to 8 percent of the final blended fluid formulation. In a concentrate, the amounts will be proportionately higher.

[0048] Another component frequently used is a viscosity modifier. Viscosity modifiers (VM) and dispersant viscosity modifiers (DVM) are well known. Examples of VMs and DVMs may include polymethacrylates, polyacrylates, polyolefins, styrene-maleic ester copolymers, and similar polymeric substances including homopolymers, copolymers and graft copolymers. The DVM may comprise a nitrogen-containing methacrylate polymer, for example, a nitrogen-containing methacrylate polymer derived from methyl methacrylate and dimethylaminopropyl amine.

[0049] Examples of commercially available VMs, DVMs and their chemical types may include the following: polyisobutylenes (such as Indopol™ from BP Amoco or Parapol™ from ExxonMobil); olefin copolymers (such as Lubrizol™ 7060, 7065, and 7067 from Lubrizol and Lucant™ HC-2000L and HC-600 from Mitsui); hydrogenated styrene-diene copolymers (such as Shellvis™ 40 and 50, from Shell and LZ® 7308, and 7318 from Lubrizol); styrene/maleate copolymers, which are dispersant copolymers (such as LZ® 3702 and 3715 from Lubrizol); polymethacrylates, some of which have dispersant properties (such as those in the Viscoplex™ series from RohMax, the Hitec™ series of viscosity index improver from Afton, and LZ 7702™, LZ 7727™, LZ 7725™ and LZ 7720C™ from Lubrizol); olefin-graft-polymethacrylate polymers (such as Viscoplex™ 2-500 and 2-600 from RohMax); and hydrogenated polyisoprene star polymers (such as Shellvis™ 200 and 260, from Shell). Also included are Asteric™ polymers from Lubrizol (methacrylate polymers with radial or star architecture). Viscosity modifiers that may be used are described in U.S. patents 5,157,088, 5,256,752 and 5,395,539. The VMs and/or DVMs may be used in the functional fluid at a concentration of up to 20% by weight. Concentrations of 1 to 12%, or 3 to 10% by weight may be used.

[0050] Another component that may be used in the composition used in the present technology is a supplemental friction modifier. These friction modifiers are well known to those skilled in the art. A list of friction modifiers that may be used is included in U.S. Patents 4,792,410, 5,395,539, 5,484,543 and 6,660,695. U.S. Patent 5,110,488 discloses metal salts of fatty acids and especially zinc salts, useful as friction modifiers. A list of supplemental friction modifiers that may be used may include:

fatty phosphites
fatty acid amides
fatty epoxides
borated fatty epoxides
fatty amines other than the fatty
    amines discussed above
glycerol esters
borated glycerol esters
alkoxylated fatty amines
oxazolines
hydroxyalkyl amides
dialkyl tartrates
borated alkoxylated fatty amines
metal salts of fatty acids
sulfurized olefins
fatty imidazolines
condensation products of carboxylic
    acids and polyalkylene-polyamines
metal salts of alkyl salicylates
amine salts of alkylphosphoric acids
ethoxylated alcohols
imidazolines
polyhydroxy tertiary amines
molybdenum compounds

— and mixtures of two or more thereof.

[0051] Representatives of each of these types of friction modifiers are known and are commercially available. For instance, fatty phosphites may be generally of the formula $(RO)_2PHO$ or $(RO)(HO)PHO$ where R may be an alkyl or alkenyl group of sufficient length to impart oil solubility. Suitable phosphites are available commercially and may be synthesized as described in U.S. Patent 4,752,416.

[0052] Borated fatty epoxides that may be used are disclosed in Canadian Patent No. 1,188,704. These oil-soluble boron- containing compositions may be prepared by reacting a boron source such as boric acid or boron trioxide with a fatty epoxide which may contain at least 8 carbon atoms. Non-borated fatty epoxides may also be useful as supplemental friction modifiers.

[0053] Borated amines that may be used are disclosed in U.S. Patent 4,622,158. Borated amine friction modifiers (including borated alkoxylated fatty amines) may be prepared by the reaction of a boron compounds, as described above, with the corresponding amines, including simple fatty amines and hydroxy containing tertiary amines. The amines useful for preparing the borated amines may include commercial alkoxylated fatty amines known by the trademark “ETHOMEEN” and available from Akzo Nobel, such as bis[2-hydroxyethyl]-coco-amine, polyoxyethylene[10]cocoamine, bis[2-hydroxyethyl]soyamine, bis[2-hydroxyethyl]-tallow-amine, polyoxyethylene-[5]tallowamine, bis[2-hydroxyethyl]oleyl-amine, bis[2-hydroxyethyl]octadecylamine, and polyoxyethylene[15]octadecylamine. Such amines are described in U.S. Patent 4,741,848.

[0054] Alkoxylated fatty amines and fatty amines themselves (such as oleylamine) may be useful as friction modifiers. These amines are commercially available.

[0055] Both borated and unborated fatty acid esters of glycerol may be used as friction modifiers. Borated fatty acid esters of glycerol may be prepared by borating a fatty acid ester of glycerol with a boron source such as boric acid. Fatty acid esters of glycerol themselves may be prepared by a variety of methods well known in the art. Many of these esters, such as glycerol monooleate and glycerol tallowate, are manufactured on a commercial scale. Commercial glycerol monooleates may contain a mixture of 45% to 55% by weight monoester and 55% to 45% by weight diester.

[0056] Fatty acids may be used in preparing the above glycerol esters; they may also be used in preparing their metal salts, amides, and imidazolines, any of which may also be used as friction modifiers. The fatty acids may contain 6 to 24 carbon atoms, or 8 to 18 carbon atoms. A useful acid may be oleic acid.

[0057] The amides of fatty acids may be those prepared by condensation with ammonia or with primary or secondary amines such as diethylamine and diethanolamine. Fatty imidazolines may include the cyclic condensation product of an acid with a diamine or polyamine such as a polyethylenepolyamine. In one embodiment, the friction modifier may be the condensation product of a C8 to C24 fatty acid with a polyalkylene polyamine, for example, the product of isostearic acid with tetraethylenepentamine. The condensation products of carboxylic acids and polyalkylenepolyamines may be imidazolines or amides.

[0058] The fatty acid may also be present as its metal salt, e.g., a zinc salt. These zinc salts may be acidic, neutral, or basic (overbased). These salts may be prepared from the reaction of a zinc containing reagent with a carboxylic acid or salt thereof. A useful method of preparation of these salts is to react zinc oxide with a carboxylic acid. Useful carboxylic acids are those described hereinabove. Suitable carboxylic acids include those of the formula RCOOH where R is an aliphatic or alicyclic hydrocarbon radical. Among these are those wherein R is a fatty group, e.g., stearyl, oleyl, linoleyl, or palmityl. Also suitable are the zinc salts wherein zinc is present in a stoichiometric excess over the amount needed to prepare a neutral salt. Salts wherein the zinc is present from 1.1 to 1.8 times the stoichiometric, e.g., 1.3 to 1.6 times the stoichiometric amount of zinc, may be used. These zinc carboxylates are known in the art and are described in U.S. Pat. 3,367,869. Metal salts may also include calcium salts. Examples may include overbased calcium salts.

[0059] Sulfurized olefins are also well known commercial materials used as friction modifiers. A suitable sulfurized olefin is one which is prepared in accordance with the detailed teachings of U.S. Patents 4,957,651 and 4,959,168. Described therein is a cosulfurized mixture of 2 or more reactants selected from the group consisting of at least one fatty acid ester of a polyhydric alcohol, at least one fatty acid, at least one olefin, and at least one fatty acid ester of a monohydric alcohol. The olefin component may be an aliphatic olefin, which usually will contain 4 to 40 carbon atoms. Mixtures of these olefins are commercially available. The sulfurizing agents useful in the process of the present technology include elemental sulfur, hydrogen sulfide, sulfur halide plus sodium sulfide, and a mixture of hydrogen sulfide and sulfur or sulfur dioxide.

[0060] Metal salts of alkyl salicylates include calcium and other salts of long chain (e.g. C12 to C16) alkyl-substituted salicylic acids.

[0061] Amine salts of alkylphosphoric acids include salts of oleyl and other long chain esters of phosphoric acid, with amines such as tertiary-aliphatic primary amines, sold under the trade name Primene™.

[0062] The amount of the supplemental friction modifier, if it is present, may be 0.1 to 1.5 percent by weight of the lubricating composition, such as 0.2 to 1.0 or 0.25 to 0.75 percent. In some embodiments, however, the amount of the supplemental friction modifier is present at less than 0.2 percent or less than 0.1 percent by weight, for example, 0.01 to 0.1 percent.

[0063] The compositions of the present technology can also include a detergent. Detergents as used herein are salts of organic acids (typically metal salts, although various ammonium salts including quaternary ammonium salts are known). The organic acid portion of the detergent may be a sulfonate, carboxylate, phenate, or salicylate. The metal portion of the detergent may be an alkali or alkaline earth metal. Suitable metals include sodium, calcium, potassium, and magnesium. Typically, the detergents are overbased, meaning that there is a stoichiometric excess of metal base over that needed to form the neutral metal salt.

[0064] Suitable overbased organic salts include the sulfonate salts having a substantially oleophilic character and which are formed from organic materials. Organic sulfonates are well known materials in the lubricant and detergent arts. The sulfonate compound should contain on average 10 to 40 carbon atoms, such as 12 to 36 carbon atoms or 14 to 32 carbon atoms on average. Similarly, the phenates, salicylates, and carboxylates have a substantially oleophilic character.

[0065] While the present technology allows for the carbon atoms to be either aromatic or in paraffinic configuration, in certain embodiments alkylated aromatics are employed. While naphthalene based materials may be employed, the aromatic of choice is the benzene moiety.

[0066] Suitable compositions thus include an overbased monosulfonated alkylated benzene such as a monoalkylated benzene. Alkyl benzene fractions may be obtained from still bottom sources and are mono- or di-alkylated. It is believed, in the present technology, that the mono-alkylated aromatics are superior to the dialkylated aromatics in overall properties.

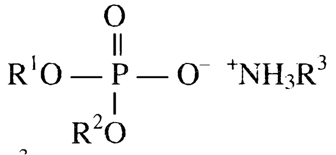
[0067] It is desired that a mixture of mono-alkylated aromatics (e.g., benzene) be utilized to obtain the mono-alkylated salt (benzene or toluene sulfonate) in the present technology. The mixtures wherein a substantial portion of the composition contains polymers of propylene as the source of the alkyl groups assist in the solubility of the salt. The use of mono-functional (e.g., mono-sulfonated) materials avoids crosslinking of the molecules with less precipitation of the salt from the lubricant.

[0068] The salt may be "overbased." By overbasing, it is meant that a stoichiometric excess of the metal base be present over that required for the anion of the neutral salt. The excess metal from overbasing has the effect of neutralizing acids which may build up in the lubricant. Typically, the excess metal will be present over that which is required to neutralize the anion at in the ratio of up to 30:1, such as 5:1 to 18:1 on an equivalent basis.

[0069] The amount of the overbased salt utilized in the composition is typically 0.025 to 3 or to 5 weight percent on an oil free basis, such as 0.1 to 1.0 percent or 0.2 to 4 percent. In other embodiments, the final lubricating composition may contain no detergent or substantially no detergent or only a low amount of detergent. That is, for a calcium overbased detergent for instance, the amount may be such as to provide less than 250 parts per million calcium, e.g., 0 to 250 or 1 to 200 or 10 to 150 or 20 to 100 or 30 to 50 parts per million calcium, or less than any of the foregoing non-zero amounts. Such low amounts of detergent may be particularly suitable for automatic transmission applications. This is in contrast with more conventional automatic transmission formulations which may contain sufficient calcium detergent to provide 300 to 600 ppm calcium. Formulations suitable for lubricating an internal combustion engine will typically have non-zero amounts of detergents, e.g., 0.1 to 5 percent. The overbased salt is usually made in up to about 50% oil and has a TBN range of 10-800 or 10-600 on an oil free basis. Borated and non-borated overbased detergents are described in U.S. Patents 5,403,501 and 4,792,410.

[0070] The compositions of the present technology can also include at least one phosphorus compound such as organic or inorganic phosphorus acids, organic or inorganic phosphorus acid salt, organic phosphorus acid esters, or derivatives thereof including sulfur-containing analogs which may, in certain embodiments, be in an amount of 0.002-1.0 weight percent. In certain embodiments, the amount of such phosphorus compound may be those that will supply 0.025 to 0.085 percent or 0.02 to 0.08 percent phosphorus to the composition. The phosphorus acids, salts, esters or derivatives thereof include phosphoric acid, phosphorous acid, phosphorus acid esters or salts thereof, phosphites, phosphorus-containing amides, phosphorus-containing carboxylic acids or esters, phosphorus-containing ethers, and mixtures thereof. Some phosphorus materials may serve as antiwear agents.

[0071] In one embodiment, the phosphorus acid, ester, or derivative can be an organic or inorganic phosphorus acid, phosphorus acid ester, phosphorus acid salt, or derivative thereof. The phosphorus acids include the phosphoric, phosphonic, phosphinic, and thiophosphoric acids including dithiophosphoric acid as well as the monothiophosphoric, thiophosphinic and thiophosphonic acids. One group of phosphorus compounds are alkylphosphoric acid mono alkyl primary amine salts as represented by the formula



$$R^1O - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R^2O}{|}}{P}} - O^- \ {}^+NH_3R^3$$

where R^1, R^2, R^3 are alkyl or hydrocarbyl groups or one of R^1 and R^2 can be H. The materials are usually a 1:1 mixture of dialkyl and monoalkyl phosphoric acid esters. Compounds of this type are described in U.S. Patent 5,354,484.

[0072] Eighty-five percent phosphoric acid is a suitable material for addition to the fully-formulated compositions and can be included at a level of 0.01 to 0.3 weight percent based on the weight of the composition, such as 0.03 to 0.2 or to 0.1 percent. The phosphoric acid may form a salt with a basic component such as a succinimide dispersant.

[0073] Other phosphorus-containing materials that may be present include dialkyl phosphites (sometimes referred to as dialkyl hydrogen phosphonates) such as dibutyl phosphite. Yet other phosphorus materials include phosphorylated hydroxy-substituted triesters of phosphorothioic acids and amine salts thereof, as well as sulfur-free hydroxy-substituted di-esters of phosphoric acid, sulphur-free phosphorylated hydroxy-substituted di- or tri-esters of phosphoric acid, and amine salts thereof. These materials are further described in U.S. patent application US 2008-0182770.

[0074] Other materials can optionally be included in the compositions of the present technology, provided that they are not incompatible with the afore-mentioned required components or specifications. Such materials include antioxidants (that is, oxidation inhibitors), including hindered phenolic antioxidants, secondary aromatic amine antioxidants such as dinonyldiphenylamine as well as such well-known variants as monononyldiphenylamine and diphenylamines with other alkyl substituents such as mono- or di-octyl, sulfurized phenolic antioxidants, oil-soluble copper compounds, phosphorus-containing antioxidants, and organic sulfides, disulfides, and polysulfides such as 2-hydroxyalkyl, alkyl thioethers or 1-t-dodecylthio-2-propanol or sulfurized 4-carbobutoxycyclohexene or other sulfurized olefins. In some embodiments the amount of antioxidant may be 0.1 to 5 percent by weight or 0.15 to 2.5 percent or 0.2 to 4 percent.

[0075] Also included may be corrosion inhibitors such as tolyl triazole and dimercaptothiadiazole and oil-soluble derivatives of such materials. Other optional components include seal swell agents, such as isodecyl sulfolane or phthalate esters, which are designed to keep seals pliable. Also permissible are pour point depressants, such as alkylnaphthalenes, polymethacrylates, vinyl acetate/fumarate or /maleate copolymers, and styrene/maleate copolymers. Other materials are anti-wear agents such as zinc dialkyldithiophosphates, tridecyl adipate, and various long-chain derivatives of hydroxy carboxylic acids, such as tartrates, tartramides, tartrimides, and citrates as described in US Application 2006-0183647. These optional materials are known to those skilled in the art, are generally commercially available, and are described in greater detail in published European Patent Application 761,805. Also included can be known materials such as corrosion inhibitors (e.g., tolyltriazole, dimercaptothiadiazoles), dyes, fluidizing agents, odor masking agents, and antifoam agents. Organic borate esters and organic borate salts can also be included.

[0076] The above components can be in the form of a fully-formulated lubricant or in the form of a concentrate within a smaller amount of lubricating oil. If they are present in a concentrate, their concentrations will generally be directly proportional to their concentrations in the more dilute form in the final blend.

[0077] The presently described compositions may be used in a method for lubricating a mechanical device, comprising supply to the mechanical device any of the lubricant compositions described herein. The mechanical device may be an automatic transmission such as found in a vehicle such as an automobile. Automatic transmissions include continuously variable transmissions and dual clutch transmissions, as well as transmissions for gasoline, diesel, and hybrid engines of various types (including gasoline/electric hybrids). Mechanical devices also include internal combustion engines, including two-stroke cycle and four-stroke cycle engines, gasoline-fueled engines, diesel-fueled engines, spark ignited engines, compression ignited engines, sump-lubricated engines, and engines in which the lubricant is supplied in admixture with fuel.

[0078] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

[0079] hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

[0080] substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this technology, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

[0081] hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this technology, contain other than carbon in a ring or chain otherwise composed of carbon atoms and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. Heteroatoms include sulfur, oxygen, and nitrogen. In general, no more than two, or no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0082] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present technology in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present technology; the present technology encompasses the composition prepared by admixing the components described above.

EXAMPLES

[0083] Preparative Example A. Reaction of Duomeen®2HT with pyromellitic dianhydride to provide a pyromellitic diimide such as that of Structure (I) above. Duomeen®2HT is a tradename of Akzo Nobel for the diamine which may be represented by $(HTallow)_2N-(CH_2)_3NH_2$, where HTallow represents hydrogenated tallow, being a mixture of about 64% C18 groups, 31% C16 groups, 4% C14 groups, and 1% C12 groups.

[0084] A 2 L round-bottom flange flask is equipped with a stirrer, nitrogen inlet, thermocouple, Dean-Stark trap, and condenser. To the flask is charged 56.7 g pyromellitic dianhydride and 750 mL xylene. The mixture is heated to about 110 °C with stirring, and 300 g of Duomeen®2HT is added dropwise over about 2 hours. The mixture is heated to 145 °C and stirred for 4 hours, then further heated to 190 °C for 1 hour under vacuum, allowing solvent and any remaining water to be removed by distillation, and then allowed to cool. The resulting diimide is obtained in an amount of 332 g.

[0085] Preparative Example B. Reaction of 2-ethylhexanol with pyromellitic dianhydride. Pyromellitic dianhydride, 21.2 g, and 2-ethylhexanol, 25.6 g, are added to a 250 mL 4-necked flask equipped with a mechanical stirrer, nitrogen inlet, thermocouple, and Dean-Stark trap topped with a condenser. The reaction mixture is heated to 150 °C over 30 minutes and held at temperature for 2 hours. Thereafter, an additional 26.2g 2-ethylhexanol and 0.24 g methanesulfonic acid are added in multiple portions as the temperature is increased to 156-160 °C and stirred at this temperature for about 2 hours. The reaction mixture is heated to 180 °C and vacuum stripped to obtain the product.

[0086] Base formulation I is prepared with the following components:

6.24% polymeric viscosity modifiers (including 30% diluent oil)
0.2% polymeric pour point depressant (including 50% diluent oil)
5.65% succinimide dispersants (including 44% diluent oil)
1.66% seal swell agent
1.02% amine and sulfur-containing antioxidants
0.30% phosphite and phosphonate friction modifiers
0.15% borate ester friction modifier
0.09% phosphoric acid (85%)
0.1% corrosion inhibitors
0.014% commercial antifoam agents
1.8% diluent oils
balance: mineral oils

[0087] Base formulation II is prepared with the following components:

9.6% polymeric viscosity modifier (including 75% diluent oil)
0.2% polymeric pour point depressant (including 50% diluent oil)
3.5% succinimide dispersants (including 44% diluent oil)
0.4% seal swell agent
0.9% amine antioxidant
0.20% phosphite friction modifier
0.10% phosphoric acid (85%)
0.037% commercial antifoam agents, dye, and other minor components
balance: mineral oils

[0088] Lubricants for testing are prepared by adding one of the test materials identified in the tables below, to the indicated base formulation. The resulting lubricants are subjected to a VSFT test, which is a variable speed friction test. The VSFT apparatus consists of a disc that can be metal or another friction material which is rotated against a metal surface. The friction materials employed in the particular tests are various commercial friction materials commonly used in automatic transmission clutches, as indicated in the Tables. The test is run over three temperatures and two load levels. The coefficient of friction measured by the VSFT is plotted against the sliding speed (50 and 200 r.p.m.) over a number speed sweeps at a constant pressure.

The results are sometimes presented as slope of the μ-V curve as a function of time, reported for 40, 80, and 120 °C and 24 kg and 40 kg (235 and 392 N) force, determined at 4 hour intervals from 0 to 52 hours. Typically, the slope will initially be positive, with a certain amount of variability, and may gradually decrease, possibly becoming negative after a certain period of time. Longer duration of positive slope is desired.

[0089] The data is initially collected as a table of slope values as a function of time, for each run. For ease of analysis and comparison, each formulation at each temperature is assigned a "slope score." At each temperature, the fraction of slope values within the first 7 time measurements (0 to 24 hours) at 24 kg and of the first 7 measurements at 40 kg (thus 14 measurements total) that are positive, as a percent, is denoted as "A". The fraction of the slope values at the two pressures (14 measurements total) within the second 24 hours (28-52 hours) that are positive are denoted as "B". The slope score is defined as A + 2B. The extra weighting given to the latter portion of the test is to reflect the greater importance (and difficulty) of preparing a durable fluid that retains a positive slope in the latter stages of the test. The maximum score of 300 denotes a fluid that exhibits a consistently positive slope through the entire test. A more detailed description of the slope score reporting summary and an illustrative calculation of a slope score is found in U.S. Patent Publication 2010-021490, Vickerman et al., August 29, 2010; see paragraphs 0093 to 0096.

Ex.	Prep.Ex.	Treat, %	Base Formulation	Friction Mat'l[a]	Slope Score		
					40°C	80°C	120°C
1*	none	–	I	6100	0	28.57	78.57
2	A	1	I	6100	78.57	171.43	235.72
3	A	2.5	I	6100	85.74	221.44	264.28
4*	none	–	II	6100	0	21.43	128.57
5	A	1	II	6100	71.43	114.29	157.14
6	A	2.5	II	6100	185.71	271.43	300
7*	none	–	II	4211	0	14.29	200
8	A	2.5	II	4211	271.43	292.86	300

* A reference or comparative example

a. Friction materials: Raybestos™ 4211 or Borg Warner™ 6100, as indicated

[0090] The results show desirable frictional performance by materials of the present technology, in particular as compared to the base formulation from which they are absent. The results also indicate that better performance is sometimes obtained at relatively higher concentrations of 2.5% compared with 1.0%.

[0091] Further frictional testing illustrates additional features of the present technology. The fluid of Example 3, containing 2.5% of the pyromellitic dimide of Preparative Example A in Base Formulation I, is subjected to a Ford 30K durability dynamic friction test (Dynax™ D-0530-31). Friction between steel and friction plates of a lubricated clutch is measured during the engagement process. The midpoint dynamic coefficient of friction is determined during the 50 ms interval centrally located at 1800 r.p.m. between 400 and 30,000 engagement cycles, repeated at 4 cycles per minute. Lubricant temperature is 135 °C.

[0092] A plot of midpoint coefficients of friction is shown in Figure 1. The upper, solid line, indicated by diamond shapes, represents the coefficient of friction for the fluid of Example 3, containing the pyromellitic diimide. The lower, dashed line, indicated by the open circles, represents the same baseline fluid without the pyromellitc diimide.

[0093] The results of the test show that by addition of the pyromellitic diimide of Preparative Example A, the dynamic friction coefficient imparted by the lubricant is significantly increased to a desirable level, and this level is maintained through 30,000 cycles. This is a unique and beneficial performance, since, traditionally, dispersants having a long polyisobutylene "tail" component are required to provide a high level of dynamic friction, but such dispersants may lead to poor performance at low temperature (such as unduly high viscosity). The present technology will permit the formulation of lubricants with high dynamic friction coefficient without or with reduced amounts of such dispersants.

[0094] The present technology will also impart good antishudder durability to the lubrication of a wet clutch as typically found in an automatic transmission.

[0095] A series of lubricant formulations is prepared containing additive components typically used in heavy duty diesel engine lubricants. The base formulation contains, in a 100-120N mineral oil, 7.6% of an olefin copolymer viscosity modifier (including 92% diluent oil), 0.15% of a pour point depressant (oil diluted), 5.1% of a succinimide dispersant (47% diluent oil), 0.63% zinc dialkyldithiophosphates (9% oil), 2.2% of a mixture of antioxidants, 1.53% overbased calcium sulfonate detergents (42% oil), 0.1% oleamide, and 90 ppm commercial antifoam agent. To the lubricants are added additional components shown in the Table below (expressed in weight percent), including in certain examples 0.2% of the tetraester of pyromellitic acid with 2-ethylhexanol as from Preparative Example B, above. The resulting lubricant formulations are subjected to a copper and lead coupon corrosion test. In this test, 50 g of lubricant sample, containing Cu and Pb coupons, is bubbled with 50 cm^3 air, typically at 135 °C, for typically 216 hours. The results of the testing are also reported in the Table:

Example:	11*	12	13*	14	15*	16
Pyromellitic ester		0.2		0.2		0.2
Glycerol monooleate	0.6	0.6			0.6	0.6
Sakuralube™ 515 [a]			0.5	0.5	0.5	0.5
1283 Test						
Pb corrosion, ppm in drain	458	357	13	16	642	281
Cu corrosion, visual rating[b]	4A	4A	4B	2B	4B	3B

* A reference or comparative example

a. Commercial molybdenum-containing composition, to provide 0.05% Mo to the lubricant formulation

b. ASTM D 130: 1A = clean or slight tarnish; 4C = heavy black deposits

[0096] Glycerol monooleate is known to lead to excessive lead corrosion. This excessive corrosion is significantly reduced by the presence of pyromellitic ester. Copper corrosion, as evaluated by visual rating, is typically improved by the presence of pyromellitic ester, especially when molybdenum is also present. (Copper corrosion as measured by ppm Cu is not significantly affected.)

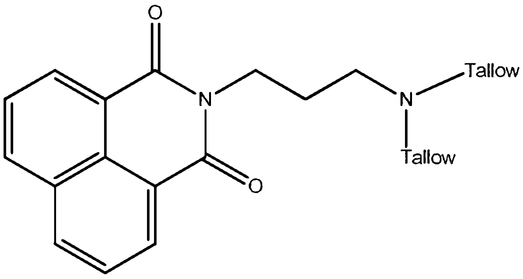
[0097] Example 17. A lubricant composition suitable for use as an engine lubricant is prepared with the following components, in weight percents:

1.0% tetraester of pyromellitic acid and 2-ethylhexanol as from Prep. Ex. B
8% polymeric viscosity modifier (including 91% diluent oil)
0.15% polymeric pour point depressant (25% oil)
5.1% succinimide dispersant (47% oil)
0.48% zinc dialkyldithiophosphate (9% oil)
1.53% overbased calcium sulfonate(s) (42% oil)

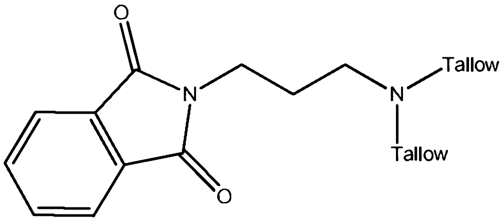
0.1% carboxylic ester friction modifier
2% hindered phenolic ester antioxidant
1% aminic antioxidant
Oil of lubricating viscosity – balance to = 100%

[0098] The lubricant composition Example 17 will exhibit one or more of good antiwear performance and good coefficient of friction.

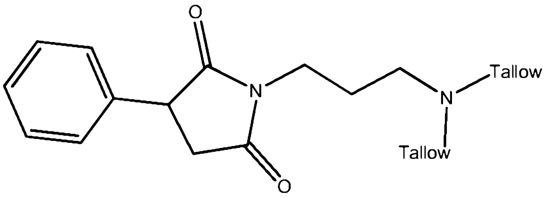
[0099] Example 18, 19, and 20. Imides are prepared having the structures shown below:



Example 18



Example 19



Example 20

[00100] Each of the materials of Examples 18, 19, and 20 is added in an amount of 2.5% by weight to each of two base formulations I and II, above, characteristic of automatic transmission fluids. They are subjected to a VSFT test (described above) using a BorgWarner™ 6100 friction material. The results are shown in the Table below, presented as "slope scores" (defined above).

Additive	Base Formulation	Slope Score		
		40°C	80°C	120°C
none	I	0	28.57	78.57
Ex. 18	I	21.43	192.87	200.01
Ex. 19	I	28.57	257.15	278.57
Ex. 20	I	92.85	142.85	242.84

None	II	0	21.43	128.57
Ex. 18	II	121.43	214.29	300
Ex. 19	II	128.58	228.58	300
Ex. 20	II	92.86	142.86	228.58

[0100] Each of the documents referred to above is incorporated herein by reference. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the technology can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration. Further, where the terms “comprise”, “comprises”, “comprised” or “comprising” are used in this specification, they are to be interpreted as specifying the presence of the stated features, integers, steps or components referred to, but not to preclude the presence or addition of one or more other feature, integer, step, component or group thereof.

The Claims defining the invention are as follows:

1. A composition comprising
   (a) an oil of lubricating viscosity and
   (b) about 0.0001 to about 10 weight percent of a condensation product of
      (i) an aromatic polycarboxylic acid or mixtures thereof or a reactive equivalent thereof, having at least two carboxylic groups attached to two adjacent carbon atoms, or attached to two carbon atoms which are separated by one atom, but not attached in positions meta to each other on an aromatic ring, the aromatic polycarboxylic acid or reactive equivalent thereof comprising an aromatic ring substituted by at least one succinic acid group or reactive equivalent thereof; with
      (ii) an aliphatic primary amine comprising N,N-dialkyl-1,3-propanediamine containing 12 to 60 carbon atoms, said condensation product comprising an imide or an amide.

2. The composition of claim 1, wherein the condensation product comprises a cyclic imide.

3. The composition of claim 1 or claim 2, wherein the aromatic polycarboxylic acid or reactive equivalent thereof comprises an aromatic group with at least 2 carboxylic acid groups, or reactive equivalents thereof, on at least two aromatic carbon atoms.

4. The composition of claim 3, wherein the aromatic polycarboxylic acid or reactive equivalent thereof comprises a benzene ring with at least two carboxylic acid groups, or reactive equivalents thereof, on adjacent carbon atoms.

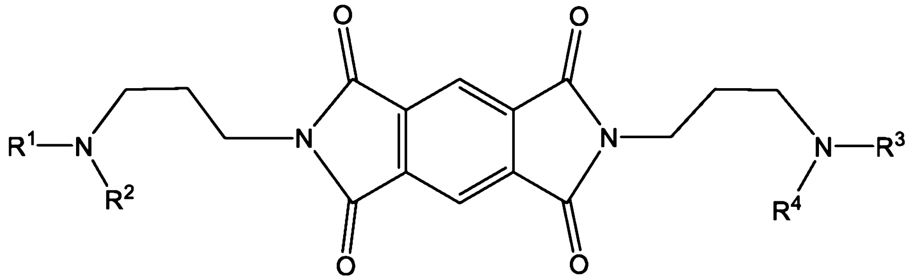
5. The composition of claim 3, wherein the aromatic polycarboxylic acid or reactive equivalent thereof comprises a naphthalene structure with two carboxylic acid groups, or reactive equivalents thereof, located in positions 1 and 8 of the naphthalene structure.

6. The composition of any one of claims 1 to 4, wherein the condensation product comprises a diimide.

7. The composition of any one of claims 1 to 4, or 6, wherein the condensation product comprises a pyromellitic diimide.

8. The composition of any one of claims 1 to 7, wherein the N,N-dialkyl-1,3-propanediamine comprises N,N-di-(hydrogenated tallow)-1,3-propanediamine, N,N-dicoco-1,3-propanediamine or N,N-diisostearyl-1,3-propanediamine.

9. The composition of any one of claims 1 to 4 or 6 to 8, wherein the condensation product comprises a material represented by



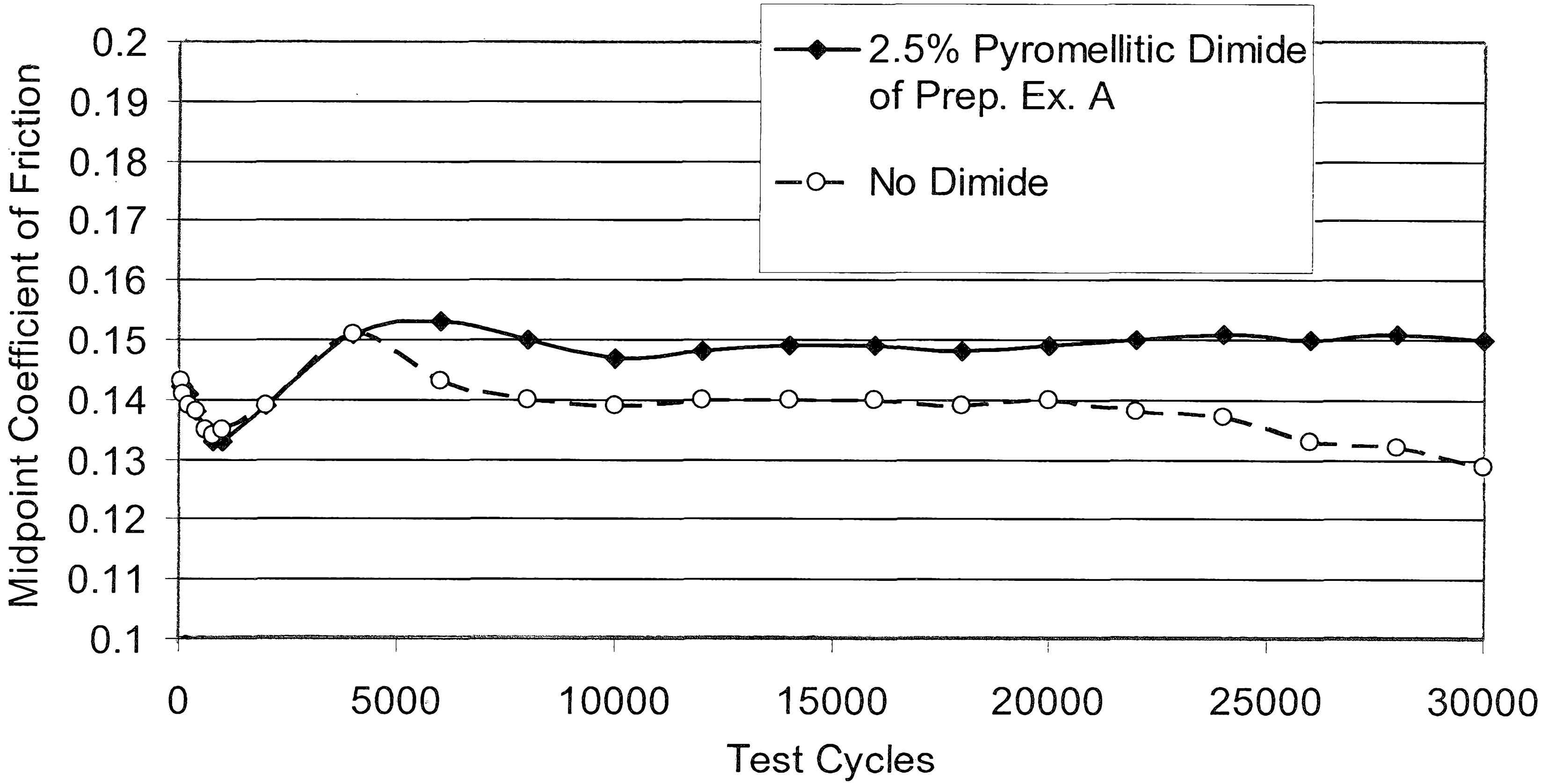
wherein each of R^1 and R^3 is independently an alkyl group of 8 to 22 carbon atoms and each of R^2 and R^4 is independently hydrogen or an alkyl group of 1 to 22 carbon atoms, provided that the total number of carbon atoms in R^1 and R^2 is at least 13 and the total number of carbon atoms in R^3 and R^4 is at least 13.

10. The composition of claim 9, wherein R^1, R^2, R^3, and R^4 are alkyl groups characteristic of tallowamine, cocoamine, or isostearylamine.

11. The composition of any one of claims 1 to 10, further comprising at least one additive selected from the group consisting of organic borate esters, organic borate salts, organic phosphorus esters, organic phosphorus salts, inorganic phosphorus salts, and inorganic phosphorus acids.

12. A method for lubricating a mechanical device, comprising supplying thereto the composition of any one of claims 1 to 11.

Fig. 1


2.5% Pyromellitic Dimide of Prep. Ex. A
No Dimide
Midpoint Coefficient of Friction
0.2
0.19
0.18
0.17
0.16
0.15
0.14
0.13
0.12
0.11
0.1
0
5000
10000
15000
20000
25000
30000
Test Cycles