

POLYAMIDE FUEL ADDITIVES

TECHNICAL FIELD

[001] This disclosure relates to fuel additive compositions and fuel compositions. More specifically, this disclosure relates to long-chain aliphatic polyamide compounds that can prevent corrosion/rust while providing anti-wear/friction protection.

BACKGROUND

[002] There has been considerable effort in recent years to improve the fuel economy of motor vehicles. In general, the efficiency of automotive engines is greatly enhanced by the presence of effective lubrication, particularly at the interface of moving parts that are prone to high friction and excessive wear. Thus, one approach for improving fuel economy has been to develop lubricants and lubricating oil additives that reduce engine friction and thus reduce energy requirements.

[003] Some of these efforts have focused on friction modifiers which are known lubricating oil additives that can reduce boundary friction by adsorbing or reacting on metal surfaces to form thin low-shear-strength films.

[004] Friction modifiers have been used in limited slip gear oils, automatic transmission fluids, slideway lubricants and multipurpose tractor fluids. In particular, with the desire for increased fuel economy, friction modifiers have been added to automotive crankcase lubricants. These friction modifiers generally operate at boundary layer conditions at temperatures where anti-wear and extreme pressure additives are not yet reactive by forming a thin mono-molecular layers of physically adsorbed polar oil-soluble products or reaction layers which exhibit a significantly lower friction compared to typical anti-wear or extreme pressure agents. However, under more severe conditions and in mixed lubrication regime these friction modifiers are added with an anti-wear or extreme pressure agent.

[005] The most common type of anti-wear or extreme pressure agent is a zinc dialkyl dithiophosphate (ZnDTP or ZDDP). ZDDP limit wear by forming a thick protective tribofilm on rubbing surfaces. Although ZDDP has been widely used in motor vehicles for many decades, some recent studies have shown that phosphorus-based anti-wear films can cause significant increase in friction in thin film, high-pressure, lubricated contacts. This, in turn, can have a negative effect on fuel efficiency.

[006] While reducing friction with lubricant additives has been important, there is potential to further improve fuel efficiency with fuel additives. Since the conditions of an internal combustion chamber are substantially different from those in a crankcase, it is not a given that a particular additive or class of additives that has provided performance benefits in a lubricating oil will provide similar benefits in fuel. Thus, there is a need to develop fuel additives that can reduce friction and/or improve fuel economy.

DESCRIPTION OF FIGURE

[007] FIG. 1 is described in the Example section.

SUMMARY OF THE INVENTION

[008] In one aspect, there is provided a method for preventing or reducing corrosion or wear in gasoline engine by supplying a fuel composition comprising a reaction product of fatty acid and polyamine.

[009] In another aspect, there is provided a method for preventing or reducing corrosion or wear in gasoline engine while providing anti-wear or friction protection by supplying a fuel composition comprising a fuel additive comprising a reaction product of fatty acid and polyamine.

DETAILED DESCRIPTION

Introduction

[010] In this specification, the following words and expressions, if and when used, have the meanings ascribed below.

[011] "Gasoline" or "gasoline boiling range components" refers to a composition containing at least predominantly C₄-C₁₂ hydrocarbons. In one embodiment, gasoline or gasoline boiling range components is further defined to refer to a composition containing at least predominantly C₄-C₁₂ hydrocarbons and further having a boiling range of from about 37.8 °C (100°F) to about 204 °C (400 °F). In an alternative embodiment, gasoline or gasoline boiling range components is defined to refer to a composition containing at least predominantly C₄-C₁₂ hydrocarbons, having a boiling range of from about 37.8 °C (100 °F) to about 204 °C (400 °F), and further defined to meet ASTM D4814.

[012] The term "diesel" refers to middle distillate fuels containing at least predominantly C₁₀-C₂₅ hydrocarbons. In one embodiment, diesel is further defined to refer to a composition containing at least predominantly C₁₀-C₂₅ hydrocarbons, and further having a boiling range of from about 165.6 °C (330 °F) to about 371.1 °C (700 °F). In an alternative embodiment, diesel is as defined above to refer to a composition containing at least predominantly C₁₀-C₂₅ hydrocarbons, having a boiling range of from about 165.6 °C (330 °F) to about 371.1 °C (700 °F), and further defined to meet ASTM D975.

[013] The term "oil soluble" means that for a given additive, the amount needed to provide the desired level of activity or performance can be incorporated by being dissolved, dispersed or suspended in an oil of lubricating viscosity. Usually, this means that at least 0.001% by weight of the additive can be incorporated in a lubricating oil composition. The term "fuel soluble" is an analogous expression for additives dissolved, dispersed or suspended in fuel.

[014] A “minor amount” means less than 50 wt% of a composition, expressed in respect of the stated additive and in respect of the total weight of the composition, reckoned as active ingredient of the additive.

[015] An “engine” or a “combustion engine” is a heat engine where the combustion of fuel occurs in a combustion chamber. An “internal combustion engine” is a heat engine where the combustion of fuel occurs in a confined space (“combustion chamber”). A “spark ignition engine” is a heat engine where the combustion is ignited by a spark, usually from a spark plug. This is contrast to a “compression-ignition engine,” typically a diesel engine, where the heat generated from compression together with injection of fuel is sufficient to initiate combustion without an external spark.

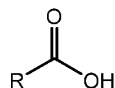
[016] The present invention provides fuel additive compositions and fuel compositions with one or more performance benefits. In some embodiments, the compositions are effective to prevent or reduce corrosion or rust. In some embodiments, the compositions are effective to prevent or reduce wear or friction. In particular, the reduction in friction may lead to gains in fuel efficiency. In some embodiments, the compositions are multifunctional in that two or more benefits (e.g., corrosion/rust and wear/friction reduction) are provided.

[017] In general, the fuel additive composition is a product of a reaction between a fatty acid and a polyamine which results in a long-chain polyamide. Whereas conventional rust and/or wear inhibitors rely on organic acid-type compositions, the polyamides of the present invention are non-acids which minimizes interactions with potential refinery process contaminants that can result in deposit formation or increased filter plugging. Other advantages will be apparent from the disclosure herein.

Fatty Acid

[018] In accordance with the present invention, the fuel additive is the product of an amidification reaction between a fatty acid and a polyamine. Any fatty acid

compatible with the present invention may be used. Typical fatty acid can have the following structure:



wherein R is an organic moiety having about 5 to 40 carbon atoms such as from 8 to 35 carbon atoms, 10 to 30 carbon atoms, or 15 to 25 carbon atoms. In some embodiments, R includes one or more heteroatoms. Suitable fatty acids include saturated and unsaturated fatty acids. The fatty acid may also be a mono-carboxylic acid or may have more one acid moiety (e.g., di-carboxylic acid).

[019] In some embodiments, the fatty acid is an aliphatic fatty acid. Examples of saturated fatty acids include aliphatic fatty acids. The aliphatic group may be linear or branched.

[020] Suitable aliphatic acids include, but are not limited to, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, 2-ethylbutyric acid, 3,3-dimethylbutyric acid, 2-methylpentanoic acid, 2-methylhexanoic acid, 4-methylhexanoic acid, 5-methylhexanoic acid, 2,2-dimethylpentanoic acid, 2-propylpentanoic acid, 2-ethylhexanoic acid, 2-methylheptanoic acid, isooctanoic acid, 3,5,5-trimethylhexanoic acid, 4-methyloctanoic acid, 4-methylnonanoic acid, isodecanoic acid, 2-butyloctanoic acid, isotridecanoic acid, 2-hexyldecanoic acid, isopalmitic acid, isostearic acid, 3-cyclohexylpropionic acid, 4-cyclohexylbutyric acid, and cyclohexanepentanoic acid.

[021] Suitable unsaturated fatty acids include fatty acids that contain double or triple carbon-carbon bond. Representative unsaturated fatty acids include palmitoleic acid, myristoleic acid, sapienic acid, oleic acid, elaidic acid, vaccenic acid, linoleic acid, linoelaidic acid, α -linoelaidic acid, arachidonic acid, eicosapentaenoic acid, erucic acid, and docosahexaenoic acid.

Polyamine

[022] Preferably, the polyamine has at least three amine nitrogen atoms per molecule, and more preferably, 4 to 12 amine nitrogens per molecule. Most preferred are polyamines having from about 6 to 10 nitrogen atoms per molecule.

[023] Preferred polyalkene polyamines also contain from about 4 to 20 carbon atoms, preferably from 2 to 3 carbon atoms per alkylene unit. The polyamine preferably has a carbon-to-nitrogen ratio of from 1:1 to 10:1.

[024] Suitable polyamines include polyalkylene polyamines. Such polyamines will typically contain about 2 to about 12 nitrogen atoms and about 2 to about 24 carbon atoms. Specific examples include diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), pentaethylene hexamine (PEHA), and heavier poly-alkylene-amines (HPA).

[025] Other specific examples of polyamines include N, N'-bis-(2-aminoethyl)piperazine (Bis AEP), N-[(2-aminoethyl) 2-aminoethyl]piperazine (PEEDA), 1-(2-aminoethyl)-4-[(2-aminoethyl)amino]ethyl]-piperazine (AEPEEDA) and 1-[2-[(2-aminoethyl)amino]ethyl]amino]ethyl]-piperazine (PEDETA).

[026] Many of the polyamines suitable for use in the present invention are commercially available and others may be prepared by methods which are well known in the art. For example, methods for preparing amines and their reactions are detailed in Sidgewick's "The Organic Chemistry of Nitrogen", Clarendon Press, Oxford, 1966; Noller's "Chemistry of Organic Compounds", Saunders, Philadelphia, 2nd Ed., 1957; and Kirk-Othmer's "Encyclopedia of Chemical Technology", 2nd Ed., especially Volume 2, pp. 99 116.

[027] The polyamine reactant may be a single compound, but typically will be a mixture of compounds reflecting commercial polyamines. Typically, the commercial polyamine will be a mixture in which one or several compounds predominate with the average composition indicated. For example, tetraethylene pentamine prepared by the polymerization of aziridine or the reaction of dichloroethylene and ammonia will have both lower and higher amine members, e.g., triethylene tetramine, substituted

piperazines and pentaethylene hexamine, but the composition will be largely tetraethylene pentamine and the empirical formula of the total amine composition will closely approximate that of tetraethylene pentamine.

[028] Other examples of suitable polyamines include admixtures of amines of various molecular weights. Included are mixtures of diethylene triamine and heavy polyamine. A preferred polyamine admixture is a mixture containing 20% by weight diethylene triamine and 80% by weight heavy polyamine.

Reaction

[029] The fuel additive of the present invention is a reaction product of fatty acid and polyamine. The reaction product is a polyamide or a fatty acid polyamide. The polyamides of the present invention may be obtained commercially or synthesized by any known method.

[030] As an illustrative example, a reaction between fatty acid and polyamine is described in U.S. Patent No. 3,169,980, which is hereby incorporated by reference. Here the polyamide is prepared by reacting the fatty acid and polyamine at temperatures in the range from about 120 °C (248 °F) to about 260 °C (500 °F). The amidification reaction requires from about 2 to 10 hours. Condensate water is subsequently removed. Reduced pressures may be needed to achieve amidification at the lower reaction temperatures. The proportion of fatty acid and polyamine may be such that the moles of fatty acid are equal to the molar equivalents of amine groups in the polyamine.

[031] A polyamide resulting from tetraethylenepentamine and a mixture of straight and branched-chain fatty acids is described by the following. A reaction vessel is charged with a mixture of tetraethylenepentamine and silicone foam inhibitor. The mixture is blanketed with nitrogen gas and heated to about 120°C. Next, a mixture of fatty acids is introduced and reaction temperature is raised to remove water. Temperature is raised again at atmospheric pressure for about an hour and then maintained under vacuum for about 7 hours.

Fuel Compositions

[032] The compounds of the present disclosure may be useful as additives in hydrocarbon fuels boiling in the gasoline or diesel range.

[033] The concentration of the polyamide compounds of the present disclosure in hydrocarbon fuel may range from 25 to 5000 parts per million (ppm) by weight (e.g., 50 to 1000 ppm).

[034] The compounds of the present disclosure may be formulated as a concentrate using an inert stable oleophilic (i.e., soluble in hydrocarbon fuel) organic solvent boiling in a range of 65 °C to 205 °C. An aliphatic or an aromatic hydrocarbon solvent may be used, such as benzene, toluene, xylene, or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols containing 2 to 8 carbon atoms, such as ethanol, isopropanol, methyl isobutyl carbinol, *n*-butanol and the like, in combination with the hydrocarbon solvents are also suitable for use with the present additives. In the concentrate, the amount of the additive may range from 10 to 70 wt% (e.g., 20 to 40 wt%).

[035] In gasoline fuels, other well-known additives can be employed including oxygenates (e.g., ethanol, methyl *tert*-butyl ether), other anti-knock agents, and detergents/dispersants (e.g., hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, succinimides, Mannich reaction products, aromatic esters of polyalkylphenoxyalkanols, or polyalkylphenoxyaminoalkanes). Additionally, friction modifiers, antioxidants, metal deactivators and demulsifiers may be present.

[036] In diesel fuels, other well-known additives can be employed, such as pour point depressants, flow improvers, cetane improvers, and the like.

[037] A fuel-soluble, non-volatile carrier fluid or oil may also be used with compounds of this disclosure. The carrier fluid is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the non-volatile residue (NVR), or solvent-free liquid fraction of the fuel additive composition while not overwhelmingly contributing to octane requirement increase. The carrier fluid may be a natural or synthetic oil, such as mineral oil, refined petroleum oils, synthetic polyalkanes and

alkenes, including hydrogenated and unhydrogenated polyalphaolefins, synthetic polyoxyalkylene-derived oils, such as those described in U.S. Patent Nos. 3,756,793; 4,191,537; and 5,004,478; and in European Patent Appl. Pub. Nos. 356,726 and 382,159.

[038] The carrier fluids may be employed in amounts ranging from 35 to 5000 ppm by weight of the hydrocarbon fuel (e.g., 50 to 3000 ppm of the fuel). When employed in a fuel concentrate, carrier fluids may be present in amounts ranging from 20 to 60 wt% (e.g., 30 to 50 wt%).

[039] The following illustrative examples are intended to be non-limiting.

EXAMPLES

[040] The polyamide tested is the reaction product of isostearic acid and tetraethylenepentamine (TEPA). Initially, 6 samples were prepared and tested for corrosion according to ASTM D665B. The samples contain either just base fuel (Samples 1 and 2) or base fuel and the polyamide (Samples 3, 4, 5, and 6) at varying amounts.

[041] Summary of the tested samples and corrosion results (ASTM D665B) is shown in Table 1 below. Visual confirmation of the corrosion test is shown clearly in FIG. 1.

Table 1

Sample	Description	Corrosion (%)	Rating
1	Base fuel	93.62	Severe Rusting
2	Base fuel	93.42	Severe Rusting
3	Base fuel + 50 PPMW polyamide	0.46	Moderate Rusting

4	Base fuel + 50 PPMW polyamide	0.20	Moderate Rusting
5	Base fuel + 100 PPMW polyamide	0.04	Light Rusting
6	Base fuel + 100 PPMW polyamide	0.04	Light Rusting (No Rusting)

[042] Additional testing was performed to measure the friction performance of the polyamide according to ASTM 6079. Sample 7 contains just the base fuel. Samples 8, 9, 10, and 11 contain either baseline formulation 1 or baseline formulation 2 and varying amounts of the polyamide.

[043] Table 2 summarizes the tested samples and the results (ASTM 6079).

Table 2

Sample	Base Fuel	Additive	Run #	X (μm)	Y (μm)	Avg (μm)	Friction Coeff
7	Base fuel	Base Fuel	Run 1	802	774	788	0.515
8	Base fuel + Methyl t-butyl ether (BL1)	50 ppmw polyamide	Run 1	563	437	500	0.283
			Run 2	546	466	506	0.281

9	Base fuel + Methyl t- butyl ether (BL1)	100 ppmw polyamide	Run 1	491	380	436	0.242
			Run 2	462	386	424	0.234
10	Base fuel + E10 (BL2)	50 ppmw polyamide	Run 1	757	730	744	0.515
			Run 2	754	726	740	0.524
11	Base fuel + E10 (BL2)	100 ppmw polyamide	Run 1	736	697	717	0.432
			Run 2	750	710	730	0.498

Baseline Formulation 1 (BL1): Base fuel + mixture of fuel detergents + 5 vol% Methyl tert-butyl ether

Baseline Formulation 2 (BL2): Base fuel + mixture of fuel detergents + E10

CLAIMS

1. A method for preventing or reducing corrosion or wear in gasoline engine by supplying a fuel composition comprising a reaction product of fatty acid and polyamine.
2. The method of claim 1, wherein the fuel composition comprises a hydrocarbon fuel boiling within range of gasoline or diesel.
3. The method of claim 1, wherein the fatty acid is an aliphatic fatty acid having 2 to 30 carbons.
4. The method of claim 3, wherein the aliphatic fatty acid is hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, 2-ethylbutyric acid, 3,3-dimethylbutyric acid, 2-methylpentanoic acid, 2-methylhexanoic acid, 4-methylhexanoic acid, 5-methylhexanoic acid, 2,2-dimethylpentanoic acid, 2-propylpentanoic acid, 2-ethylhexanoic acid, 2-methylheptanoic acid, isooctanoic acid, 3,5,5-trimethylhexanoic acid, 4-methyloctanoic acid, 4-methylnonanoic acid, isodecanoic acid, 2-butyloctanoic acid, isotridecanoic acid, 2-hexyldecanoic acid, isopalmitic acid, isostearic acid, 3-cyclohexylpropionic acid, 4-cyclohexylbutyric acid, or cyclohexanepentanoic acid.
5. The method of claim 1, wherein the polyamine has about 2 to about 12 nitrogen atoms and about 2 to about 24 carbon atoms.
6. The method of claim 1, wherein the polyamine is diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylene hexamine, polyalkylene-amines, N, N'-bis-(2-aminoethyl)piperazine, N-[(2-aminoethyl) 2-

aminoethyl]piperazine), 1-(2-aminoethyl)-4-[(2-aminoethyl)amino]ethyl]-piperazine) or 1-[2-[[2-[(2-aminoethyl)amino]ethyl]amino]ethyl]-piperazine).

7. A method for preventing or reducing corrosion or wear in gasoline engine while providing anti-wear or friction protection by supplying a fuel composition comprising a fuel additive comprising a reaction product of fatty acid and polyamine.

8. The method of claim 7, wherein the fuel composition comprises a hydrocarbon fuel boiling within range of gasoline or diesel.

9. The method of claim 7, wherein the fatty acid is an aliphatic fatty acid having 2 to 30 carbons.

10. The method of claim 9, wherein the aliphatic fatty acid is hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, 2-ethylbutyric acid, 3,3-dimethylbutyric acid, 2-methylpentanoic acid, 2-methylhexanoic acid, 4-methylhexanoic acid, 5-methylhexanoic acid, 2,2-dimethylpentanoic acid, 2-propylpentanoic acid, 2-ethylhexanoic acid, 2-methylheptanoic acid, isooctanoic acid, 3,5,5-trimethylhexanoic acid, 4-methyloctanoic acid, 4-methylnonanoic acid, isodecanoic acid, 2-butyloctanoic acid, isotridecanoic acid, 2-hexyldecanoic acid, isopalmitic acid, isostearic acid, 3-cyclohexylpropionic acid, 4-cyclohexylbutyric acid, or cyclohexanepentanoic acid.

11. The method of claim 7, wherein the polyamine has about 2 to about 12 nitrogen atoms and about 2 to about 24 carbon atoms.

12. The method of claim 7, wherein the polyamine is diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylene hexamine, poly-

alkylene-amines, N, N'-bis-(2-aminoethyl)piperazine, N-[(2-aminoethyl) 2-aminoethyl]piperazine, 1-(2-aminoethyl)-4-[(2-aminoethyl)amino]ethyl]-piperazine) or 1-[2-[[2-[(2-aminoethyl)amino]ethyl]amino]ethyl]-piperazine).