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(54) **Title:** COMPOSITION AND METHOD FOR PREVENTING OR REDUCING LOW SPEED PRE-IGNITION IN SPARK-IGNITED INTERNAL COMBUSTION ENGINES

(57) **Abstract:** Fuel and lubricant compositions are provided that contain a primary low-speed pre-ignition (LSPI)-reducing additive comprising (i) an amino additive, (ii) an amine additive, (iii) a triazole additive, (iv) a benzamidinium additive, (v) a benzoxazole additive, or (vi) a N=C-X motif additive. Methods for preventing or reducing low speed pre-ignition events in spark-ignited engines using these compositions are also provided.

WO 2020/194041 A2

COMPOSITION AND METHOD FOR PREVENTING OR REDUCING LOW SPEED PRE-IGNITION IN SPARK-IGNITED INTERNAL COMBUSTION ENGINES

TECHNICAL FIELD

[001] This disclosure relates to fuel and lubricant compositions for spark-ignited engines and methods for preventing or reducing low speed pre-ignition events using the same.

BACKGROUND

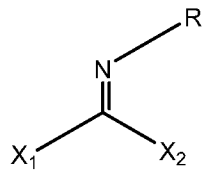
[002] Turbocharged or supercharged engines (i.e., boosted internal combustion engines) may exhibit an abnormal combustion phenomenon known as stochastic pre-ignition or low-speed pre-ignition (or "LSPI"). LSPI is an event that may include very high pressure spikes, early combustion during an inappropriate crank angle, and knock. All of these, individually and in combination, have the potential to cause degradation and/or severe damage to the engine. However, because LSPI events occur only sporadically and in an uncontrolled fashion, it is difficult to identify the causes for this phenomenon and to develop solutions to suppress it.

[003] Pre-ignition is a form of combustion that results in ignition of the air-fuel mixture in the combustion chamber prior to the desired ignition of the air-fuel mixture by the igniter. Pre-ignition has typically been a problem during high load engine operation since heat from operation of the engine may heat a part of the combustion chamber to a sufficient temperature to ignite the air-fuel mixture upon contact. This type of pre-ignition is sometimes referred to as hot-spot pre-ignition.

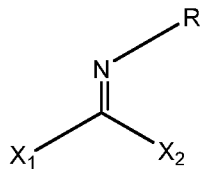
[004] More recently, intermittent abnormal combustion has been observed in boosted internal combustion engines at low speeds and medium-to-high loads. For example, during operation of the engine at 3000 rpm or less, under load, with a brake mean effective pressure (BMEP) of at least 10 bar, low-speed pre-ignition (LSPI) may occur in a random and stochastic fashion. During low speed engine operation, the compression stroke time is longest.

[005] Previous studies have demonstrated that turbocharger use, engine design, engine coatings, piston shape, fuel choice, and/or engine oil additives may contribute to an increase in LSPI events. Accordingly, there is a need for fuel and engine oil additive components and/or combinations that are effective to reduce or eliminate LSPI.

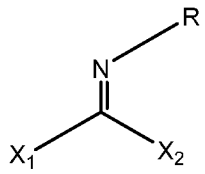
SUMMARY

[006] In one aspect, there is provided a fuel composition comprising (1) greater than 50 wt % of a hydrocarbon fuel boiling in the gasoline or diesel range and (2) a minor amount of one or more of: a primary low-speed pre-ignition (LSPI)-reducing additive comprising (i) an amino additive, (ii) an amine additive, (iii) a triazole additive, (iv) a benzamidinium additive, (v) a benzoxazole additive, or (vi) a N=C-X motif additive having a structure of 

, wherein X_1 and X_2 are independently H, C, N, O, or S; and wherein X_1 or X_2 independently includes one or more C_1-C_{20} alkyl group or one or more aromatic group.

[007] In another aspect, there is provided a fuel concentrate comprising (1) from 90 to 30 wt % of an organic solvent boiling in a range of from 65°C to 205°C and (2) from 10 to 70 wt % of an additive component selected from one or more of (i) an amino additive, (ii) an amine additive, (iii) a triazole additive, (iv) a benzamidinium additive, (v) a benzoxazole additive, or (vi) a N=C-X motif additive having a structure of 

, wherein X_1 and X_2 are independently H, C, N, O, or S; and wherein X_1 or X_2 independently includes one or more C_1-C_{20} alkyl group or one or more aromatic group.

[008] In a further aspect, there is provided a lubricating oil composition comprising (1) greater than 50 wt % of a base oil and (2) 0.01 to 15 wt % of a component selected from one or more of a primary low-speed pre-ignition (LSPI)-reducing additive comprising (i) an amino additive, (ii) an amine additive, (iii) a triazole additive, (iv) a benzamidinium additive, (v) a benzoxazole additive, or (vi) a N=C-X motif additive having a structure of 

, wherein X_1 and X_2 are independently H, C, N, O, or S; and wherein X_1 or X_2 independently includes one or more C_1-C_{20} alkyl group or one or more aromatic group.

DETAILED DESCRIPTION

Introduction

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

[010] "Gasoline" or "gasoline boiling range components" refers to a composition containing at least predominantly C_4-C_{12} hydrocarbons. In one embodiment, gasoline or gasoline boiling range components is further defined to refer to a composition containing at least predominantly C_4-C_{12} hydrocarbons and further having a boiling range of from about 100°F (37.8°C) to about 400°F (204°C). In an alternative embodiment, gasoline or gasoline boiling range components is defined to refer to a composition containing at least predominantly C_4-C_{12} hydrocarbons, having a boiling range of from about 100°F (37.8°C) to about 400°F (204°C), and further defined to meet ASTM D4814.

[011] The term "diesel" refers to middle distillate fuels containing at least predominantly C_{10}-C_{25} hydrocarbons. In one embodiment, diesel is further defined to refer to a composition containing at least predominantly C_{10}-C_{25} 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 C_{10}-C_{25} 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.

[012] 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.

[013] The term "alkyl" refers to saturated hydrocarbon groups, which can be linear, branched, cyclic, or a combination of cyclic, linear and/or branched.

[014] An "alkanol" is an alkyl group, as described herein, having a hydroxy substituent (i.e., an —OH group).

[015] 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.

[016] An "analog" is a compound having a structure similar to another compound but differing from it in respect to a certain component such as one or more atoms, functional groups, substructures, which are replaced with other atoms, groups, or substructures.

[017] A "homolog" is a compound belonging to a series of compounds that differ from each other by a repeating unit. Alkanes are examples of homologs. For example, ethane and propane are homologs because they differ only in the length of a repeating unit (-CH_2-). A homolog may be considered a specific type of analog.

[018] A "derivative" is a compound that is derived from a similar compound via a chemical reaction (e.g., acid-base reaction, hydrogenation, etc.). In the context of substituent groups, a derivative may be a combination of one or more moiety. For example, a phenol moiety may be considered a derivative of aryl moiety and hydroxyl

moiety. A person of ordinary skill in the related art would know the metes and bounds of what is considered a derivative. The term "substituted" refers to a substitution or replacement of an atom or atoms of a compound. As an illustrative example, a "substituted alkyl group" may refer to, among other things, an ethanol.

[019] 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.

Low Speed Pre-Ignition (LSPI)

[020] Low Speed Pre-Ignition (LSPI) is most or more likely to occur in direct-injected, boosted (turbocharged or supercharged), spark-ignited (gasoline) internal combustion engines that, in operation, generate a brake mean effective pressure level of greater than 1000 kPa (10 bar) at engine speeds of from 1500 to 2500 rotations per minute (rpm), such as at engine speeds of from 1500 to 2000 rpm. "Brake mean effective pressure" (BMEP) is defined as the work accomplished during on engine cycle, divided by the engine swept volume, the engine torque normalized by engine displacement. The word "brake" denotes the actual torque or power available at the engine flywheel, as measured on a dynamometer. Thus, BMEP is a measure of the useful energy output of the engine.

[021] It has now been found that the fuel compositions or lubricating oil compositions of this disclosure which are particularly useful in high pressure spark-ignited internal combustion engines and, when used in the high-pressure spark-ignited internal combustion engines, will prevent or minimize engine knocking and pre-ignition problems.

Primary LSPI-Reducing Additives

[022] The following are descriptions of primary additives that can be utilized as a fuel or lubricant additive to reduce LSPI activity. Primary LSPI-reducing additives can be used as standalone additives and/or with other primary additive(s) and/or with of one or more secondary LSPI-reducing additive (described later). When more than one additive is used, the additives may be in salt form. Moreover, when two or more additives are used, there may be synergy between the two or more additives. In general, these additives are fuel or oil soluble at concentrations needed to achieved a desired LSPI reduction level. Table 1 summarizes the primary additive types.

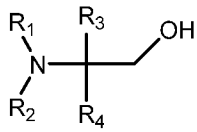
Table 1

Primary Additive Types
1. Amino Additives Beta-amino alkanol Amino acid Amino ester
2. N=C-X Motif Additives Amidine Guanidine Imidazole Benzamidine Benzamidazole Aminobenzimidazole
3. Triazole Additives
4. Benzamidium Additives
5. Benzoxazole Additives
6. Amine Additives Aromatic amine Aliphatic amine

1. Amino Additives

β-Amino Alkanol

[023] The fuel additive or lubricating oil additive of this disclosure may be a β-amino alkanol, a substituted β-amino alkanol, a derivative thereof or an acceptable salt thereof. Useful β-amino alkanols include those that can be represented by the following general formula:

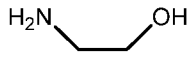


Formula 1

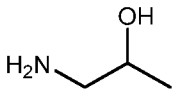
wherein R_1, R_2, R_3, and R_4 are each independently selected from hydrogen and a C_1-C_{20} alkyl (e.g., C_1-C_6 alkyl) group; and two or more of R_1, R_2, R_3, and R_4 optionally can be bonded together to form a ring structure (e.g., a five-, six-, or seven-membered ring). In some embodiments, R_1, R_2, R_3, and R_4 may independently include one or more aromatic rings.

[024] The β-amino alkanol has at least 2 carbon atoms (e.g., from 4 to 30 carbon atoms, from 4 to 20 carbon atoms, from 4 to 16 carbon atoms, from 4 to 12 carbon atoms, from 5 to 30 carbon atoms, from 5 to 20 carbon atoms, from 5 to 16 carbon atoms, or from 5 to 12 carbon atoms).

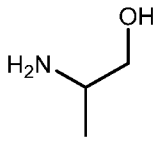
[025] Representative examples of suitable β-amino alkanols include ethanolamine (**Formula 1A**), 1-amino-2-propanol (**Formula 1B**), alaninol (**Formula 1C**), 2-(methylamino)ethanol (**Formula 1D**), 2-(ethylamino)ethanol (**Formula 1E**), 2-amino-2-methyl-1-propanol (**Formula 1F**), 2-amino-1-butanol (**Formula 1G**), 2-amino-1-pentanol (**Formula 1H**), valinol (**Formula 1I**), 2-amino-1-hexanol (**Formula 1J**), leucinol (**Formula 1K**), isoleucinol (**Formula 1L**), cycloleucinol (**Formula 1M**), cyclohexylglycinol (**Formula 1N**), prolinol (**Formula 1O**), 2-(hydroxymethyl)piperidine (**Formula 1P**), 2-aminocyclopentanol (**Formula 1Q**), and 2-aminocyclohexanol (**Formula 1R**). Representative structures are shown below.



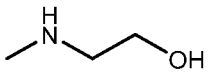
Formula 1A



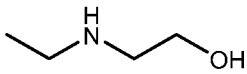
Formula 1B



Formula 1C

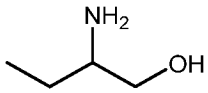


Formula 1D

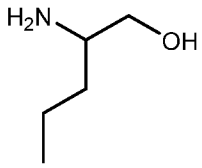


Formula 1E

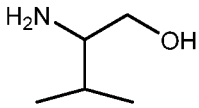
Formula 1F



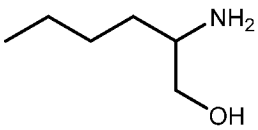
Formula 1G



Formula 1H



Formula 1I



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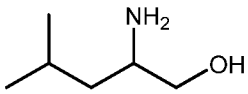

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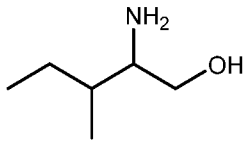
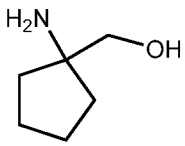
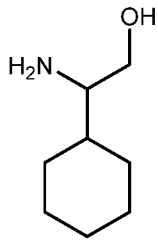


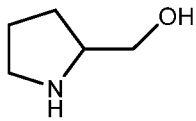
Formula 1L



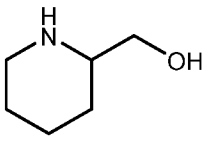
Formula 1M



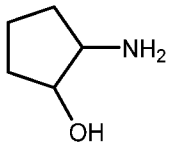
Formula 1N



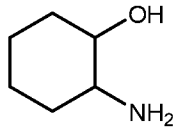
Formula 1O



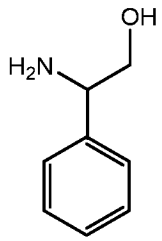
Formula 1P



Formula 1Q



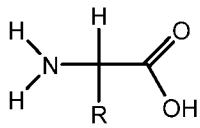
Formula 1R



Formula 1S

Amino Acid

[026] The fuel additive or lubricating oil additive of this disclosure may be an aliphatic amino acid, a substituted aliphatic amino acid, or a derivative thereof, or an acceptable salt thereof. Useful amino acids include those that can be represented by the following general formula:



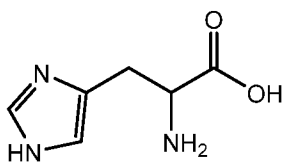
Formula 2

wherein R is an "aliphatic" or "aromatic" side chain. Amino acid side chains can be broadly classified as aromatic or aliphatic. An aromatic side chain includes an aromatic ring. Examples of amino acids with aromatic side chains include for example, histidine (**Formula 2A**), phenylalanine (**Formula 2B**), tyrosine (**Formula 2C**), tryptophan (**Formula 2D**) and the like. Non-aromatic side chains are broadly grouped as "aliphatic" and include, for example, alanine (**Formula 2E**), glycine (**Formula 2F**), cysteine (**Formula 2G**), and the like.

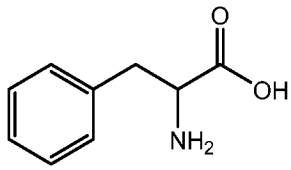
[027] The amino acid(s) can be natural and/or non-natural α-amino acids. Natural amino acids are those encoded by the genetic code, as well as amino acids derived therefrom. These include, for example, hydroxyproline (**Formula 2H**), γ-carboxyglutamate (**Formula 2I**), and citrulline (**Formula 2J**). In this specification, the term "amino acid" also includes amino acid analogs and mimetics. Analogs are

compounds having the same general structure of a natural amino acid, except that the R group is not one found among the natural amino acids.

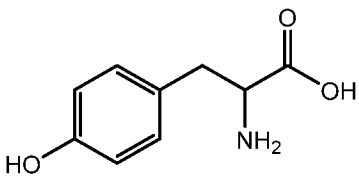
[028] Representative examples of analogs of naturally occurring amino acids include homoserine (**Formula 2K**), norleucine (**Formula 2L**), homoproline (**Formula 2M**) and proline (**Formula 2N**). An amino acid mimetic is a compound that has a structure different from the general chemical structure of an α-amino acid but functions in a manner similar to one. The amino acid may be an L- or D-amino acid. Representative structures are shown below.



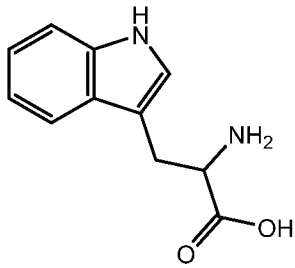
Formula 2A



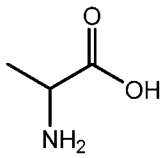
Formula 2B



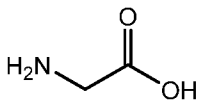
Formula 2C



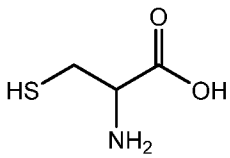
Formula 2D



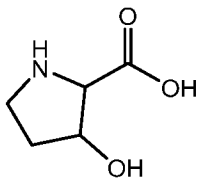
Formula 2E



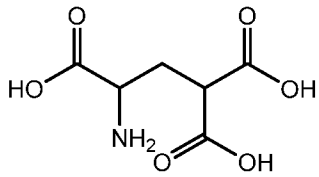
Formula 2F



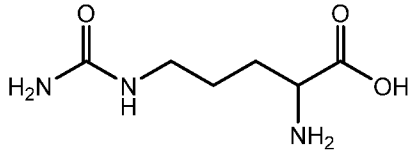
Formula 2G



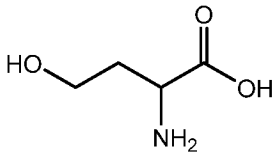
Formula 2H



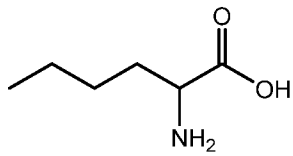
Formula 2I



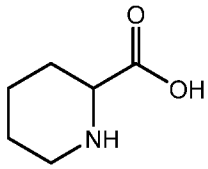
Formula 2J



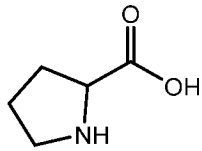
Formula 2K



Formula 2L



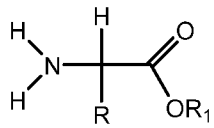
Formula 2M



Formula 2N

Amino Ester

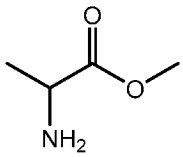
[029] The fuel additive or lubricating oil additive of this disclosure may be an amino ester, a substituted amino ester, or a derivative thereof, or an acceptable salt thereof. Amino esters can be derived from amino acids (as described above) and alcohols. Amino esters and amino acids may be considered derivatives of each other. Useful amino esters include those that can be represented by the following general formula:



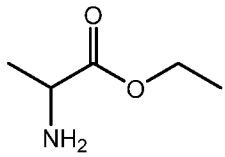
Formula 3

wherein R is an aliphatic side chain and R_1 is a carbon chain 1 to 20 carbon atoms in length, preferably 1 to 4 carbon atoms, in particular, methanol or ethanol, preferably methanol.

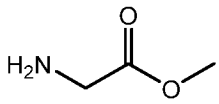
[030] The amino esters may include aromatic or aliphatic side chains. Representative examples of amino esters include methyl alaninate (**Formula 3A**), ethyl alaninate (**Formula 3B**), methyl glycinate (**Formula 3C**), and ethyl glycinate (**Formula 3D**). Representative structures are shown below.



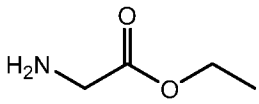
Formula 3A



Formula 3B



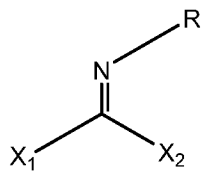
Formula 3C



Formula 3D

2. N=C-X Motif Additives

[031] A fuel additive or lubricating oil additive of this disclosure may have a N=C-X motif as shown in the generalized structure below



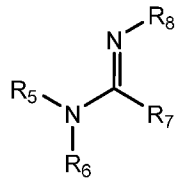
Formula 4

wherein R is H, monovalent organic group, or monovalent heterorganic group (described in greater detail below), X_1 and X_2 are independently H, C, N, O, or S and wherein X_1 or X_2 independently includes one or more C_1-C_{20} alkyl group (e.g., C_1-C_6

alkyl) or one or more aromatic ring. In some embodiments, X_1 and X_2 may include a cyclic structure (e.g., a five-, six-, or seven-membered ring). Cyclic structures may be aromatic or non-aromatic, as well as vary from being fully saturated to fully unsaturated. Suitable examples of additives compatible with Formula 4 include amidines, guanidines, imidazoles, benzamidines, benzimidazoles, and aminobenzimidazoles.

Amidine

[032] The fuel additive or lubricating oil additive of this disclosure may be an amidine, a substituted amidine, or a derivative thereof or an acceptable salt thereof. Useful amidines include those that can be represented by the following general formula:

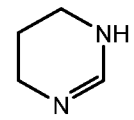


Formula 5

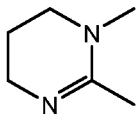
wherein R_5, R_6, R_7 and R_8 are each independently selected from hydrogen, monovalent organic groups, monovalent heterorganic groups (e.g., comprising nitrogen, oxygen, sulfur or phosphorus, in the form of groups or moieties that are bonded through a carbon atom and that do not contain acid functionality such as carboxylic or sulfonic), and combinations thereof; and wherein any two or more of R_5, R_6, R_7 and R_8 optionally can be bonded together to form a cyclic structure (e.g., a five-, six, or seven-membered ring). The cyclic structures may be aromatic or non-aromatic, as well as vary from being fully saturated to fully unsaturated. The organic and heterorganic groups may have from 1 to 10 carbon atoms (e.g., 1 to 6 carbon atoms).

[033] Representative examples of suitable amidines include 1,4,5,6-tetrahydropyrimidine (**Formula 5A**), 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine (**Formula 5B**), 1,2-diethyl-1,4,5,6-tetrahydropyrimidine (**Formula 5C**), 1,5-

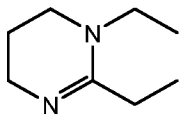
diazabicyclo[4.3.0]non-5-ene (DBN; **Formula 5D**), 1,8-diazabicyclo[5.4.0]-undeca-7-ene (DBU; **Formula 5E**), benzamidine (**Formula 5F**), benzimidazole (**Formula 5G**) and 2-phenyl-1H-benzo[d]imidazole (**Formula 5M**). Representative structures are shown below.



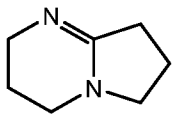
Formula 5A



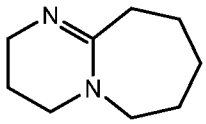
Formula 5B



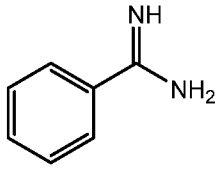
Formula 5C



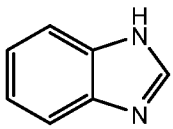
Formula 5D



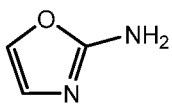
Formula 5E



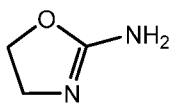
Formula 5F



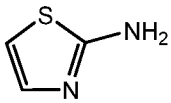
Formula 5G



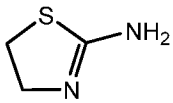
Formula 5H



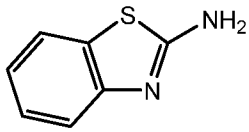
Formula 5I



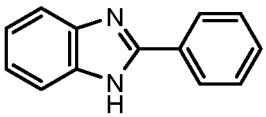
Formula 5J



Formula 5K



Formula 5L

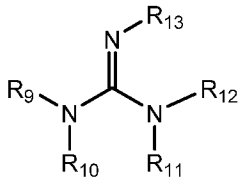


Formula 5M

Guanidine

[034] The fuel additive or lubricating oil additive of this disclosure may be a guanidine, a substituted guanidine, or a derivative thereof, or an acceptable salt

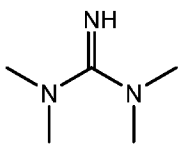
thereof. Useful guanidines include those that can be represented by the following general formula,



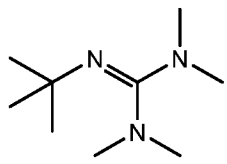
Formula 6

wherein R_9, R_{10}, R_{11}, R_{12} and R_{13} are each independently selected from hydrogen, monovalent organic groups, monovalent heterorganic groups (e.g., comprising nitrogen, oxygen, sulfur or phosphorus, in the form of groups or moieties that are bonded through a carbon atom and that do not contain acid functionality such as carboxylic or sulfonic), and combinations thereof; and wherein any two or more of R_9, R_{10}, R_{11}, R_{12} and R_{13} optionally can be bonded together to form a cyclic structure (e.g., a five-, six, or seven-membered ring). The cyclic structures may be aromatic or non-aromatic, as well as vary from being fully saturated to fully unsaturated. The organic and heterorganic groups may have from 1 to 10 carbon atoms (e.g., 1 to 6 carbon atoms).

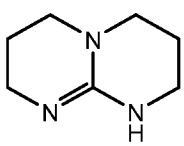
[035] Representative examples of suitable guanidines include 1,1,3,3-tetramethylguanidine (TMG; **Formula 6A**), 2-tert-butyl-1,1,3,3-tetramethylguanidine (BTMG; **Formula 6B**), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; **Formula 6C**), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD; **Formula 6D**) and 1,2-diphenylguanidine (**Formula 6I**). Representative structures shown below.



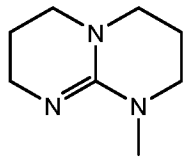
Formula 6A



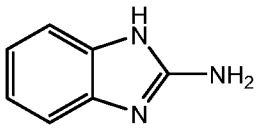
Formula 6B



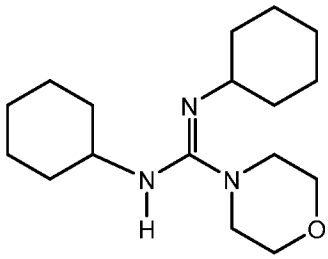
Formula 6C



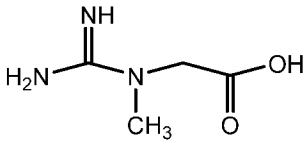
Formula 6D



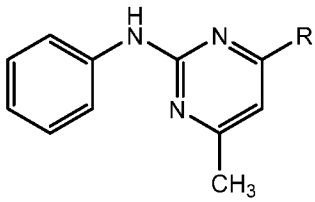
Formula 6E



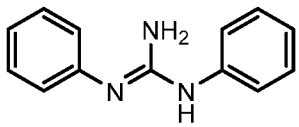
Formula 6F



Formula 6G



Formula 6H

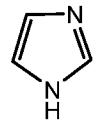


Formula 6I

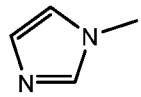
Imidazoles

[036] The fuel additive or lubricating oil additive of this disclosure may be an imidazole, a substituted imidazole, or a derivative thereof, or an acceptable salt thereof. Suitable imidazoles include imidazole (**Formula 7A**), 1-methylimidazole (**Formula 7B**), 1-ethylimidazole (**Formula 7D**), 1-propylimidazole (**Formula 7E**), 1-n-butylimidazole (**Formula 7F**), 1-decylimidazole, 1-dodecylimidazole, 2-methylimidazole (**Formula 7G**), 2-ethylimidazole, 2-isopropylimidazole (**Formula 7H**), 4-methylimidazole (**Formula 7I**), 1,2-dimethylimidazole (**Formula 7J**), 2-ethyl-4(5)-

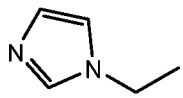
methylimidazole (**Formula 7K**), and 1-vinylimidazole (**Formula 7L**). Representative structures are shown below.



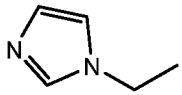
Formula 7A



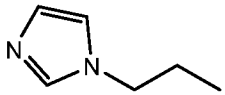
Formula 7B



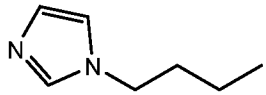
Formula 7C



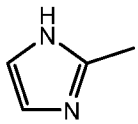
Formula 7D



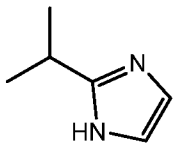
Formula 7E



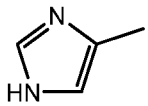
Formula 7F



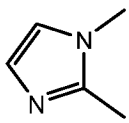
Formula 7G



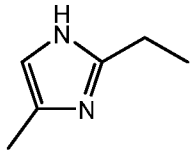
Formula 7H



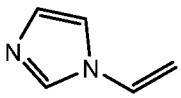
Formula 7I



Formula 7J



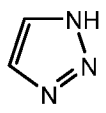
Formula 7K



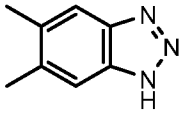
Formula 7L

3. Triazole Additives

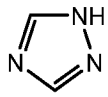
[037] The fuel additive or lubricating oil additive of this disclosure may be a triazole, a substituted triazole, or a derivative thereof, or an acceptable salt thereof. Suitable triazoles include 1, 2, 3-triazole (**Formula 8A**), 5,6-dimethylbenzotriazole (**Formula 8B**), and 1, 2, 4-triazole (**Formula 8C**). Representative structures are shown below.



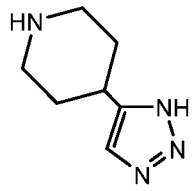
Formula 8A



Formula 8B



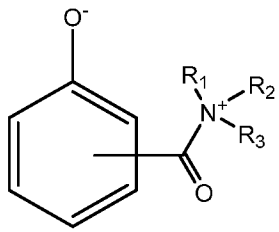
Formula 8C



Formula 8D

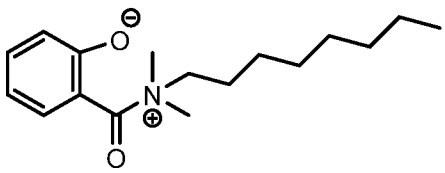
4. Benzamidinium Additives

[038] The fuel additive or lubricating oil additive of this disclosure may be a benzamidinium, a substituted benzamidinium, or a derivative thereof, or an acceptable salt thereof. Useful benzamidinium additives include those that can be represented by the following general formula 9, wherein R_1, R_2, and R_3 are independently C_1-C_{20} alkyl groups.

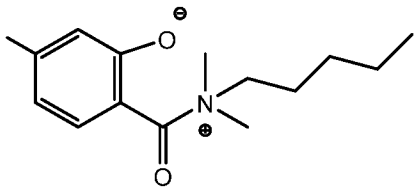


Formula 9

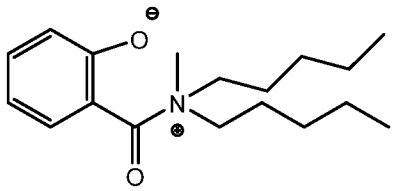
[039] Suitable benzamidiniums include N,N-dimethyl-N-octylbenzamidium-2-oxide (**Formula 9A**). Representative structures are shown below.



Formula 9A



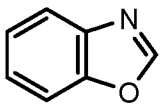
Formula 9B



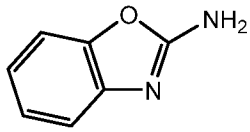
Formula 9C

5. Benzoxazole Additives

[040] The fuel additive or lubricating oil additive of this disclosure may be a benzoxazole, a substituted benzoxazole, or a derivative thereof, or an acceptable salt thereof. Suitable benzoxazoles include benzoxazole (**Formula 10A**) and 2-aminobenzoxazole (**Formula 10B**). Representative structures are shown below.



Formula 10A

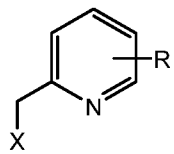


Formula 10B

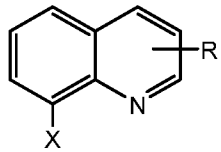
6. Amine Additives

Aromatic amine

[041] The fuel additive or lubricating oil additive of this disclosure may be an aromatic amine, a substituted aromatic amine, or a derivative thereof, or an acceptable salt thereof. Aromatic amine additives can have the generalized structure shown in Formula 11-1 or 11-2,



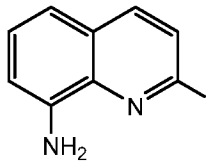
Formula 11-1



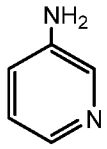
Formula 11-2

wherein R is independently one or more H or C_1-C_{20} alkyl group and X is N (e.g., R-N-R) or O^-.

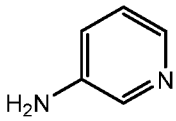
[042] Suitable aromatic amines include 2-methylquinolin-8-amine (**Formula 11A**). Representative structures are shown below.



Formula 11A



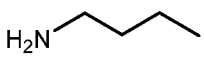
Formula 11B



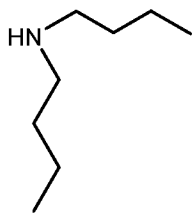
Formula 11C

Aliphatic amine

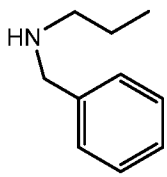
[043] Suitable aliphatic amines are shown below.



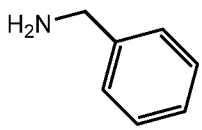
Formula 12A



Formula 12B



Formula 12C



Formula 12D

Secondary LSPI-Reducing Additives

[044] The following are descriptions of secondary LSPI-reducing additives that can be utilized as fuel or lubricating additives to reduce LSPI activity. In general, a secondary LSPI-reducing additive, a substituted secondary LSPI-reducing additive, or a derivative thereof will be used in their salt form and in combination with a primary additive to reduce LSPI activity. For example, β-amino alkanol (primary additive) and aliphatic acid (secondary additive) can be combined and utilized as an LSPI additive. Table 2 lists the secondary additive types. Some additives can act as a primary additive and/or secondary additive.

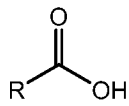
Table 2

Secondary Additive Types
7. Acid Additives Aliphatic acid Unsaturated acid Alkylaromatic acid Aromatic acid Hydroxy acid Amino acid
8. Phenol Additives
9. 1, 3 Dicarbonyl Additives 1,3 Diketone 1,3 Ketoester
10. Hydroxamide Additives
11. Antioxidant Additives
12. Salicylate Additives

7. Acid Additives

Aliphatic Acid

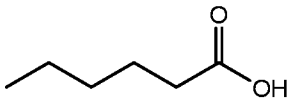
[045] Aliphatic acids are non-aromatic carboxylic acids. Suitable aliphatic acids include mono-carboxylic acids having the following structure



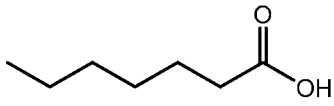
Formula 13

wherein R is an aliphatic group having between 2 to 20 carbon atoms. The aliphatic group may be linear or branched and may contain heteroatoms.

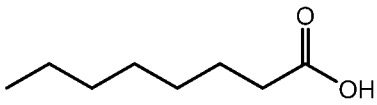
[046] Suitable aliphatic acids include hexanoic acid (**Formula 13A**), heptanoic acid (**Formula 13B**), octanoic acid (**Formula 13C**), nonanoic acid (**Formula 13D**), decanoic acid (**Formula 13E**), undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid (C_{20}), behenic acid (C_{22}), 2-ethylbutyric acid (**Formula 13F**), 3,3-dimethylbutyric acid, 2-methylpentanoic acid (C_6), 2-methylhexanoic acid (C_7), 4-methylhexanoic acid (C_7), 5-methylhexanoic acid (C_7), 2,2-dimethylpentanoic acid (C_7), 2-propylpentanoic acid (C_8), 2-ethylhexanoic acid (**Formula 13G**), 2-methylheptanoic acid (C_8), isooctanoic acid (C_8), 3,5,5-trimethylhexanoic acid (C_9), 4-methyloctanoic acid (C_9), 4-methylnonanoic acid, (C_{10}), isodecanoic acid (C_{10}), 2-butyloctanoic acid (C_{12}), isotridecanoic acid (C_{13}), 2-hexyldecanoic acid (C_{16}), isopalmitic acid (C_{16}), isostearic acid (**Formula 13H**), 3-cyclohexylpropionic acid, 4-cyclohexylbutyric acid (**Formula 13I**), and cyclohexanepentanoic acid. Representative structures are shown below.



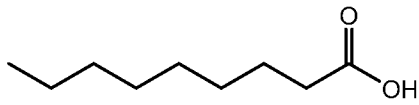
Formula 13A



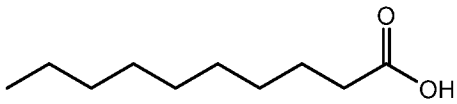
Formula 13B



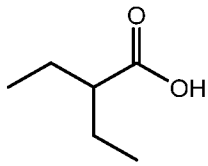
Formula 13C



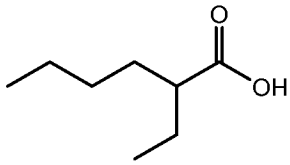
Formula 13D



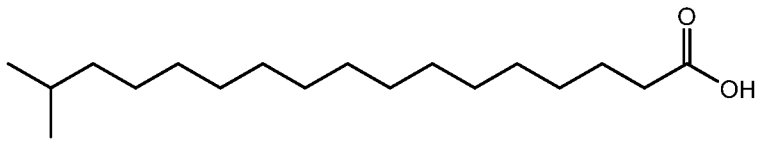
Formula 13E



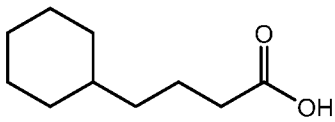
Formula 13F



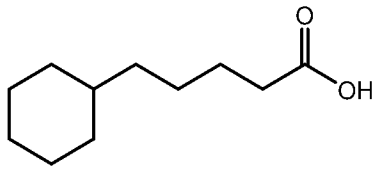
Formula 13G



Formula 13H



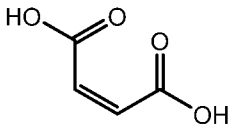
Formula 13I



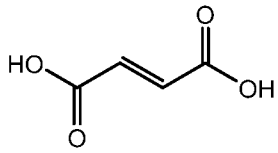
Formula 13J

Unsaturated Acid

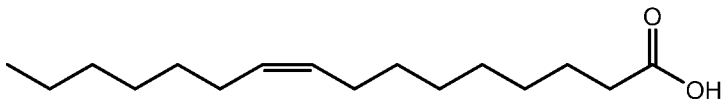
[047] Suitable unsaturated acids include any organic acids that contain double or triple carbon-carbon bond. Representative unsaturated acids include maleic acid (**Formula 14A**), fumaric acid (**Formula 14B**), as well as unsaturated fatty acids such as palmitoleic acid (**Formula 14C**) and oleic acid (**Formula 14D**). Representative structures are shown below.



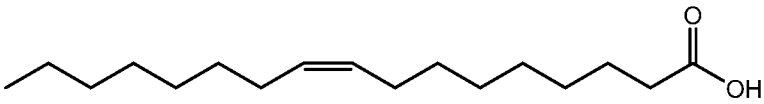
Formula 14A



Formula 14B



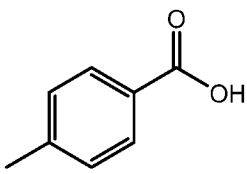
Formula 14C



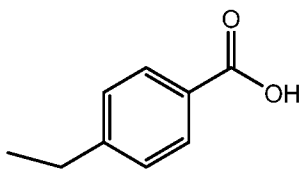
Formula 14D

Alkylaromatic Acid

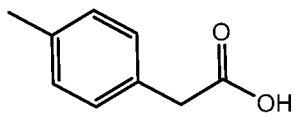
[048] Suitable alkylaromatic acids include both mono-carboxylic acids and dicarboxylic acids. The alkyl carboxylic acid may have 6 or more carbon atoms (e.g., 6 to 24 carbon atoms, 6 to 20 carbon atoms, 8 to 24 carbon atoms, 8 to 20 carbon atoms, or even 8 to 18 carbon atoms). The alkyl moiety may be optionally substituted with one or more substituents such as hydroxy, alkoxy and carbonyl (e.g., aldehydic or ketonic) groups. Suitable examples of alkylaromatic acid include methylbenzoic acid (**Formula 15A**) and ethylbenzoic acid (**Formula 15B**). Representative structures are shown below.



Formula 15A



Formula 15B

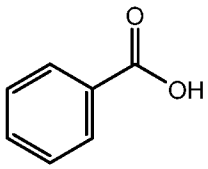


Formula 15C

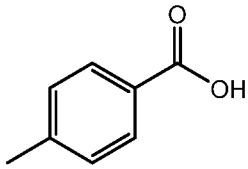
Aromatic Acid

[049] Suitable aromatic acids include both mono-carboxylic acids and dicarboxylic acids. The alkyl carboxylic acid may have 6 or more carbon atoms (e.g., 6

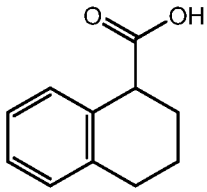
to 24 carbon atoms, 6 to 20 carbon atoms, 8 to 24 carbon atoms, 8 to 20 carbon atoms, or even 8 to 18 carbon atoms). The alkyl moiety may be optionally substituted with one or more substituents such as hydroxy, alkoxy and carbonyl (e.g., aldehydic or ketonic) groups. Suitable aromatic acids include benzoic acid (**Formula 16A**), hydroxybenzoic acid (**Formula 16B**), and tetralin carboxylic acid (**Formula 16C**). Representative structures are shown below.



Formula 16A



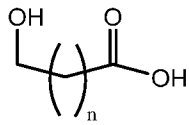
Formula 16B



Formula 16C

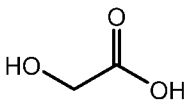
Hydroxy Acid

[050] Suitable hydroxy acids include those that can be represented by the following general formula:

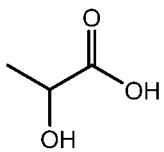


Formula 17

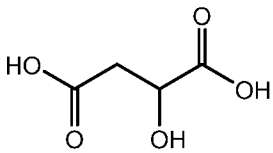
wherein n = 1 to 3. Suitable examples of hydroxy acid include glycolic acid (**Formula 17A**), lactic acid (**Formula 17B**), malic acid (**Formula 17C**), tartaric acid (**Formula 17D**), and citric acid (**Formula 17E**). Representative structures are shown below.



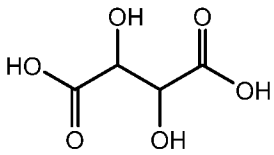
Formula 17A



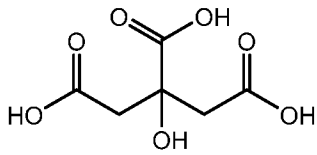
Formula 17B



Formula 17C



Formula 17D



Formula 17E

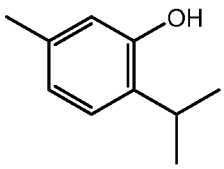
Amino Acid

[051] Amino acids can be utilized as primary and/or secondary additives. Suitable amino acids were previously described above.

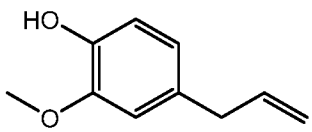
8. Phenol Additives

Phenol

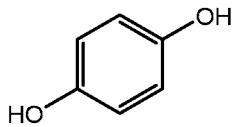
[052] Suitable phenols include, thymol (**Formula 18A**), eugenol (**Formula 18B**), hydroquinone (**Formula 18C**), resorcinol (**Formula 18D**), cresol (**Formula 18E**) and 2-methylquinolin-8-ol (**Formula 18G**). Representative structures are shown below.



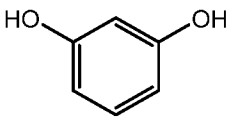
Formula 18A



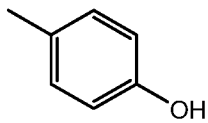
Formula 18B



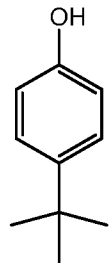
Formula 18C



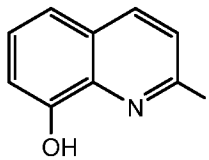
Formula 18D



Formula 18E



Formula 18F

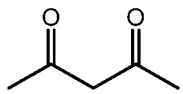


Formula 18G

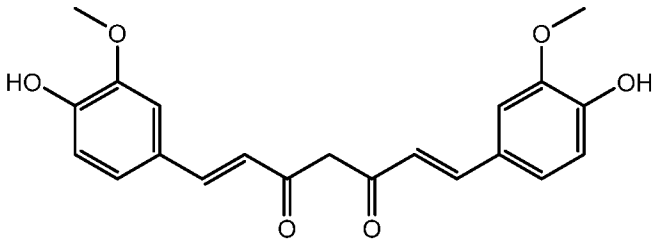
9. 1,3 Dicarbonyl Additives

1, 3 Diketone

[053] Suitable examples of 1,3 diketone compounds include acetylacetone (**Formula 19A**), , and curcumin (**Formula 19B**). Representative structures are shown below.



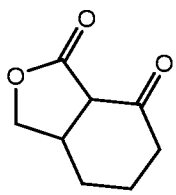
Formula 19A



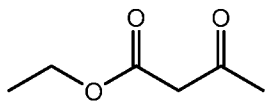
Formula 19B

1,3 Ketoester

[054] Suitable 1,3 ketoesters are shown below.



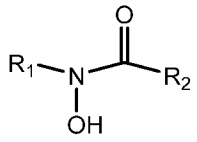
Formula 20A



Formula 20B

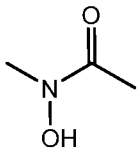
10. Hydroxamide Additives

[055] A hydroxamide is a hydroxy derivative of an amide. Useful hydroxamides include those that can be represented by the following general formula:

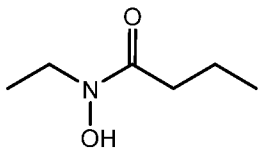


Formula 21

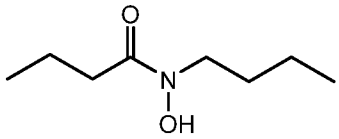
wherein R_1 and R_2 are each independently selected from hydrogen or C_1-C_{20} (e.g., C_3-C_{12}) alkyl group. Suitable hydroxamide includes hydroxy methylacetamide (**Formula 21A**). Representative structures are shown below.



Formula 21A



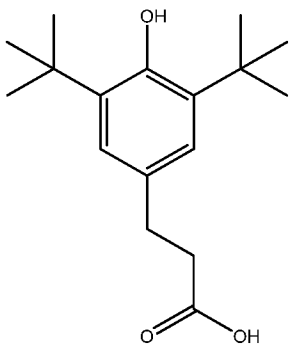
Formula 21B



Formula 21C

11. Antioxidant Additives

[056] Suitable antioxidants include both mono-carboxylic acids and dicarboxylic acids. The alkyl carboxylic acid may have 6 or more carbon atoms (e.g., 6 to 24 carbon atoms, 6 to 20 carbon atoms, 8 to 24 carbon atoms, 8 to 20 carbon atoms, or even 8 to 18 carbon atoms). The alkyl moiety may be optionally substituted with one or more substituents such as hydroxy, alkoxy and carbonyl (e.g., aldehydic or ketonic) groups. Suitable antioxidants include the following.

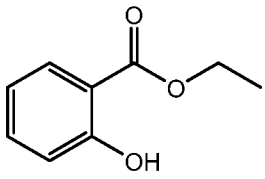


Formula 22A

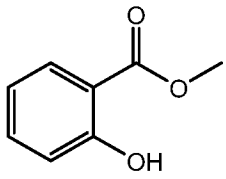
12. Salicylate Additives

Salicylate

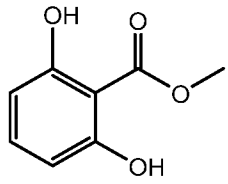
[057] Suitable salicylates include 2-hydroxy-5-(tetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecayn-1-yl)benzoic acid--dihydrogen (**Formula 23E**). Suitable salicylates are shown below.



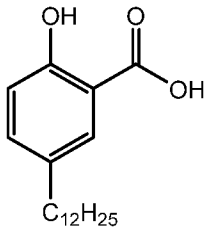
Formula 23A



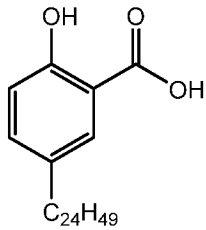
Formula 23B



Formula 23C



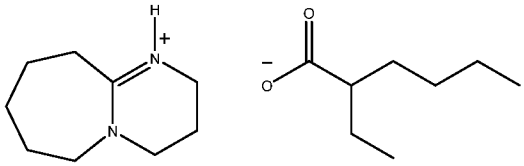
Formula 23D



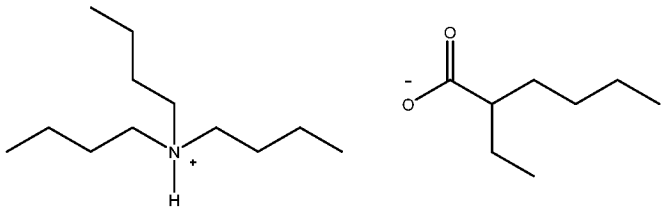
Formula 23E

Salts

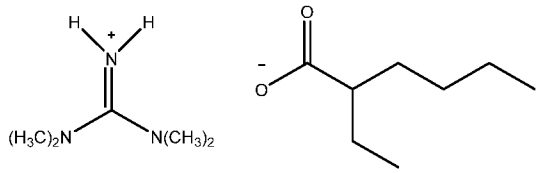
[058] The salts of this disclosure may be prepared by conventional means, for example, by mixing the primary additive with a suitable secondary additive in an aprotic solvent. The order in which one additive is added to the other is not important. The primary additive and secondary additive are usually mixed together in an approximately equimolar ratio. An excess of the primary or secondary additive component may be used. For example, the molar ratio of base relative to the alkyl carboxylic acid may be about 1.05:1 to 2:1 (e.g., 1.1:1 to 1.5:1). Representative salts are shown below.



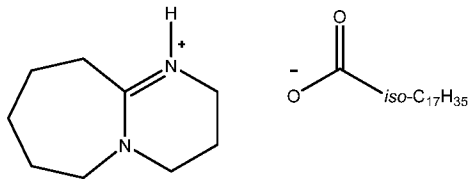
Formula 24A



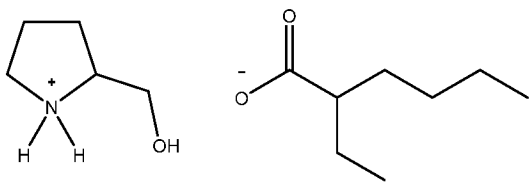
Formula 24B



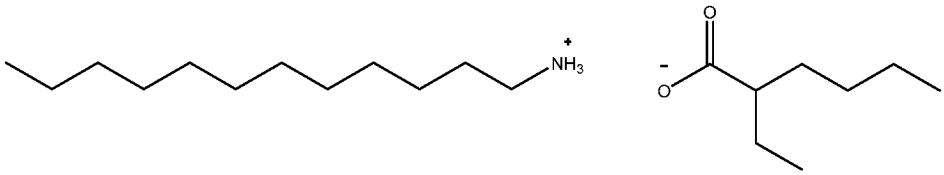
Formula 24C



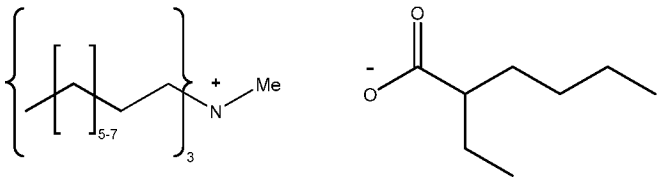
Formula 24D



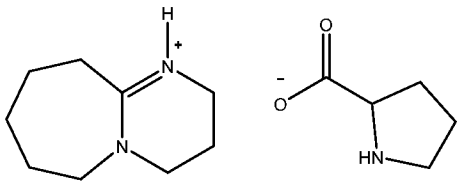
Formula 24E



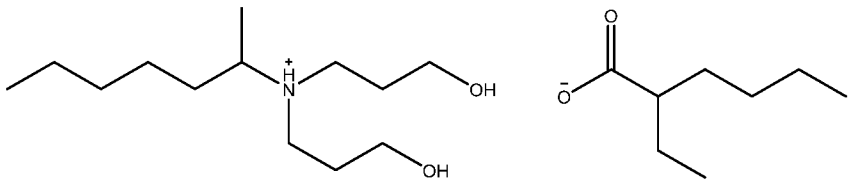
Formula 24F



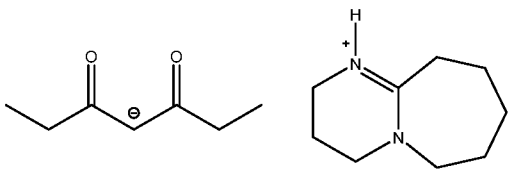
Formula 24G



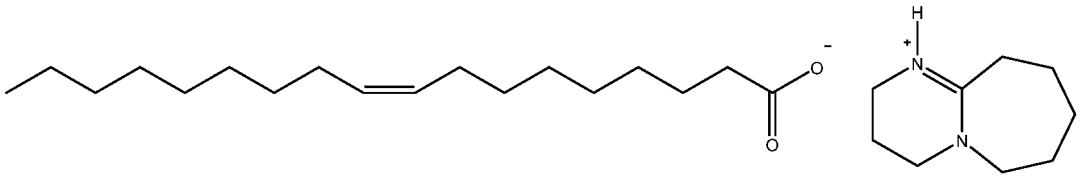
Formula 24H



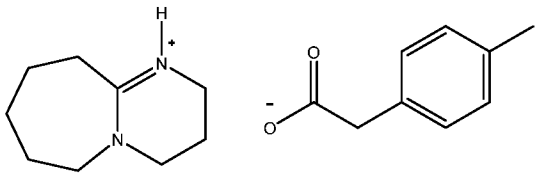
Formula 24I



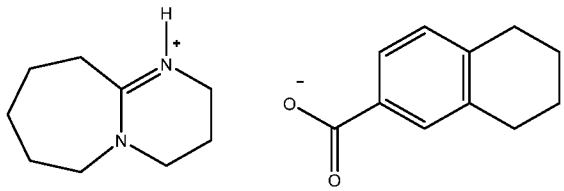
Formula 24J



Formula 24K



Formula 24L



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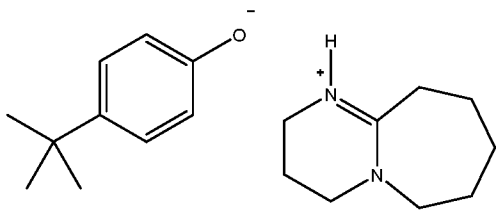

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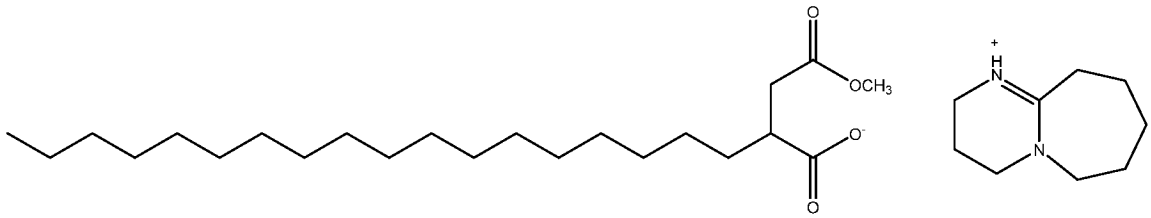
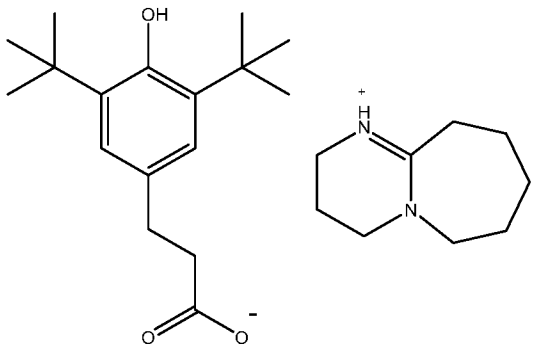
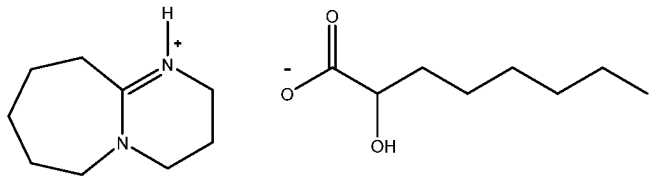


Formula 24O



Formula 24P



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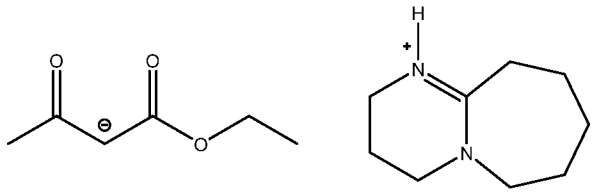

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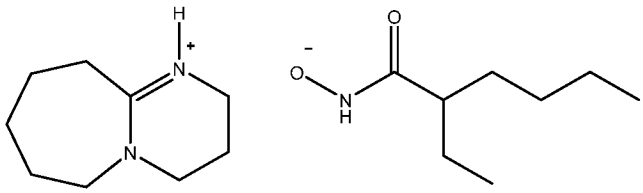
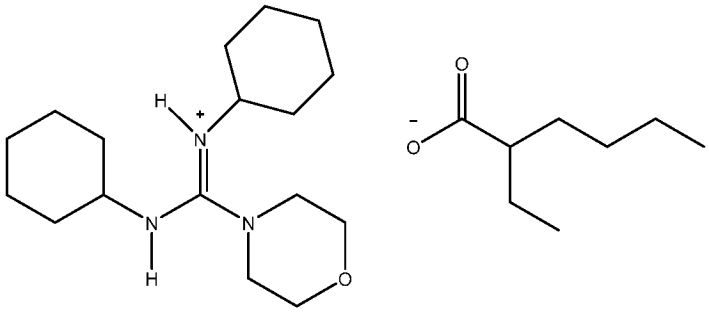
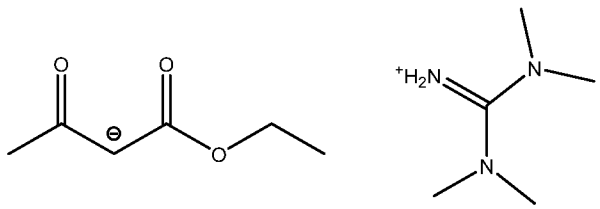


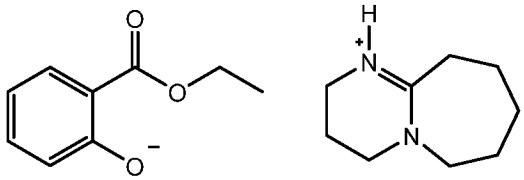
Formula 24S



Formula 24T



Formula 24U



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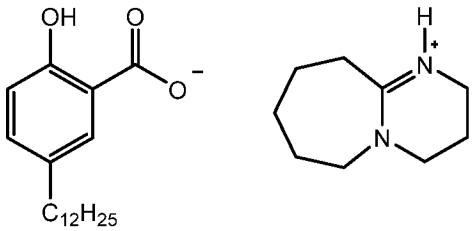
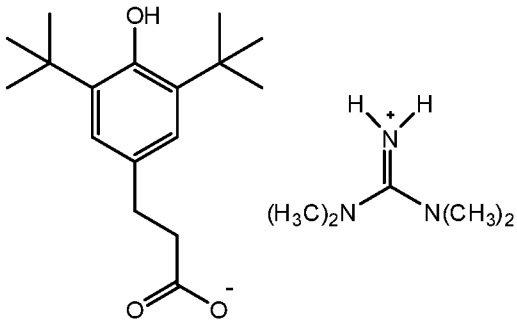
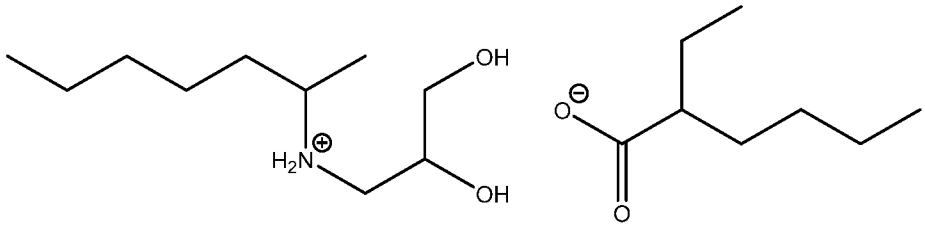


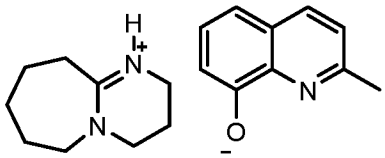
Formula 24W



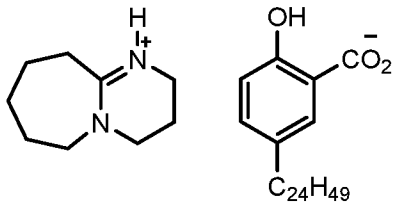
Formula 24X



Formula 24Y



Formula 24Z



Formula 24AA

Fuel Compositions

[059] The compounds of the present disclosure may be useful as additives in hydrocarbon fuels to prevent or reduce engine knock or pre-ignition events in spark-ignited internal combustion engines.

[060] The concentration of the 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).

[061] 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 %).

[062] 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.

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

[064] 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.

[065] 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 %).

Lubricating Oil Compositions

[066] The compounds of the present disclosure may be useful as additives in lubricating oils to prevent or reduce engine knock or pre-ignition events in spark-ignited internal combustion engines.

[067] The concentration of the compounds of the present disclosure in the lubricating oil composition may range from 0.01 to 15 wt % (e.g., 0.5 to 5 wt %), based on the total weight of the lubricating oil composition.

[068] The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil, which is useful for making concentrates as well as for making lubricating oil compositions therefrom, may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

[069] Definitions for the base stocks and base oils in this disclosure are the same as those found in American Petroleum Institute (API) Publication 1509 Annex E ("API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils," December 2016). Group I base stocks contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1. Group II base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test

methods specified in Table E-1. Group III base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[070] Natural oils include animal oils, vegetable oils (e.g., castor oil and lard oil), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[071] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C_8 to C_{14} olefins, e.g., C_8, C_{10}, C_{12}, C_{14} olefins or mixtures thereof, may be utilized.

[072] Other useful fluids for use as base oils include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance characteristics.

[073] Non-conventional or unconventional base stocks/base oils include one or more of a mixture of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomerate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-

petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[074] Base oils for use in the lubricating oil compositions of present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils, and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils, and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[075] Typically, the base oil will have a kinematic viscosity at 100°C (ASTM D445) in a range of 2.5 to 20 mm^2/s (e.g., 3 to 12 mm^2/s, 4 to 10 mm^2/s, or 4.5 to 8 mm^2/s).

[076] The present lubricating oil compositions may also contain conventional lubricant additives for imparting auxiliary functions to give a finished lubricating oil composition in which these additives are dispersed or dissolved. For example, the lubricating oil compositions can be blended with antioxidants, ashless dispersants, anti-wear agents, detergents such as metal detergents, rust inhibitors, dehazing agents, demulsifying agents, friction modifiers, metal deactivating agents, pour point depressants, viscosity modifiers, antifoaming agents, co-solvents, package compatibilizers, corrosion-inhibitors, dyes, extreme pressure agents and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the invention by the usual blending procedures.

[077] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is an ashless dispersant, a functionally effective amount of this ashless dispersant would be an amount sufficient to impart the desired dispersancy characteristics to the lubricant. Generally, the concentration of each of these additives, when used, may range, unless otherwise specified, from about 0.001 to about 20 wt %, such as about 0.01 to about 10 wt %.

EXAMPLES

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

EXAMPLES 1-45

[079] The test compounds were blended in gasoline or lube oil and their capacity for reducing LSPI events were determined using the test method described below.

[080] A GM 2.0 L LHU 4-cylinder gasoline turbocharged direct-injected engine was used for LSPI testing. Each cylinder was equipped with a combustion pressure sensor.

[081] A six-segment test procedure was used to determine the number of LSPI events that occurred under conditions of an engine speed of 2000 rpm and a load of 275 Nm. The LSPI test condition is run for 28 minutes with each segment separated by an idle period. The first segment is used to condition the oil and the number of LSPI events are not counted. Each segment is slightly truncated to eliminate the transient portion. Each truncated segment typically has approximately 100,000 combustion cycles (25,000 combustion cycles per cylinder). In total, the five truncated segments where LSPI events are counted have approximately 500,000 combustion cycles (125,000 combustion cycles per cylinder). There may be instances of shortened tests in the event the engine cannot complete all six segments.

[082] LSPI-impacted combustion cycles were determined by monitoring peak cylinder pressure (PP) and crank angle at 5% total heat release (AI5). LSPI-impacted combustion cycles are defined as having both (1) a PP greater than five standard deviations than the average PP for a given cylinder and truncated segment and (2) an AI5 greater than five standard deviations less than the average for a given cylinder and truncated segment.

[083] The LSPI frequency is reported as the number of LSPI-impacted combustion cycles per million combustion cycles and is calculated as follows:

LSPI Frequency = [(*Total Number of LSPI Impacted Combustion Cycles in five Truncated Segments*)/(*Total Number of Combustion Cycles in five Truncated Segments*)] × 1,000,000

[084] An additive associated with a test fuel and/or test lubricant that reduces the LSPI frequency, when compared to the corresponding baseline fuel and/or baseline lubricant, is considered an additive that mitigates LSPI frequency. For testing herein, the baseline fuel was a conventional 49-state premium unleaded gasoline fuel without any deposit control additives and the baseline lubricant was representative of a conventional engine oil meeting ILSAC GF-5 and API SN specifications. In some of the tests, tetralin was added to the gasoline to promote LSPI. The test results are set forth in Table 2.

TABLE 2

Ex. No.	Additive Component	Additive Concentration	Base Fluid	LSPI Activity (events/million combustion cycles)	Reference (events/million combustion cycles)	Drop in LSPI Activity	Formula
1	Prolinol	1000 ppmw	Fuel	108	268	60%	1O
2	Prolinol	1000 ppmw	Fuel	155	268	42%	1O
3	DBU/2-ethylhexanoate	1000 ppmw	Fuel	14	250	94%	24A
4	DBU/2-ethylhexanoate	500 ppmw	Fuel	28	225	87%	24A
5	DBU/2-ethylhexanoate	250 ppmw	Fuel	65	255	75%	24A
6	Tributylammonium/2-ethylhexanoate	1114 ppmw	Fuel	166	265	37%	24B
7	TMG/2-ethylhexanoate	875 ppmw	Fuel	52	217	76%	24C
8	DBU/isostearate	1473 ppmw	Fuel	48	240	80%	24D
9	DBU/isostearate	1.9 wt %	Lube Oil	113	285	60%	24D
10	Prolinol/2-ethylhexanoate	828 ppmw	Fuel	193	316	39%	24E

11	Prolinol/2-ethylhexanoate	1.1 wt %	Lube Oil	131	316	59%	24E
12	Monosubstituted amine/2-ethylhexanoate	1114 ppmw	Fuel	213	300	29%	24F
13	Aliquat/2-ethylhexanoate	High	Fuel	243	350	31%	24G
14	DBU/Proline	901 ppmw	Fuel	50	350	86%	24H
15	DBU/diketone	946 ppmw	Fuel	62	374	83%	24J
16	DBU/oleate	1466 ppmw	Fuel	38	520	93%	24K
17	DBU/Toluene	1020 ppmw	Fuel	74	531	86%	24L
18	DBU/Tetralin Carboxylate	1108 ppmw	Fuel	106	540	80%	24M
19	DBU/Phenoxide	1020 ppmw	Fuel	36	600	94%	24N
20	DBU	514 ppmw	Fuel	78	419	81%	5E
21	TMG	389 ppmw	Fuel	154	463	67%	6A
22	DBU/Phenol	2338 ppmw	Fuel	218	462	53%	24W
23	DBU/SA analog	1814 ppmw	Fuel	152	396	62%	24O
24	DBU Antioxidant	2421 ppmw	Fuel	24	416	94%	24P

25	DBU/Hydroxy acid	1757 ppmw	Fuel	159	367	57%	24Q
26	DBU/Ketoester	1577 ppmw	Fuel	10	510	98%	24R
27	DBU/Hydroxamide	1750 ppmw	Fuel	123	536	77%	24S
28	MorphGuam	1650 ppmw	Fuel	119	478	75%	6F
29	TMG/antioxidant	2213 ppmw	Fuel	24	498	95%	24X
30	Benzamidine	676 ppmw	Fuel	59	444	87%	5F
31	MorphGuam/2-ethylhexanoate	2461 ppmw	Fuel	26	352	93%	24T
32	Benzamidazole	664 ppmw	Fuel	151	353	57%	5G
33	Imidazole	383 ppmw	Fuel	112	330	66%	7A

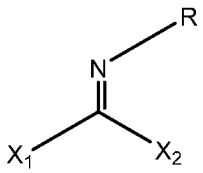
34	2-aminobenzimidazole	749 ppmw	Fuel	16	281	94%	6E
35	TMG/Ketoester	1382 ppmw	Fuel	99	381	74%	24U
36	DBU/Ethyl Salicylate	1790 ppmw	Fuel	34	472	93%	24V
37	N-(2,3-dihydroxypropyl)heptan-2-aminium (AHPD)/2-ethylhexanoate	1000 ppmw	Fuel	84	312	73%	24Y
38	benzoxazole	401.5 ppmw	Fuel	197	344	43%	10A
39	2-aminobenzoxazole	805.4 ppmw	Fuel	239	338	29%	10B
40	N,N-dimethyl-N-octylbenzamidinium-2-oxide	1665.7 ppmw	Fuel	10	246	96%	9A
41	5,6-dimethylbenzotriazole	991.9 ppmw	Fuel	109	235	54%	8B
42	DBU/phenoxide	1869.9 ppmw	Fuel	0	215	100%	24Z
43	DBU/salicylate	4162.2 ppmw	Fuel	46	197	77%	24AA
44	2-phenyl-1H-benzo[d]imidazole	1166.1 ppmw	Fuel	121	192	37%	5M

45	1,2-diphenylguanidine	1725.5 ppmw	Fuel	12	134	91%	6l

CLAIMS

1. A fuel composition comprising (1) greater than 50 wt % of a hydrocarbon fuel boiling in the gasoline or diesel range and (2) a minor amount of one or more of:

a primary low-speed pre-ignition (LSPI)-reducing additive comprising (i) an amino additive, (ii) an amine additive, (iii) a triazole additive, (iv) a benzamidinium additive, (v) a benzoxazole additive, or (vi) a N=C-X motif additive having a structure of



,

wherein X_1 and X_2 are independently H, C, N, O, or S; and

wherein X_1 or X_2 independently includes one or more C_1-C_{20} alkyl group or one or more aromatic group.

2. The fuel composition of claim 1, wherein the amino additive is a beta-amino alkanol, an amino acid, or an amino ester.

3. The fuel composition of claim 1, wherein the amine additive is aromatic amine or aliphatic amine.

4. The fuel composition of claim 1, wherein the triazole additive is 5,6-dimethylbenzotriazole.

5. The fuel composition of claim 1, wherein the primary LSPI-reducing additive is prolinol, aliquat, morphguam, 2-aminobenzimidazole, AHPD, N,N-dimethyl-N-octylbenzamidinium-2-oxide, benzoxazole, 2-methylquinolin-8-amine, or 2-aminobenzoxazole.

6. The fuel composition of claim 1, wherein the N=C-X motif additive is an amidine, a guanidine, an imidazole, a benzamidine, a benzimidazole, or an amino benzimidazole.

7. The fuel composition of claim 6, wherein the amidine is 1,4,5,6-tetrahydropyrimidine, 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine, 1,2-diethyl-1,4,5,6-tetrahydropyrimidine, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 2-phenyl-1H-benzo[d]imidazole, or 1,8-diazabicyclo[5.4.0]-undece-7-ene (DBU).

8. The fuel composition of claim 6, wherein the guanidine is 1,1,3,3-tetramethylguanidine (TMG), 2-tert-butyl-1,1,3,3-tetramethylguanidine(BTMG), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,2-diphenylguanidine, or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD).

9. The fuel composition of claim 1, further comprising:

a secondary LSPI-reducing additive comprising an acid additive, a phenol additive, a 1,3 dicarbonyl additive, a hydroxamide additive, antioxidant additive, or salicylate additive.

10. The fuel composition of claim 9, wherein the primary LSPI-reducing additive and the secondary LSPI-reducing additive form a salt.

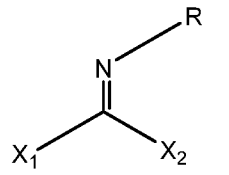
11. The fuel composition of claim 9, wherein the acid additive is an aliphatic acid, an unsaturated acid, an alkylaromatic acid, an aromatic acid, a hydroxy acid, or an amino acid.

12. The fuel composition of claim 9, wherein the secondary LSPI-reducing additive is 2-ethylhexanoate, isostreate, proline, diketone, oleate, toluene, tetraline carboxylate,

phenoxide, phenol carboxylate, hydroxy acid, 2-hydroxy-5-(tetracosa-1,3,5,7,9,11,13,15,17,19,21,23-dodecayn-1-yl)benzoic acid--dihydrogen or ketoester.

13. A fuel concentrate comprising (1) from 90 to 30 wt % of an organic solvent boiling in a range of from 65°C to 205°C and (2) from 10 to 70 wt % of an additive component selected from one or more of

(i) an amino additive, (ii) an amine additive, (iii) a triazole additive, (iv) a benzamidinium additive, (v) a benzoxazole additive, or (vi) a N=C-X motif additive having a structure of



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wherein X_1 and X_2 are independently H, C, N, O, or S; and

wherein X_1 or X_2 independently includes one or more C_1-C_{20} alkyl group or one or more aromatic group.

14. The fuel concentrate of claim 13, wherein the amino additive is a beta-amino alkanol, an amino acid, or an amino ester.

15. The fuel concentrate of claim 13, wherein the amine additive is aromatic amine or aliphatic amine.

16. The fuel concentrate of claim 13, wherein the triazole additive is 5,6-dimethylbenzotriazole.

17. The fuel concentrate of claim 13, primary LSPI-reducing additive is prolinol, aliquat, morphguam, 2-aminobenzimidazole, AHPD, N,N-dimethyl-N-

octylbenzamidinium-2-oxide, benzoxazole, 2-methylquinolin-8-amine, or 2-aminobenzoxazole.

18. The fuel concentrate of claim 13, wherein the N=C-X motif additive is an amidine, a guanidine, an imidazole, a benzamidine, a benzimidazole, or an amino benzimidazole.

19. The fuel concentrate of claim 18, wherein the amidine is 1,4,5,6-tetrahydropyrimidine, 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine, 1,2-diethyl-1,4,5,6-tetrahydropyrimidine, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 2-phenyl-1H-benzo[d]imidazole, or 1,8-diazabicyclo[5.4.0]-undece-7-ene (DBU).

20. The fuel concentrate of claim 18, wherein the guanidine is 1,1,3,3-tetramethylguanidine (TMG), 2-tert-butyl-1,1,3,3-tetramethylguanidine(BTMG), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,2-diphenylguanidine, or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD).

21. The fuel concentrate of claim 13, further comprising:

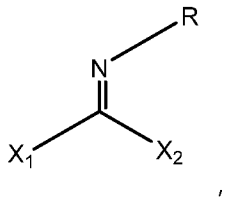
a secondary LSPI-reducing additive comprising an acid additive, a phenol additive, a 1,3 dicarbonyl additive, a hydroxamide additive, an antioxidant additive, or a salicylate additive.

22. The fuel concentrate of claim 21, wherein the acid additive is an aliphatic acid, an unsaturated acid, an alkylaromatic acid, an aromatic acid, a hydroxy acid, or an amino acid.

23. The fuel concentrate of claim 21, wherein the secondary LSPI-reducing additive is 2-ethylhexanoate, isostreate, proline, diketone, oleate, toluene, tetraline carboxylate, phenoxide, phenol carboxylate, hydroxy acid, or ketoester.

24. A lubricating oil composition comprising (1) greater than 50 wt % of a base oil and (2) 0.01 to 15 wt % of a component selected from one or more of

a primary low-speed pre-ignition (LSPI)-reducing additive comprising (i) an amino additive, (ii) an amine additive, (iii) a triazole additive, (iv) a benzamidinium additive, (v) a benzoxazole additive, or (vi) a N=C-X motif additive having a structure of



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wherein X_1 and X_2 are independently H, C, N, O, or S; and

wherein X_1 or X_2 independently includes one or more C_1-C_{20} alkyl group or one or more aromatic group.

25. The lubricating oil composition of claim 24, wherein the amino additive is a beta-amino alkanol, an amino acid, or an amino ester.

26. The lubricating oil composition of claim 24, wherein the amine additive is aromatic amine or aliphatic amine.

27. The lubricating oil composition of claim 24, wherein the triazole additive is 5,6-dimethylbenzotriazole.

28. The lubricating oil composition of claim 24, wherein the primary LSPI-reducing additive is prolinol, aliquat, morphguam, 2-aminobenzimidazole, AHPD, N,N-dimethyl-N-octylbenzamidinium-2-oxide, benzoxazole, 2-methylquinolin-8-amine, or 2-aminobenzoxazole.

29. The lubricating oil composition of claim 24, wherein the N=C-X motif additive is an amidine, a guanidine, an imidazole, a benzamidine, a benzimidazole, or an amino benzimidazole.

30. The lubricating oil composition of claim 29, wherein the amidine is 1,4,5,6-tetrahydropyrimidine, 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine, 1,2-diethyl-1,4,5,6-tetrahydropyrimidine, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 2-phenyl-1H-benzo[d]imidazole, or 1,8-diazabicyclo[5.4.0]-undece-7-ene (DBU).

31. The lubricating oil composition of claim 29, wherein the guanidine is 1,1,3,3-tetramethylguanidine (TMG), 2-tert-butyl-1,1,3,3-tetramethylguanidine(BTMG), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,2-diphenylguanidine, or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD).

32. The lubricating oil composition of claim 24, further comprising:

a secondary LSPI-reducing additive comprising an acid additive, a phenol additive, a 1,3 dicarbonyl additive, a hydroxamide additive, antioxidant additive, or salicylate additive.

33. The lubricating oil composition of claim 32, wherein the secondary LSPI-reducing additive is 2-ethylhexanoate, isostreate, proline, diketone, oleate, toluene, tetraline carboxylate, phenoxide, phenol carboxylate, hydroxy acid, or ketoester.

34. A method for preventing or reducing low speed pre-ignition events in a spark-ignited internal combustion engine, the method comprising supplying to the engine the lubricating oil composition comprising of claim 24.

35. The method of claim 34, wherein the spark-ignited internal combustion engine is operated at a speed of less than 3000 rpm.

36. The method of claim 34, wherein the spark-ignited internal combustion engine is operated under a load with a brake mean effective pressure of at least 10 bar (1 MPa).

37. A method for preventing or reducing low speed pre-ignition events in a spark-ignited internal combustion engine, the method comprising supplying to the engine the fuel composition comprising of claim 1.

38. The method of claim 37, wherein the spark-ignited internal combustion engine is operated at a speed of less than 3000 rpm.

39. The method of claim 37, wherein the spark-ignited internal combustion engine is operated under a load with a brake mean effective pressure of at least 10 bar (1 MPa).