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(54) Title: METHOD FOR REDUCING LOW SPEED PRE-IGNITION

(57) Abstract: Use of an unleaded gasoline fuel composition for reducing the occurrence of Low Speed Pre-Ignition (LSPI) in a spark-ignition internal combustion engine, wherein the unleaded gasoline fuel composition comprises a gasoline base fuel and detergent additive package, wherein the detergent additive package comprises a Mannich base detergent mixture, wherein the mixture comprises a first Mannich base detergent component derived from a di- or polyamine and a second Mannich base detergent component derived from a monoamine, wherein the weight ratio of the first Mannich base detergent to the second Mannich base detergent mixture ranges from about 1:6 to about 3:1, and wherein the spark-ignition internal combustion engine is lubricated with a lubricant composition comprising from 1200ppmw to 3000ppmw of calcium, based on the total lubricant composition.



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METHOD FOR REDUCING LOW SPEED PRE-IGNITION

Cross-Reference To Related Applications

This application claims priority to U.S. Provisional Application Serial No. 62/573,723 filed October 18, 2017, the entire disclosure of which is hereby incorporated by reference.

5 Field of the Invention

The present invention relates to a method for reducing low speed pre-ignition in a spark-ignition internal combustion engine.

Background of the Invention

10 Under ideal conditions, normal combustion in a conventional spark-ignited engine occurs when a mixture of fuel and air is ignited within the combustion chamber inside the cylinder by the production of a spark originating from a spark plug. Such normal combustion is generally characterized by the expansion of the flame front across the combustion chamber in an orderly and controlled manner.

15 However, in some instances, the fuel/air mixture may be prematurely ignited by an ignition source prior to the spark plug firing, thereby resulting in a phenomenon known as pre-ignition. Pre-ignition is undesirable as it typically results in the presence of greatly increased temperatures and pressures within the combustion chamber, which may have a significant, negative impact on the overall efficiency and performance of an engine. Pre-ignition may cause damage to the cylinders, pistons and valves in the
20 engine and in some instances may even culminate in engine failure.

25 Recently, low-speed pre-ignition (“LSPI”) has been recognized amongst many original equipment manufacturers (“OEMs”) as a potential problem for highly boosted, down-sized spark-ignition engines. Contrary to the pre-ignition phenomenon observed in the late 50’s at high speeds, LSPI typically occurs at low speeds and high loads. LSPI is a constraint that restricts improvements in torque at low engine speeds, which could impact fuel economy and drivability. The occurrence of LSPI may ultimately lead to so-called “monster knock” or “mega-knock” where potentially devastating pressure waves can result in severe damage to the piston and/or cylinder. As such, any technology that can mitigate the risk of pre-ignition, including LSPI, would be highly
30 desirable.

There are multiple mechanisms leading to LSPI events discussed in the

literature. One of those mechanisms involves ignition of the flaked-off deposits present inside the combustion chamber (e.g. around the piston crevice region or on the injector) leading to LSPI events while another mechanism is based on the ignition of oil droplets inside the combustion chamber. It could be a combination of these two mechanisms
5 (deposits and oil droplets) that results in LSPI or a yet to be determined mechanism.

It has been found that LSPI is more common in engines, such as modern turbocharged engines, that operate using an engine oil with high calcium content and a market-average gasoline fuel. Most commercial engine oils currently available in the market have high calcium content, ranging from 1200 ppm to 3000 ppm. Typically, as
10 mentioned above, this LSPI phenomenon is common in the high torque, low speed operating conditions. Most Original Equipment Manufacturers (OEMs) calibrate their engine management systems to avoid engine operation in these regimes to prevent LSPI from occurring. However, operating in these regimes would potentially give the OEMs additional opportunity to decrease fuel consumption.

One solution to the problem of LSPI is to formulate engine oils such that they have a new composition. Examples of those methods can be found in WO2015/171978A1, WO2016/087379A1, WO2015/042341A1. One such solution is to formulate engine oils having a very low calcium content (<100ppm). The effects of lower calcium content in the engine oils in lowering LSPI occurrences have been
20 described in SAE 2016-01-2275. Such a formulation potentially modifies the chemical pathways in terms of the oil droplets that lead to LSPI. However, most current commercial engine oils have high calcium content and therefore it would be desirable to come up with an alternative solution for the problem of LSPI without having to reformulate the engine oil formulation.

It has now been found by the present inventors that by using a gasoline formulation which comprises a certain type of detergent additive package and/or certain detergent additive components, a surprising reduction in LSPI events can be achieved, especially in the case when used in engines which are lubricated with engine oils having high levels of calcium.

30 Summary of the Invention

According to the present invention there is provided the use of an unleaded gasoline fuel composition for reducing the occurrence of Low Speed Pre-Ignition (LSPI) in a spark-ignition internal combustion engine, wherein the unleaded gasoline

fuel composition comprises a gasoline base fuel and a detergent additive package, wherein the detergent additive package comprises a Mannich base detergent mixture, wherein the mixture comprises a first Mannich base detergent component derived from a di- or polyamine and a second Mannich base detergent component derived from a monoamine, wherein the weight ratio of the first Mannich base detergent to the second Mannich base detergent mixture ranges from about 1:6 to about 3:1, and wherein the spark-ignition internal combustion engine is lubricated with a lubricant composition comprising from 1200ppmw to 3000ppmw of calcium, based on the total lubricant composition.

According to the present invention there is further provided the use of an unleaded gasoline fuel composition for reducing the occurrence of Low Speed Pre-Ignition (LSPI) in a spark-ignition internal combustion engine, wherein the unleaded gasoline fuel composition comprises a major amount of gasoline base fuel, a minor amount of a first Mannich base detergent derived from a di- or polyamine and a second Mannich base detergent derived from a monoamine, an antiwear component, preferably selected from a hydrocarbyl amide and a hydrocarbyl imide, and a polyether carrier fluid, and optionally a succinimide detergent, wherein the weight ratio of the first Mannich base detergent to the second Mannich base detergent mixture ranges from about 1:6 to about 3:1, and wherein the spark-ignition internal combustion engine is lubricated with a lubricant composition comprising from 1200ppmw to 3000ppmw of calcium, based on the total lubricant composition.

According to the present invention there is further provided a method for reducing the occurrence of Low Speed Pre-Ignition (LSPI) in an internal combustion engine, the method comprising supplying to the engine a fuel composition comprising an unleaded gasoline fuel composition comprising a detergent additive package wherein the detergent additive package comprises a Mannich base detergent mixture, wherein the mixture comprises a first Mannich base detergent component derived from a di- or polyamine and a second Mannich base detergent component derived from a monoamine, wherein the weight ratio of the first Mannich base detergent to the second Mannich base detergent mixture ranges from about 1:6 to about 3:1, and wherein the spark-ignition internal combustion engine is lubricated with a lubricant composition comprising from 1200ppmw to 3000ppmw of calcium, based on the total lubricant composition.

The features and advantages of the present invention will be apparent to those skilled in the art. While numerous changes may be made by those skilled in the art, such changes are within the spirit of the invention.

Detailed Description of the Invention

5 Accordingly, the disclosure herein provides the use of an unleaded gasoline fuel composition comprising a specified additive package or comprising a certain combination of specified additive components for reducing the occurrence of Low Speed Pre-Ignition (LSPI) in a spark-ignition internal combustion engine.

10 The level of occurrence of pre-ignition in a spark-ignited engine may be assessed using any suitable method. In general, such a method may involve running a spark-ignited engine using the relevant fuel and/or lubricant composition, and monitoring changes in engine pressure during its combustion cycles, i.e., changes in pressure versus crank angle. A pre-ignition event will result in an increase in engine pressure before sparking: this may occur during some engine cycles but not others.

15 Instead, or in addition to, changes in engine performance may be monitored, for example by maximum attainable brake torque, engine speed, intake pressure and/or exhaust gas temperature. Instead, or in addition to, a suitably experienced driver may test-drive a vehicle which is driven by the spark-ignited engine, to assess the effects of a particular fuel and/or lubricant composition on, for example, the degree of engine knock

20 or other aspects of engine performance. Instead, or in addition to, levels of engine damage due to pre-ignition, for example due to the associated engine knock, may be monitored over a period of time during which the spark-ignited engine is running using the relevant fuel and/or lubricant composition.

25 A reduction in the occurrence of pre-ignition may be a reduction in the number of engine cycles at which pre-ignition events occur or a reduction in the rate at which pre-ignition events occur within the engine, and/or in the severity of the pre-ignition events which occur (for example, the degree of pressure change which they cause). It may be manifested by a reduction in one or more of the effects which pre-ignition can have on engine performance, for example impairment of brake torque or inhibition of

30 engine speed. It may be manifested by a reduction in the amount or severity of engine knock, in particular by a reduction in, or elimination of, “mega knock”. Preferably, in the present invention, a reduction in the occurrence of pre-ignition is a reduction in the number of engine cycles in which pre-ignition events occur.

Since pre-ignition, particularly if it occurs frequently, can cause significant engine damage, the fuel compositions disclosed herein may also be used for the purpose of reducing engine damage and/or for the purpose of increasing engine longevity.

5 The uses and methods of the present invention may be used to achieve any degree of reduction in the occurrence of pre-ignition in the engine, including reduction to zero (i.e., eliminating pre-ignition). It may be used to achieve any degree of reduction in a side effect of pre-ignition, for example engine damage. It may be used for the purpose of achieving a desired target level of occurrence or side effect. The method and use herein preferably achieves a 5% reduction or more in the occurrence of pre-ignition in the engine, more preferably a 10% reduction or more in the occurrence of pre-ignition in the engine, even more preferably a 15% reduction or more in the occurrence of pre-ignition in the engine, and especially a 30% reduction or more in the occurrence of pre-ignition in the engine.

15 Examples of suitable methods for measuring Low Speed Pre-Ignition events can be found in the following SAE papers: SAE 2014-01-1226, SAE 2011-01-0340, SAE 2011-01-0339 and SAE 2011-01-0342. Another example of a suitable method for measuring Low Speed Pre-Ignition events is that described in the Examples hereinbelow.

20 Fuel compositions for use herein generally comprise a gasoline base fuel and optionally one or more fuel additives in addition to the detergent additive package or the specified combination of additive components described herein.

In one aspect of the present invention, the unleaded gasoline fuel composition comprises a gasoline base fuel and a detergent additive package. The detergent additive package is typically used at a concentration from 6 PTB (23 ppmw) to 528 PTB (2000 ppmw), preferably from 8 PTB (30 ppmw) to 300 PTB (1125 ppmw), more preferably from 30 PTB (113 ppmw) to 250 PTB (942 ppmw) (where PTB stands for pounds of additive per thousand barrels of gasoline).

30 The detergent additive package for use herein comprises a Mannich base detergent mixture that comprises a first Mannich base detergent component derived from a di- or polyamine and a second Mannich base detergent component derived from a monoamine, wherein the weight ratio of the first Mannich base detergent to the second Mannich base detergent in the mixture ranges from about 1:6 to about 3:1,

such as from 1:4 to 2:1 or from 1:3 to 1:1. Suitable detergent additive packages for use herein are disclosed in US2016/0289584, incorporated herein by reference.

In one embodiment herein, a suitable fuel additive package comprises (a) a first Mannich base detergent component derived from a di- or polyamine, (b) a second Mannich base detergent component derived from a monoamine, (c) an antiwear component, and (d) optionally, a carrier fluid component selected from the group consisting of a polyether monool and polyether polyol. The ratio weight of the first Mannich base detergent to the second Mannich base detergent in the fuel additive package ranges from about 1:6 to about 3:1, such as from 1:4 to 2:1, or from 1:3 to 1:1.

In another aspect of the present invention, the gasoline fuel composition comprises a combination of Mannich base detergent additives instead of a detergent additive package. In this aspect of the present invention, the Mannich base detergent additives are added to the gasoline base fuel, either by premixing the individual detergent additives together, optionally together with one or more antiwear additives and/or one or more succinimide detergents and/or one or more carrier fluids, and then adding the premix to the gasoline base fuel, or by adding the individual detergent additives and the individual antiwear additives and carrier fluids, directly to the gasoline base fuel.

Mannich Base Detergents

The Mannich base detergents useful in the present invention are the reaction products of an alkyl-substituted hydroxy aromatic compound, an aldehyde and an amine. The alkyl-substituted hydroxyaromatic compound, aldehyde and amine used in making the Mannich detergent reaction products described herein may be any such compounds known and applied in the art, provided the Mannich based detergents include at least a first Mannich base detergent derived from a di- or polyamine and at least a second Mannich base detergent derived from a dialkyl monoamine.

Representative alkyl-substituted hydroxyaromatic compounds that may be used in forming the Mannich base reaction products are polypropylphenol (formed by alkylating a phenol with polypropylene), polybutylphenols (formed by alkylating a phenol with polybutenes and/or polyisobutylene) and polybutyl-co-polypropylphenol (formed by alkylating phenol with a copolymer of butylene and/or butylene and propylene). Other similar long-chain alkylphenols may also be used.

Examples include phenols alkylated with copolymers of butylene and/or isobutylene and/or propylene, and one or more mono-olefinic co-monomers copolymerizable therewith (e.g., ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene, etc.) where the copolymer molecule contains at least 50% by weight, of butylene and/or isobutylene and/or propylene units. The comonomers polymerized with propylene, butylenes and/or isobutylene may be aliphatic and may also contain non-aliphatic groups, e.g., styrene, o-methylstyrene, p-methylstyrene, di-vinyl benzene and the like. Thus in any case the resulting polymers and copolymers used in forming the alkyl-substituted hydroxyaromatic compounds are substantially aliphatic hydrocarbon polymers.

In one embodiment herein, polybutylphenol (formed by alkylating a phenol with polybutylene) is used in forming the Mannich base detergents. Unless otherwise specified herein, the term "polybutylene" is used in a generic sense to include polymers made from "pure" or "substantially pure" 1-butene or isobutene, and polymers made from mixtures of two or all three of 1-butene, 2-butene and isobutene. Commercial grades of such polymers may also contain insignificant amounts of other olefins. So-called high reactivity polybutylenes having relatively high proportions of polymer molecules having a terminal vinylidene group, formed by methods such as described, for example, in U.S. Pat. No. 4,152,499 and W. German Offenlegungsschrift 29 04 314, are also suitable for use in forming the long chain alkylated phenol reactant.

The alkylation of the hydroxyaromatic compound is typically performed in the presence of an alkylating catalyst at a temperature in the range of about 50° to about 200 °C. Acidic catalysts are generally used to promote Friedel-Crafts alkylation. Typical catalysts used in commercial production include sulfuric acid, BF₃, aluminum phenoxide, methanesulphonic acid, cationic exchange resin, acidic clays and modified zeolites.

The long chain alkyl substituents on the benzene ring of the phenolic compound are derived from polyolefin having a number average molecular weight (MW) of from about 500 to about 3000 Daltons (preferably from about 500 to about 2100 Daltons) as determined by gel permeation chromatography (GPC). It is also desirable that the polyolefin used have a polydispersity (weight average molecular weight/number average molecular weight) in the range of about 1 to about 4 (suitably from about 1 to about 2) as determined by GPC.

The Mannich detergents may be made from a long chain alkylphenol. However, other phenolic compounds may be used including high molecular weight alkyl-substituted derivatives of resorcinol, hydroquinone, catechol, hydroxydiphenyl, benzylphenol, phenethylphenol, naphthol, tolylnaphthol, among others. Particularly
5 suitable for the preparation of the Mannich condensation products are the polyalkylphenol and polyalkylcresol reactants, e.g., polypropylphenol, polybutylphenol, polypropylcresol, polyisobutylcresol, and polybutylcresol, wherein the alkyl group has a number average molecular weight of about 500 to about 2100, while the most suitable alkyl group is a polybutyl group derived from polybutylene
10 having a number average molecular weight in the range of about 800 to about 1300 Daltons.

The configuration of the alkyl-substituted hydroxyaromatic compound is that of a para-substituted monoalkylphenol or a para-substituted mono-alkyl ortho-cresol. However, any alkylphenol readily reactive in the Mannich condensation reaction
15 may be used. Thus, Mannich products made from alkylphenols having only one ring alkyl substituent, or two or more ring alkyl substituents are suitable for use in making the Mannich base detergents described herein. The long chain alkyl substituents may contain some residual unsaturation, but in general, are substantially saturated alkyl groups. Long chain alkyl phenols, according to the disclosure, include cresol.

Representative reactants include, but are not limited to, linear, branched or
20 cyclic alkylene monoamines and di- or polyamines having at least one suitably reactive primary or secondary amino group in the molecule. Other substituents such as hydroxyl, cyano, amido, etc., may be present in the amine compound. In one embodiment, the first Mannich base detergent is derived from an alkylene di- or
25 polyamine. Such di- or polyamines may include, but are not limited to, polyethylene polyamines, such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethyleneheptamine, heptaethyleneoctamine, octaethylenenonamine, nonaethylenedecamine, decaethyleneundecamine and mixtures of such amines having nitrogen contents
30 corresponding to alkylene polyamines of the formula $H_2N-(A-NH-)_nH$, where A is divalent ethylene and n is an integer of from 1 to 10. The alkylene polyamines may be obtained by the reaction of ammonia and dihaloalkanes, such as dichloro alkanes. Thus, the alkylene polyamines obtained from the reaction of 2 to 11 moles of

ammonia with 1 to 10 moles of dichloro alkanes having 2 to 6 carbon atoms and the chlorines on different carbon atoms are suitable alkylene polyamine reactants.

In one embodiment, the first Mannich base detergent is derived from an aliphatic linear, branched or cyclic diamine or polyamine having one primary or secondary amino group and one tertiary amino group in the molecule. Examples of suitable polyamines include N,N,N",N"-tetraalkyl-dialkylenetriamines (two terminal tertiary amino groups and one central secondary amino group), N,N,N",N"-tetraalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), N,N,N,N",N"-pentaalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal secondary amino group), N,N-dihydroxyalkyl-alpha, omega-alkylenediamines (one terminal tertiary amino group and one terminal primary amino group), N,N,N'-trihydroxy-alkyl-alpha, omega-alkylenediamines (one terminal tertiary amino group and one terminal secondary amino group), tris(dialkylaminoalkyl)aminoalkylmethanes (three terminal tertiary amino groups and one terminal primary amino group), and like compounds, wherein the alkyl groups are the same or different and typically contain no more than about 12 carbon atoms each, and which suitably contain from 1 to 4 carbon atoms each. In one embodiment, the alkyl groups of the polyamine are methyl and/or ethyl groups. Accordingly, the polyamine reactants may be selected from N,N-dialkylalpha, omega-alkylenediamine, such as those having from 3 to about 6 carbon atoms in the alkylene group and from 1 to about 12 carbon atoms in each of the alkyl groups. A particularly useful polyamine is N,N-dimethyl-1,3-propanediamine and N-methyl piperazine.

Examples of polyamines having one reactive primary or secondary amino group that can participate in the Mannich condensation reaction and at least one sterically hindered amino group that cannot participate directly in the Mannich condensation reaction to any appreciable extent include N-(tert-butyl)-1,3-propanediamine, N-neopentyl-1,3-propanediamine, N-(tert-butyl)-1-methyl-1,2-ethanediamine, N-(tert-butyl)-1-methyl-1,3-propanediamine, and 3,5-di(tert-butyl)aminoethyl-1-piperazine.

The second Mannich base detergent may be derived from an alkyl-monoamine, that includes, without limitation, a di-alkyl monoamine such as

methylaniline, dimethyl amine, ethylaniline, di-ethylaniline, propylaniline,
isopropylaniline, dipropyl amine, di-isopropyl amine, butylaniline, isobutylaniline, di-
butyl amine, di-isobutylaniline, pentylaniline, dipentyl amine, neopentylaniline, di-
neopentyl amine, hexylaniline, dihexyl amine, heptylaniline, diheptyl amine,
5 octylaniline, dioctyl amine, 2-ethylhexylaniline, di-2-ethylhexyl amine, nonylaniline,
dinonyl amine, decylaniline, didecyl amine, dicyclohexylaniline, and the like.

Representative aldehydes for use in the preparation of the Mannich base
products include the aliphatic aldehydes such as formaldehyde, acetaldehyde,
propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde,
10 stearaldehyde. Aromatic aldehydes which may be used include benzaldehyde and
salicylaldehyde. Illustrative heterocyclic aldehydes for use herein are furfural and
thiophene aldehyde, etc. Also useful are formaldehyde-producing reagents such as
paraformaldehyde, or aqueous formaldehyde solutions such as formalin. A
particularly suitable aldehyde may be selected from formaldehyde and formalin.

15 The condensation reaction among the alkylphenol, the specified amine(s) and
the aldehyde may be conducted at a temperature in the range of about 40°C to about
200 °C. The reaction may be conducted in bulk (no diluent or solvent) or in a solvent
or diluent. Water is evolved and may be removed by azeotropic distillation during
the course of the reaction. Typically, the Mannich reaction products are formed by
20 reacting the alkyl-substituted hydroxyaromatic compound, the amine and aldehyde in
the molar ratio of 1.0:0.5-2.0:1.0-3.0, respectively.

Suitable Mannich base detergents for use in the disclosed embodiments
include those detergents taught in U.S. Pat. Nos. 4,231,759, 5,514,190, 5,634,951,
5,697,988, 5,725,612, 5,876,468 and 6,800,103, the disclosures of which are
25 incorporated herein by reference.

When formulating the fuel compositions used herein, a mixture of the
Mannich base detergents is used. The mixture of Mannich base detergents includes a
weight ratio of from about 1:6 to about 3:1 of the first Mannich base detergent to the
second Mannich base detergent. In another embodiment, the mixture of Mannich
30 base detergents includes a weight ratio of from about 1:4 to about 2:1, such as from
about 1:3 to about 1:1, of the first Mannich base detergent to the second Mannich
base detergent. The total amount of Mannich base detergent in a gasoline fuel

composition according to the disclosure may range from about 10 to about 400 parts per million by weight based on a total weight of the fuel composition.

An optional component of the fuel compositions and/or additive package(s) described herein is a succinimide detergent. The succinimide detergent suitable for use in various embodiments of the disclosure may impart a dispersant effect on the fuel composition when added in an amount effective for that purpose. The presence of the succinimide, together with the mixed Mannich base detergents, in the fuel composition is observed to result in enhanced deposit formation control, relative to the performance of the succinimide together with either the first or second Mannich base detergent.

The succinimide detergents, for example, include alkenyl succinimides comprising the reaction products obtained by reacting an alkenyl succinic anhydride acid, acid-ester or lower alkyl ester with an amine containing at least one primary amine group.

Suitable succinimide base detergents for use herein include those disclosed in US2016/0289584, incorporated by reference herein.

When the succinimide detergent is present in the fuel compositions/additive packages herein, the weight ratio of succinimide detergent to Mannich base detergent mixture preferably ranges from about 0.04:1 to about 0.2:1.

In another embodiment, the Mannich base detergent mixture and the succinimide detergent may be used with a liquid carrier or induction aid. Such carriers may be of various types, such as for example liquid poly-alphaolefin oligomers, mineral oils, liquid poly(oxyalkylene) compounds, liquid alcohols or polyols, polyalkenes, liquid esters, and similar liquid carriers. Mixtures of two or more such carriers may be used. Suitable carrier fluids for use herein include those disclosed in US2016/0289584, incorporated herein by reference.

When the carrier fluid is present, the weight ratio of carrier fluid to Mannich base detergent mixture preferably ranges from about 0.25:1 to about 1:1.

The anti-wear component for the fuel compositions, and additive packages described herein may be selected from a hydrocarbyl amide and a hydrocarbyl imide. In one embodiment, the hydrocarbyl amide is an alkanol amide derived from diethanol amine and oleic acid. In another embodiment, the hydrocarbyl imide is a succinimide derived from polyisobutenyl succinic anhydride and ammonia. In one

embodiment, the hydrocarbyl amide compound may be one or more fatty acid alkanol amide compounds.

Suitable anti-wear additives for use herein include those disclosed in US2016/0289584, incorporated herein by reference.

5 If the liquid fuel compositions of the present invention contain a gasoline base fuel, the liquid fuel composition is a gasoline fuel composition. The gasoline may be any gasoline suitable for use in an internal combustion engine of the spark-ignition (gasoline) type known in the art, including automotive engines as well as in other types of engine such as, for example, off road and aviation engines. The gasoline
10 used as the base fuel in the liquid fuel composition of the present invention may conveniently also be referred to as 'base gasoline'.

Gasolines typically comprise mixtures of hydrocarbons boiling in the range from 25 to 230°C (EN-ISO 3405), the optimal ranges and distillation curves typically varying according to climate and season of the year. The hydrocarbons in a gasoline
15 may be derived by any means known in the art, conveniently the hydrocarbons may be derived in any known manner from straight-run gasoline, synthetically-produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbons, hydro-cracked petroleum fractions, catalytically reformed hydrocarbons or mixtures of these.

20 The specific distillation curve, hydrocarbon composition, research octane number (RON) and motor octane number (MON) of the gasoline are not critical.

Conveniently, the research octane number (RON) of the gasoline may be at least 80, for instance in the range of from 80 to 110, preferably the RON of the gasoline will be at least 90, for instance in the range of from 90 to 110, more
25 preferably the RON of the gasoline will be at least 91, for instance in the range of from 91 to 105, even more preferably the RON of the gasoline will be at least 92, for instance in the range of from 92 to 103, even more preferably the RON of the gasoline will be at least 93, for instance in the range of from 93 to 102, and most preferably the RON of the gasoline will be at least 94, for instance in the range of
30 from 94 to 100 (EN 25164); the motor octane number (MON) of the gasoline may conveniently be at least 70, for instance in the range of from 70 to 110, preferably the MON of the gasoline will be at least 75, for instance in the range of from 75 to 105, more preferably the MON of the gasoline will be at least 80, for instance in the range

of from 80 to 100, most preferably the MON of the gasoline will be at least 82, for instance in the range of from 82 to 95 (EN 25163).

Typically, gasolines comprise components selected from one or more of the following groups; saturated hydrocarbons, olefinic hydrocarbons, aromatic hydrocarbons, and oxygenated hydrocarbons. Conveniently, the gasoline may
5 comprise a mixture of saturated hydrocarbons, olefinic hydrocarbons, aromatic hydrocarbons, and, optionally, oxygenated hydrocarbons.

Typically, the olefinic hydrocarbon content of the gasoline is in the range of from 0 to 40 percent by volume based on the gasoline (ASTM D1319); preferably,
10 the olefinic hydrocarbon content of the gasoline is in the range of from 0 to 30 percent by volume based on the gasoline, more preferably, the olefinic hydrocarbon content of the gasoline is in the range of from 0 to 20 percent by volume based on the gasoline.

Typically, the aromatic hydrocarbon content of the gasoline is in the range of from 0 to 70 percent by volume based on the gasoline (ASTM D1319), for instance
15 the aromatic hydrocarbon content of the gasoline is in the range of from 10 to 60 percent by volume based on the gasoline; preferably, the aromatic hydrocarbon content of the gasoline is in the range of from 0 to 50 percent by volume based on the gasoline, for instance the aromatic hydrocarbon content of the gasoline is in the range
20 of from 10 to 50 percent by volume based on the gasoline.

The benzene content of the gasoline is at most 10 percent by volume, more preferably at most 5 percent by volume, especially at most 1 percent by volume based on
the gasoline.

The gasoline preferably has a low or ultra low sulphur content, for instance at
25 most 1000 ppmw (parts per million by weight), preferably no more than 500 ppmw, more preferably no more than 100, even more preferably no more than 50 and most preferably no more than even 10 ppmw.

The gasoline also preferably has a low total lead content, such as at most
30 0.005 g/l, most preferably being lead free – having no lead compounds added thereto (i.e. unleaded).

When the gasoline comprises oxygenated hydrocarbons, at least a portion of non-oxygenated hydrocarbons will be substituted for oxygenated hydrocarbons. The

oxygen content of the gasoline may be up to 35 percent by weight (EN 1601) (e.g. ethanol per se) based on the gasoline. For example, the oxygen content of the gasoline may be up to 25 percent by weight, preferably up to 10 percent by weight. Conveniently, the oxygenate concentration will have a minimum concentration
5 selected from any one of 0, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 percent by weight, and a maximum concentration selected from any one of 5, 4.5, 4.0, 3.5, 3.0, and 2.7 percent by weight.

Examples of oxygenated hydrocarbons that may be incorporated into the gasoline include alcohols, ethers, esters, ketones, aldehydes, carboxylic acids and
10 their derivatives, and oxygen containing heterocyclic compounds. Preferably, the oxygenated hydrocarbons that may be incorporated into the gasoline are selected from alcohols (such as methanol, ethanol, propanol, 2-propanol, butanol, tert-butanol, iso-butanol and 2-butanol), ethers (preferably ethers containing 5 or more carbon atoms per molecule, e.g., methyl tert-butyl ether and ethyl tert-butyl ether)
15 and esters (preferably esters containing 5 or more carbon atoms per molecule); a particularly preferred oxygenated hydrocarbon is ethanol.

When oxygenated hydrocarbons are present in the gasoline, the amount of oxygenated hydrocarbons in the gasoline may vary over a wide range. For example, gasolines comprising a major proportion of oxygenated hydrocarbons are currently
20 commercially available in countries such as Brazil and U.S.A., e.g. ethanol per se and E85, as well as gasolines comprising a minor proportion of oxygenated hydrocarbons, e.g. E10 and E5. Therefore, the gasoline may contain up to 100 percent by volume oxygenated hydrocarbons. E100 fuels as used in Brazil are also included herein. Preferably, the amount of oxygenated hydrocarbons present in the
25 gasoline is selected from one of the following amounts: up to 85 percent by volume; up to 70 percent by volume; up to 65 percent by volume; up to 30 percent by volume; up to 20 percent by volume; up to 15 percent by volume; and, up to 10 percent by volume, depending upon the desired final formulation of the gasoline. Conveniently, the gasoline may contain at least 0.5, 1.0 or 2.0 percent by volume oxygenated
30 hydrocarbons.

Examples of suitable gasolines include gasolines which have an olefinic hydrocarbon content of from 0 to 20 percent by volume (ASTM D1319), an oxygen content of from 0 to 5 percent by weight (EN 1601), an aromatic hydrocarbon

content of from 0 to 50 percent by volume (ASTM D1319) and a benzene content of at most 1 percent by volume.

Also suitable for use herein are gasoline blending components which can be derived from a biological source. Examples of such gasoline blending components can be found in WO2009/077606, WO2010/028206, WO2010/000761, European
5 patent application nos. 09160983.4, 09176879.6, 09180904.6, and US patent application serial no. 61/312307.

Whilst not critical to the present invention, the base gasoline or the gasoline composition of the present invention may conveniently include one or more optional
10 fuel additives, in addition to the essential Mannich detergents mentioned above. The concentration and nature of the optional fuel additive(s) that may be included in the base gasoline or the gasoline composition used in the present invention is not critical. Non-limiting examples of suitable types of fuel additives that can be included in the
15 base gasoline or the gasoline composition used in the present invention include anti-oxidants, corrosion inhibitors, antiwear additives or surface modifiers, flame speed additives, detergents, dehazers, antiknock additives, metal deactivators, valve-seat recession protectant compounds, dyes, solvents, carrier fluids, diluents and
20 markers. Examples of suitable such additives are described generally in US Patent No. 5,855,629.

Conveniently, the fuel additives can be blended with one or more solvents to form an additive concentrate, the additive concentrate can then be admixed with the base gasoline or the gasoline composition of the present invention.

The (active matter) concentration of any optional additives present in the base gasoline or the gasoline composition of the present invention is preferably up to 1
25 percent by weight, more preferably in the range from 5 to 2000 ppmw, advantageously in the range of from 300 to 1500 ppmw, such as from 300 to 1000 ppmw.

Lubricant compositions for use in the spark ignition engines described herein generally generally comprise a base oil and one or more performance additives, and
30 should be suitable for use in a spark-ignited internal combustion engine. In some embodiments, the lubricant compositions described herein may be particularly useful in a turbocharged spark-ignited engine, more particularly a turbocharged spark-ignited engine which operates, or may operate, or is intended to operate, with an inlet pressure

of at least 1 bar.

The present invention has been found to be particularly useful in high calcium engine oil environments. Hence, the lubricant compositions for use herein generally have a calcium content of from 1200ppmw to 3000ppmw, on the basis of the total
5 lubricating composition. In one embodiment, the lubricant compositions for use herein have a calcium content from 2000 ppmw to 3000 ppmw, as measured according to ASTM D5185. In another embodiment, the lubricant compositions herein have a calcium content from 2500 ppmw to 3000 ppmw.

The fuel compositions may be conveniently prepared using conventional
10 formulation techniques by admixing one or more base fuels with one or more performance additive packages and/or one or more additive components.

To facilitate a better understanding of the present invention, the following examples of certain aspects of some embodiments are given. In no way should the following examples be read to limit, or define, the entire scope of the invention.

15 Examples

Two different fuels were used in the present examples. Example 1 (according to the present invention) was a base fuel in combination with a fuel additive package containing a combination of detergents meeting the requirements of Claim 1 herein. The base fuel used in Example 1 was an E10 fuel (10% v/v ethanol) containing 16.9%
20 v/v aromatics, 7.3% v/v olefins and 75.8% v/v saturates (all results determined according to ASTM D1319), and having an anti-knock index $((RON+MON)/2)$ of 93. The base fuel was obtained from a US terminal and therefore met the ASTM D4814 specification as required by regulations. Comparative Example 1 was the same base fuel as in Example 1 in combination with an additive package typically used in a
25 market-average LAC gasoline. (LAC denotes Lowest Additive Concentration). It is mandated by the U.S. Environmental Protection Agency for all gasoline sold in the US to have a minimum concentration of detergent, and it is common for the gasoline with the minimum concentration of detergent to be called LAC gasoline. Comparative Example 1 and Example 1 contained the respective fuel additive packages at the same
30 treat rates, eliminating any changes in LSPI measurements due to the change in treat rates of the additive packages.

Example 1 and Comparative Example 1 were subjected to the following test method for measuring LSPI events and the frequency thereof.

Test Method for Measuring LSPI

The test protocol used for measuring LSPI events involved running a quasi-steady state test on a modern turbocharged gasoline direct injection engine with a displacement of 2.0 L. The test included operation at an engine condition where the low speed pre-ignition phenomenon was known to occur. At this condition the engine controls were fixed to prevent distortion of the results by the engine settings. For this condition, the engine was held at steady conditions for 25,000 engine cycles (one test segment). Each test sequence consisted of six such test segments and was four hours long. The test sequence was run two times for each fuel without an oil drain or a flush in between. Therefore, each test for each fuel was eight hours long and had 12 segments of 25,000 engine cycles each. The LSPI measurements in each test were done during these 25,000 engine cycles test segments, when the conditions were steady. The measurement metric for the test was to measure the combustion pressure in all four cylinders of the engine and to identify combustion cycles where low speed pre-ignition occurred. Those cycles were counted and the total number of cycles in which LSPI occurred per test was used to quantify the behaviour of each fuel.

The following test conditions were used during the test:

1. The load (BMEP) and torque fluctuated slightly between tests because the operating condition was defined by the fuel flow rate, equivalence ratio, and CA50 location rather than the engine load.
2. The torque range in the two tests were between 250 Nm and 275 Nm.
3. BMEP varied between 15.8 – 17.3 bar.
4. Engine speed = 2000 rpm.
5. Lubricant type: A GF-5 certified high calcium containing lubricant of 5W-30 viscosity grade having a calcium content of 2900 ppmw as measured according to ASTM D5185.

Table 1 below sets out the total number of LSPI cycles per test for the fuels of Example 1 and Comparative Example 1.

Table 1

Example:	Total Number of LSPI cycles per test
Example 1	60
Comparative Example 1	98

The results in Table 1 show that the fuel of Example 1 was associated with a

reduced LSPI occurrence compared with the fuel of Comparative Example 1. It is to be noted that each LSPI event in an engine has the potential to result in a “mega knock,” which is characterized by extremely high pressures inside the engine cylinder that could lead to a rapid and catastrophic degradation of the engine. Therefore, the reduction in the number of LSPI cycles obtained by Example 1, as shown in Table 1, is very significant.

CLAIMS

1. Use of an unleaded gasoline fuel composition for reducing the occurrence of Low Speed Pre-Ignition (LSPI) in a spark-ignition internal combustion engine,
5 wherein the unleaded gasoline fuel composition comprises a gasoline base fuel and detergent additive package, wherein the detergent additive package comprises a Mannich base detergent mixture, wherein the mixture comprises a first Mannich base detergent component derived from a di- or polyamine and a second Mannich base detergent component derived from a monoamine, wherein the weight ratio of the first
10 Mannich base detergent to the second Mannich base detergent mixture ranges from about 1:6 to about 3:1, and wherein the spark-ignition internal combustion engine is lubricated with a lubricant composition comprising from 1200ppmw to 3000ppmw of calcium, based on the total lubricant composition.
2. Use according to Claim 1 wherein the detergent package further comprises a
15 carrier fluid, preferably selected from the group consisting of a polyether monool and polyether polyol, wherein the weight ratio of carrier fluid to Mannich base detergent mixture ranges from about 0.25:1 to about 1:1.
3. Use according to Claim 1 or 2 wherein the weight ratio of the first Mannich
20 base detergent to the second Mannich base detergent ranges from about 1:1 to about 1:3.
4. Use according to any of Claims 1 to 3 wherein the detergent package further
comprises an antiwear component, preferably selected from a hydrocarbyl amide and a hydrocarbyl imide. Use according to any of Claims 1 to 4 wherein the detergent
25 additive package further comprises a succinimide detergent, wherein the weight ratio of succinimide detergent to Mannich base detergent mixture ranges from about 0.04:1 to about 0.2:1.
5. Use according to any of Claims 1 to 5 wherein the unleaded gasoline fuel
composition comprises from about 23 ppm to 2000 ppm by weight of the detergent
additive package.
- 30 6. Use according to Claim 1 wherein the detergent additive package is present in the form of an additive concentrate which comprises the detergent additive package and an antiwear component selected from a hydrocarbyl amide and a hydrocarbyl imide.

7. Use according to Claim 7 wherein the unleaded gasoline fuel composition comprises from about 23 ppm to about 2000 ppm by weight of the additive concentrate.
8. Use according to any of Claims 1 to 8 wherein the first Mannich base detergent and the second Mannich base detergent are derived from polyisobutenyl phenol wherein the polyisobutenyl group has a molecular weight ranging from 500 to 1000 Daltons, as determined by gel permeation chromatography.
9. Use of an unleaded gasoline fuel composition for reducing the occurrence of Low Speed Pre-Ignition (LSPI) in a spark-ignition internal combustion engine, wherein the unleaded gasoline fuel composition comprises a major amount of gasoline base fuel, a minor amount of a first Mannich base detergent derived from a di- or polyamine and a second Mannich base detergent derived from a monoamine, an antiwear component, preferably selected from a hydrocarbyl amide and a hydrocarbyl imide, and a polyether carrier fluid, and optionally a succinimide detergent, wherein the weight ratio of the first Mannich base detergent to the second Mannich base detergent mixture ranges from about 1:6 to about 3:1, and wherein the spark-ignition internal combustion engine is lubricated with a lubricant composition comprising from 1200ppmw to 3000ppmw of calcium, based on the total lubricant composition.
10. Method for reducing the occurrence of Low Speed Pre-Ignition (LSPI) in an internal combustion engine, the method comprising supplying to the engine a fuel composition comprising an unleaded gasoline fuel composition comprising a detergent additive package wherein the detergent additive package comprises Mannich base detergent mixture, wherein the mixture comprises a first Mannich base detergent component derived from a di- or polyamine and a second Mannich base detergent component derived from a monoamine, wherein the weight ratio of the first Mannich base detergent to the second Mannich base detergent mixture ranges from about 1:6 to about 3:1, and wherein the spark-ignition internal combustion engine is lubricated with a lubricant composition comprising from 1200ppmw to 3000ppmw of calcium, based on the total lubricant composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/056008

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C10L1/22
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AKRAM ZAHDEH ET AL: "Fundamental Approach to Investigate Pre-Ignition in Boosted SI Engines", SAE INTERNATIONAL JOURNAL OF ENGINES, vol. 4, no. 1, 12 April 2011 (2011-04-12), pages 246-273, XP055203891, ISSN: 1946-3944, DOI: 10.4271/2011-01-0340 page 259 - page 260; figure 31 -----	1-10
A	US 2009/071065 A1 (MALFER DENNIS J [US] ET AL) 19 March 2009 (2009-03-19) claims 26,33 -----	1-10
A	US 2015/322372 A1 (GAO JASON ZHISHENG [US] ET AL) 12 November 2015 (2015-11-12) claims 97-104 -----	1-10

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Pöllmann, Klaus
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2018/056008

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009071065	A1	19-03-2009	NONE

US 2015322372	A1	12-11-2015	EP 3140373 A1 15-03-2017
			SG 11201608062V A 28-10-2016
			US 2015322372 A1 12-11-2015
			WO 2015171292 A1 12-11-2015
