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(54) CLEAN-BURNING GASOLINE ADDITIVE TO ELIMINATE VALVE SEAT RECESSION AND TOXIC DEPOSITS

(57) A fuel additive for fuel formulations comprising calcium sulfonates in an amount effective to limit or eliminate valve seat recession in engines utilizing such fuel formulations. The fuel additive may also include a detergent, particularly in an amount to enhance the VSR limiting effect of the calcium sulfonates. Also included are fuel formulations containing calcium sulfonates in a concentration effective to limit vale seat recession in engines utilizing the fuel formulations. Methods for treating VSR in piston engines are also provided.

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Description

Field of Invention

[0001] Valve Seat Recession (VSR) can occur in any internal combustion engine due to the repetitive impact of the valves in the cylinder, particularly the exhaust valve, contacting the cylinder head socket (valve seat) under intense temperature and pressure over the operating life of a piston engine.

Background

[0002] Combustion of gasoline products in the combustion chamber of a piston engine often results in residue and deposits forming around the intake valve and exhaust port and around the cylinder and piston head. The composition of gasoline typically comprises C_7 - C_{10} aromatic hydrocarbons and C_4 - C_{12} aliphatic compounds that upon incomplete combustion result in engine deposits and combustion residue.

[0003] The cleanest combustion examples, i.e. those unleaded gasolines that contain only C_4 - C_{10} aliphatic compounds and high-octane oxygenated compounds (e.g. ETBE, MTBE, TAME, alcohols, etc.), tend to offer much cleaner combustion characteristics due to the presence of oxygen in their chemistry. However, many high performance gasolines with more exotic high-octane chemistries often do not fully combust. This can result in the combustion chamber being effectively "too clean" without the help of an effective valve seat recession additive.

[0004] Alternatively, these fuels may utilize specific compounds known as octane boosters, e.g. aromatic amines, organometallic compounds, or >5% (m/m) aromatic hydrocarbons. Typical high-octane compounds used to boost octane rating in gasoline engines, but that often result in heavier engine, sparkplug and valve-seat deposits, may include any of the following: aromatic hydrocarbons (e.g., toluene, xylenes, and trimethylbenzenes); aromatic amines (e.g., aniline, m-toluidine and Cumidine); and organometallic compounds (e.g. tetraethyllead (TEL), MMT (Methylcyclopentadienyl manganese tricarbonyl and ferrocene).

[0005] The octane boosters increase octane ratings of the fuel but tend to cause dirty build-up of deposits and grime in the combustion chamber. This can create a physical barrier, primarily around the exhaust port, which serves to resist valve seat recession. However, this type of build-up can become excessive, leading to loss of compression in the combustion chamber or even engine shut-down - thus such excessive deposits require frequent servicing and diligent cleaning of the spark plugs, often every 25 to 50 hours of engine operation in certain engine applications.

[0006] There is a long history of using VSR additives in gasoline to prevent or minimize valve seat recession. However, such additives have focused for decades on the use of phosphorous-based compounds, potassium, sodium and manganese organometallic chemistries (see Technical Committee on Petroleum Additive Manufacturers in Europe - (ATC) document 113 published in September 2013).

[0007] Traditional phosphorous, potassium, sodium and manganese anti-VSR additives blended with gasoline or aviation gasoline in an aircraft engine tend to develop specific unwanted effects, such as increased wear at other parts of the engine and layers of sludge on the combustion chamber making an uncontrollable amount of deposits that may require a chemical scavenger to abate. Chemical scavengers often add to toxicity concerns and add complexity to the combustion and exhaust behavior of the fuel.

[0008] Fuel additives determine much about the useful nature of any gasoline. TEL is toxic and although it is present in small amounts (~ 2.1g Pb /gallon), it has a large impact on airborne and municipal water toxicity levels across the nation. Aviation gasoline is one type of premium-quality gasoline for somewhat lower-compression piston engines that has historically contained TEL, which tends to create what is sometimes referred to as a lubricity effect which serves to prevent valve seat recession.

[0009] Such leaded gasoline is also coupled (2:1) with ethylene dibromide, an even more toxic compound as a chemical scavenger of the lead. Together these compounds directly affect the level of sludge in an engine, the frequency of oil changes, the frequency of sparkplug changes due to lead fouling, the consternation of communities dealing with exhaust toxicity of micro-particulates of lead dust. The seemingly small quantity of additives determines a lot about the nature of the fuel. See Table 1.

Table 1 - Old Fuel Additives

	Impact of Key Fuel Additives		
	Anti-VSR	Detergents	Unintended Side Effects
Auto Gasoline	NR; 5-50% aromatics	Already in use	Toxic exhaust without catalytic convertor
100LL Avgas	NR; Lead deposits	Lead too thick	Frequent service to remove lead; Toxic exhaust
100R Avgas Test	Min 10 ppm calcium	Up to 250 ppm	None - Results in longer service intervals

(continued)

	Impact of Key Fuel Additives		
	Anti-VSR	Detergents	Unintended Side Effects
100-MMT Avgas	NR; MMT deposits	MMT too thick	Frequent service to remove MMT; Toxic exhaust
100-Amine Avgas	NR; >5% aromatics	May be useful	Monitor fuel system for amine damage
NR = Not Required due to the chemistry of the fuel causing excessive combustion chamber deposits			

Summary of Invention

[0010] A fuel additive is provided to limit valve seat recession in piston engines. The additive provides calcium sulfonates in an amount in fuel formulation effective to limit VSR in engines using the fuel formulation. The calcium sulfonates preferably comprise calcium petroleum sulfonates, and the fuel additive may also include detergents, antioxidants and anti-microbial agents. The additives find particular use with clean-burning aircraft fuels. Also provided are methods for treating vale seat recession in engines by combining the fuel additives to the fuel used by such engines. Further provided are fuel formulations containing calcium sulfonates, and optionally detergents and other components, which result in limited valve seat recession in the engines using such fuels.

[0011] Key features of the Additive package in this invention are its ability to limit, or even prevent, valve seat recession (VSR), eliminate intake deposits, and protect against corrosion and microbial growth in the aircraft.

[0012] This invention utilizes a new technology - a specialized gasoline additive - to limit valve seat recession (VSR), including when using a clean-burning gasoline, preferably an unleaded gasoline.

[0013] Furthermore, such gasolines, particularly clean-burning gasolines, using this invention result in far less corrosion in the engine and oil system (typically caused by the presence of organometallics) leading to longer engine life and longer time between engine overhauls.

[0014] A preferred embodiment is a high-octane premium-quality aviation gasoline comprised of aliphatic hydrocarbons and oxygenates with no or very low levels of aromatics, amines or metals as outlined herein.

[0015] Further forms, objects, features, aspects, benefits, advantages, and embodiments of the present invention will become apparent from a detailed description and drawings provided herewith.

Description

[0016] For the purpose of promoting an understanding of the principles of the invention, reference will now be made to the embodiments and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended. Any alterations and further modifications in the described embodiments, and any further applications of the principles of the invention as described herein are contemplated as would normally occur to one skilled in the art to which the invention relates. One embodiment of the invention is shown in great detail, although it will be apparent to those skilled in the relevant art that some features that are not relevant to the present invention may not be shown for the sake of clarity.

[0017] This invention uses a special formulation of components blended in solution as a fuel Additive (the "Additive") which is added at a specified treat rate to appropriate gasoline or aviation gasoline compositions. This invention provides a unique and novel approach to anti-VSR additives, resulting in a soft, easy-to-clean, non-toxic thin residue film which coats the combustion area of the cylinder, piston head, intake and exhaust port areas, thereby treating VSR (wear-and-tear) to the mechanical parts.

[0018] The Additive of the present invention is tailored to work with any gasoline, but also finds particular advantage in use with clean-burning gasoline to treat VSR. Without being bound to any particular mechanism of action, it appears that the VSR Additive produces a very thin layer of a soft, easy to clean, non-toxic residue which accumulates and then stabilizes in the combustion chamber. This produces a minimal but useful buildup of soft, white residue in and around the intake and exhaust ports during the combustion process. The result is a thin, soft residue that serves as a barrier to treat valve seat recession and to leave the combustion chamber with virtually no wear-and-tear on the valve seat and with freedom from harmful deposits.

[0019] The Additive is useful limiting VSR. As used herein, the reference to "limiting" VSR is meant to include a reduction of VSR as compared to operation of the engine with the same fuel formulation, but without the Additive. This reduction may include, for example, a reduction in VSR of at least 10%, preferably at least 25%, and most preferably at least 50%. In some embodiments, the Additive is effective to substantially eliminate VSR, meaning that VSR is reduced by at least 90%. In embodiments, use of the Additive eliminates VSR.

[0020] A major difference between the Additive of this invention and those commonly known in the prior art is its low treatment rate the Additive results in harmless deposits and less residue with a cleaner combustion chamber, which extends maintenance cycles and engine life while allowing for ease of cleaning of spark plugs. It is a particular feature of this invention that the Additive package is free of an octane booster and/or a chemical scavenger, and in an aspect the final fuel formulation including the Additive is free, and preferably substantially free, of an octane booster and/or a chemical scavenger. Being substantially free refers to the final fuel formulation constituting less than 1 wt % of octane booster and/or chemical scavenger.

Calcium Sulfonates

[0021] The inventive Additive includes one or more fuel-soluble calcium sulfonates. The calcium sulfonates preferably comprise calcium petroleum sulfonates. In one embodiment, the calcium is provide to provide a low treat rate ranging from about 5 to about 100 ppm (as Ca^{2+}), alternatively at least 5 or 10 ppm, in the fuel formulation.

[0022] Sulfonates can be derived from petroleum fractions, from lignin, and from fatty oils. These materials are mixtures of indeterminate or variable composition, probably comprising one or more of the main chemical types of sulfonates together with sulfates and other sulfur compounds. Such compositions are made largely by empirical procedures. Natural petroleum sulfonates are defined as those manufactured by sulfonation of crude oil, crude distillates, or any portion of these distillates in which hydrocarbons present are not substantially different from their state in the original crude oil. For further information, see https://www.primaryinfo.com/technology/calcium-petroleum-sulfonate.htm, the content of which is hereby incorporated by reference.

[0023] These natural materials, then, are quite different from synthetic sulfonates, which are derived most commonly from sulfonation of olefinic polymers or alkyl aromatic hydrocarbons. Calcium petroleum sulfonate is calcium salt of sulfonic acid made by processing heavy alkaline benzene of suitable fraction with sulfuric acid or sulfur trioxide and refining by liquid extraction by using suitable alcoholic solvent and precipitating insoluble salts by control of PH and centrifuging. Petroleum sulfonate is mainly obtained by treating high-boiling petroleum fractions in a stirred tank reactor (STR) or in a falling-film reactor (FFR). Synthesis of petroleum sulfonate surfactant may be made with ultra-low interfacial tension in a rotating packed bed reactor.

[0024] Sulfonation may be defined as any chemical process by which the sulfonic acid group (SO_2OH) or the corresponding salt or sulfonyl halide group (e.g. $-SO_2Cl$) is introduced into an organic compound. Recently a process has been developed for the manufacture of superior metal petroleum sulfonates, particularly calcium petroleum sulfonates, by the sulfonation of a highly viscous, highly refined paraffinic oil fraction having a viscosity of at least about 200 to 230 SUS at 210 F, and having a viscosity index of about 85 to 100 or higher.

Carriers

[0025] The calcium compound is preferably formulated in a compatible, low-toxicity carrier suitable for use in combination with gasoline fuels. As known in the art, such carriers include, for example, C_7 to C_9 arene hydrocarbons.

Detergents

[0026] The Additive further may comprise one or more detergents. The detergents typically comprise, for example, from 50 to 200 ppm of the Additive. By way of example, a polyolefin alkyl phenol alkyl amine is a suitable detergent. The use of such detergents in combination with the calcium sulfonates provides an unexpectedly superior impact on gasoline fuels by forming a thin soft residue layer without undesired build-up, while still being sufficient to treat valve seat recession when an engine is operated continuously under load.

[0027] Detergents leave the intake clean, while the calcium forms a soft white film during combustion which is easily cleaned by a light brush or rinsed with water and air dried. This is dramatically easier to clean than removing TEL or MMT organometallic deposits which form once fuel is combusted and caked onto engine parts - requiring frequent and excessive physical effort to clean off the spark plugs.

[0028] The use of a detergent will depend on the nature of the fuel. For clean-burning fuels there will be less need for a detergent, whereas fuels which are not clean-burning may benefit from addition of a detergent. This is demonstrated in the examples provided hereafter. The determination of the use of a detergent, and the amount, is within the ordinary skill in the art based on assessment of the results of using the calcium sulfonate with a given fuel.

[0029] In a particular aspect, the detergent is used with the calcium sulfonates for addition to a fuel formulation requiring the detergent to make the calcium sulfonates effective to limit VSR. As disclosed herein, certain fuels benefit from the combination of calcium sulfonates and detergents in order to enhance the effect of either alone in limiting VSR. In this respect, the calcium sulfonates and the detergents are used in amounts and proportions that increase the VSR limiting effect of the calcium sulfonates. Preferably, the combination of the one or more calcium sulfonates and the one or more detergents provides enhanced limiting of VSR that is at least 25%, preferably at least 50%, better than use of the calcium sulfonates alone for a given fuel and engine. For example, if the calcium sulfonates limit VSR to 12%, then the addition of the detergent results in a limitation of VSR to at most 9%, or at most 6%.

Antioxidant

[0030] An additional component may comprise an antioxidant, suitable for use with fuel formulations. An example of a suitable antioxidant is 2,6-ditertiary butyl-4-methylphenol. The determination of the use of an antioxidant, and the amount, is within the ordinary skill in the art based on assessment of the results of using the calcium sulfonate with a given fuel.

Other Excipients

[0031] Other known excipients may also be included in the Additive. For example, an anti-microbial agent, such as 4,4,6-trimethyl-1,3,2- dioxaborolane, may optionally be included. It may also be desirable to add a color dye to the Additive formulation, for example Blue (1,4-dialkylaminoanthraquinone), or Red (alkylazobenzene-4-azo-2-naphthol) dyes, or possibly other colors. The addition of such coloring agent may be prescribed by international fuel regulatory organizations (e.g. ASTM International) for quality control and color calibration when used in aviation gasolines.

Fuels

[0032] The use of > 5% (m/m) aromatic hydrocarbons in aircraft piston engines has an adverse effect on the output of exhaust emissions (particularly in the absence of catalytic convertors as required in automobiles) and heavy combustion deposits of carbon. Using 30 - 50 % aromatics (m/m) in the fuel, as is often the case in Autogas used in aircraft, increases the density of the fuel above 6 lbs. per gallon which may create a concern on managing center-of-gravity and weight/balance attributes of an aircraft. Accordingly, the preferred clean-burning gasoline is one with < 5% aromatic hydrocarbons.

[0033] This invention is a specially designed Additive uniquely tailored to work with specific fuels, particularly clean-burning aviation gasolines that combust with very little or no organometallic, amines or hydrocarbon deposits - i.e. those fuels comprised of less than 5% (m/m) aromatic hydrocarbons, less than about 1.5% (m/m) aromatic amines and less than 0.005% (m/m) organometallic compounds that upon combustion leave very little or no residue on the valves. Such clean-burning fuels might expose the exhaust valves to direct (unlubricated) impact with the cylinder head, leading to valve seat recession.

[0034] Use of aromatic hydrocarbons >30% (m/m) increases the density of the fuel plus contributes to carbon fouling which has shown evidence of impacting sparkplug performance; also, excessive carbon fouling can contribute to sticking / blow-by in the cylinder walls.

[0035] This Additive can be applied to any gasoline formulation for use in a piston engine, no matter the formulation, but is particularly useful when used in very clean-burning unleaded gasoline blends comprised of aliphatic hydrocarbons or any combination of aliphatic hydrocarbons and oxygenates as described herein.

[0036] The cleanest burning high-octane gasoline preferred an oxygenate compound. Our scientists tested various known high-octane aviation gasolines (100LL, 100-octane with MMT, 100-octane with aniline) were tested. In addition we tested 100R, the cleanest burning oxygenated aviation gasoline, which in various embodiments contained > 80% Ethyl Tert-Butyl Ether and ideally > 95% ETBE, however some combination of other ethers (MTBE, TAME, THME, Diisopropyl Ether, etc.) and trace amount of alcohols (methanol, ethanol, etc.) in the fuel as acceptable within industry limits on water solubility.

[0037] A further aspect of this invention is the Additive formulation in a clean-burning fuel eliminates the use of harmful chemicals that can cause acidity, corrosion, organometallic deposits and sparkplug fouling, and sludge build-up that by their chemical nature can cause unwanted wear-and-tear throughout the piston engine. Using this special Additive with clean-burning gasoline results in less frequent and less extensive engine maintenance requirements, conducted at longer time intervals between servicing, thereby creating an economic benefit to operators of aircraft piston engines.

Additive Package

[0038] In one aspect, the present invention provides an Additive package suited for addition to an existing fuel formulation. This addition could occur at any point in the preparation and use of a given fuel formulation. For example, during initial formulation of a fuel the calcium sulfonate may be added to the other fuel components. The calcium sulfonate may be provided by itself, or it may be in combination with other intended fuel components. In a particular aspect, the calcium sulfonate forms a components of an Additive package that includes other components intended to work in combination with the calcium sulfonates, such as those described herein including detergents and/or antioxidants. The Additive package may then also comprise a carrier effective to suspend or otherwise support, including by solution, the calcium sulfonates

[0039] In a related aspect, the Additive package is configured to be used for addition to a fuel formulation as provided to an end user. For example, the Additive package may be separately contained and added directly to the fuel in a storage receptacle or in the fuel tank of an aircraft or the like. In this respect, the Additive package may be specifically supplied with a combination of related components, e.g., the calcium sulfonates and other components such as carrier, detergent, antioxidant, dye, etc.

Method of Treating VSR

[0040] The present invention further includes a method of treating VSR using the Additive. The method comprises adding the Additive to a fuel formulation to provide the calcium sulfonates at a level to provide the concentrations of calcium in the final fuel formulation as set forth herein. The method may comprise adding the Additive during the blending of the fuel formulation. The method may also comprise adding the Additive to the fuel formulation as it is received from the producer. This may occur by way of adding the Additive to the fuel while in storage or as present in a fuel tank, such as the tank of an aircraft.

Example 1 - Prior Art

[0041] An aviation gasoline blend comprising at least one C_4 - C_{10} aliphatic hydrocarbon and at least one oxygenated compound, with less than 5% arene hydrocarbons and no amines or organometallic compounds, having a motor octane of at least 99.6 MON was tested without any anti-VSR additive. The result was an excessive level of valve recession as the fuel combustion ran "too clean" and the metal-on-metal impact of the valves undesirably eroded the facing edge of the valves with the valve seat making the valve seat, out-of-tolerance after the 250 hours test of engine operation.

Example 2 - Phosphate

[0042] Aviation gasoline blend comprising at least one C_4 - C_{10} aliphatic hydrocarbon and at least one oxygenated compound, with less than 5% arene hydrocarbons and no amines or organometallic compounds, having a motor octane of at least 99.6 MON was tested with a phosphorous-based anti-VSR additive. The result was a limited level of valve recession, still within tolerance, but sludge and grime were excessive and difficult to remove.

Example 3 - Potassium

[0043] Aviation gasoline blend comprising at least one C_4 - C_{10} aliphatic hydrocarbon and at least one oxygenated compound, with less than 5% arene hydrocarbons and no amines or organometallic compounds, having a motor octane of at least 99.6 MON was tested with a potassium -based anti-VSR additive. The result was a limited level of valve recession, still within tolerance, but sludge and grime were excessive and difficult to remove. Potassium tends to cake-up and form chunks of debris which can be dangerous when dislodged in the combustion or exhaust chamber.

Example 4 - Manganese

[0044] Aviation gasoline blend comprising at least one C_4 - C_{10} aliphatic hydrocarbon and at least one oxygenated compound, with less than 5% arene hydrocarbons and no amines or organometallic compounds, having a motor octane of at least 99.6 MON was tested with a manganese-based anti-VSR additive (MMT). The result was a limited level of valve recession, but sludge and grime were excessive. Spark plug deposits shut down the engine between regular cleaning intervals. MMT tends to cake-up and form chunks of debris which can be dangerous when dislodged in the combustion chamber.

Example 5 - Anti-VSR Additive

[0045] The response of the Additive package of this invention was tested in several different test engine runs using SAE standard testing for the response of the Additive package. The standard calls for a 250-hour test, with the engine under full load. In total, 13 of these test engines were run the full 250 hours to evaluate additive response. This test was conducted on a nominal blend of 100R, a clean-burning aviation gasoline with 75% aliphatic hydrocarbons and 25% oxygenates (m/m) with the maximum treat rate prescribed by the SPEC-100R-18 specification. In addition, 8 other full runs were conducted with decreasing amounts of the Additive package in this invention.

[0046] The piston engines were purchased new, fully dimensionally measured, and reassembled before the run. Oil was changed initially at 25 hours and thereafter every 50 hours. For comparison of data, 100LL avgas with tetraethyllead and ethanol-free automotive gasoline were each run on a full additive test engine. At the completion of each run, the test engine was torn down and completely measured, evaluated, and photographed.

[0047] The following items were of specific focus as they relate to additive response and an overall assessment of each attribute was compiled. Note that VSR pass / fail was only one criteria of the test:

- Intake Valve seat wear
- Exhaust valve seat wear
- Spark Plug - evaluation and photos
- Cylinder head - evaluation and photos
- Intake runner - evaluation and photos
- Intake Valve stem- evaluation and photos
- Exhaust Valve stem- evaluation and photos
- Intake Valve face- evaluation and photos
- Exhaust Valve face- evaluation and photos

[0048] Experiments were conducted comparing prior art fuel formulations as compared to fuel formulations according to the present invention. In accordance with the guidance in D7826, the final test engine was run on a 100R with 4x treat rate of the recommended 10 ppm calcium Additive package (i.e. 40ppm of calcium).

[0049] Results are summarized in the following tables. A FAIL criterion was established for valve seat wear above 19% change from the pre-test measurements based upon industry service and manufacturer norms for valve seat tolerance. The percent of VSR was determined by comparing the change in measurement of a suitable structure of the engine, e.g., a ridge on the edge of the valve seat. The tests were run based on a 200 hour engine test.

Table 2

Fuel ID	Composition	Additive Pack Treat Rate	Intake Seat Wear	Exhaust Seat Wear	PASS/FAIL
100LL AVGAS	100LL fromKLAF	UNKNOWN - directly from pump	9.23%	1.30%	PASS
[illegible]	[illegible]	UNKNOWN - directly from pump	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	NONE	[illegible]	[illegible]	[illegible]

[0050] As evidenced in Table 2, 100LL avgas created lead deposits which allowed the fuel to meet valve seat recession requirements. However, the lead deposits required 25- to 50-hour inspections and cleaning. Autogas typically has up to 50% aromatics and high boiling compounds which impact the heavy exhaust valve deposits; autogas detergents may clean the intake. The 100R baseline fuel with <u>no</u> additives was spotless on both valve seats, but regrettably the amount of valve seat wear was "high" due to the metal-on-metal impact (i.e., without appropriate additives the fuel burns "too clean", with no deposits).

Table 3

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[0051] Table 3 reports the results of using very clean-burning unleaded avgas 100R (second column), and using small amounts of calcium (2.5 ppm, 5 ppm and 7.5 ppm) from calcium petroleum sulfonate, with 10 mg/L of antioxidant (2,6-ditertiary butyl-4-methylphenol). The use of 7.5 ppm of Ca for test blend TA 402 yielded a passing result with respect to VSR. Addition of 50 ppm of detergent for test blend TA 401 helped clean the intake on TA401 and provided passing results.

Table 4

TA396	2.75 IsoB / 72.25 IsoOct(P) / 25 ETBE	[VSR] 10ppm Ca, [AO] 10mg/L	0.00%	0.00%	PASS
TA407	2.75 IsoB / 72.25 IsoOct(K) / 25 ETBE	[VSR] 10ppm Ca, [DET] 50ppm, [AO] 10mg/L	0.00%	0.00%	PASS
TA409	2.75 IsoB / 72.25 IsoOct(K) / 25 ETBE	[VSR] 40ppm Ca, [DET] 200ppm, [AO] 10mg/L	0.00%	0.00%	PASS

[0052] Using very clean-burning unleaded avgas 100R for the results in Table 4, and additive treat rates of at least 10 ppm of calcium, plus adding detergents from 0 ppm up to 250 ppm and the antioxidant, made the entire valve seat recession disappear and the combustion chamber was very clean from any deposits.

[0053] Using very clean-burning unleaded aviation gasoline, blended in a minimum 99.6 MON formulation comprising at least one C_4 - C_{10} aliphatic and at least one oxygenated-compound, with no more than 5% aromatic content and with no amines or organometallic compounds, provided passing results using an Additive containing at least 10ppm calcium petroleum sulfonates plus anti-oxidants to result in no valve seat recession.

[0054] Furthermore, the optional addition of 50 ppm to 250 ppm of detergents and the option of an anti-microbial agent results in cleaner piston-engine intakes and long-time storability of the fuel, thereby extending overall engine life.

[0055] In one experiment, an aviation gasoline blend comprising at least one C_4 - C_{10} aliphatic hydrocarbon and at least oxygenated compound, with less than 5% arene hydrocarbons and no amines or organometallic compounds, having a motor octane of at least 99.6 MON was tested with the calcium-based anti-VSR Additive. The result was a level of valve recession of zero wear - like new. The calcium component of the additive formed a thin white layer of soft film which prevented the valve seat from wearing during the 250-hour engine test. Additional testing found that the addition of detergents kept the intake clear from any deposits and dirt buildup. The antioxidant reduced the impact of any gum-forming compounds. The anti-microbial agent reduced the risk of microbial growth in unleaded fuels that might be exposed to growth propagating conditions.

Example 6

[0056] Exemplary formulations for the Additive are provided in Table 5.

Table 5

	Tested VSR Additive Formulations (m/m)				
	Anti-VSR	Antioxidant	Detergent/CI	Anti-microbial	Carrier + Dye
Additive 1	30-60%				40-70%
Additive 2	10-40%	5-10%	20-50%	0%	20-40%
Additive 3	20-30%	5-10%	20-30%	20-30%	20-40%
Additive 4	10-30%	5-10%	20-60%	5-20%	20-40%

[0057] The terms in Table 5 have the following meanings:

- Anti-VSR = Calcium petroleum sulfonates
- Anti-Oxidant = 2,6-ditertiary butyl-4-methylphenol
- Detergent/CI = Polyolefin alkyl phenol alkyl amine
- Anti-microbial = 4, 4, 6 - trimethyl-1, 3, 2-dioxaborinane (Optional)
- Blue Dye = 1,4-dialkylaminoanthraquinone (Optional)

- Red Dye = alkylazobenzene-4-azo-2-naphthol (Optional)
- Carrier in Solution = C_7 to C_9 arene hydrocarbon

Aspects of the Invention

[0058] As described herein, the present invention has many aspects. These further include the following.

[0059] In a first aspect, the fuel Additive may be comprised of at least 10 ppm of calcium petroleum sulfonates in solution with a liquid carrier (an C_7 to C_9 arene hydrocarbon), blended with any gasoline composition, which upon combustion prevents valve seat recession, intake coking, and reduces post-combustion deposits in the exhaust chamber.

[0060] In a second aspect, the fuel Additive in the first aspect may be blended specifically with any aviation gasoline composition used in piston aircraft, which upon combustion prevents valve seat recession, intake coking, and reduces post-combustion deposits in the exhaust chamber.

[0061] The fuel Additive of the first or second aspect may be combined with 50 to 250 ppm of detergent - such as Polyolefin alkyl phenol alkyl amine.

[0062] The fuel Additive of the first or second aspect may be combined with up to 20 mg/L of antioxidant - 2,6-ditertiary butyl-4-methylphenol.

[0063] The fuel Additive of the first or second aspect may be combined with up to 40 mg/L of an anti-microbial agent - 4, 4, 6 - trimethyl-1, 3, 2-dioxaborinane.

[0064] The fuel Additive of the first or second aspect may be combined with any approved dyes for quality control and color calibration for fuel safety.

[0065] In a third aspect, a fuel Additive may be comprised of at least 10 ppm of calcium petroleum sulfonates in solution with a liquid carrier (an C_7 to C_9 arene hydrocarbon), blended with any clean-burning aviation gasoline with at least a 99.6 MON octane rating, comprised of at least one C_4 to C_8 aliphatic hydrocarbon and at least one oxygenated-compound and with no more than 5% aromatic hydrocarbons, and no amines or organometallic compounds, which upon combustion prevents valve seat recession, intake coking, and reduces post-combustion deposits in the exhaust chamber.

[0066] The fuel Additive of the third aspect may be combined with 50 to 250 ppm of detergent - such as Polyolefin alkyl phenol alkyl amine.

[0067] The fuel Additive of the third aspect may be combined with up to 20 mg/L of antioxidant - such as 2,6-ditertiary butyl-4-methylphenol.

[0068] The fuel Additive of the third aspect may be combined with up to 40 mg/L of an anti-microbial agent - such as 4, 4, 6 - trimethyl-1, 3, 2-dioxaborinane.

[0069] The fuel Additive of the third aspect may be combined with any approved dyes for quality control and color calibration for fuel safety - such as Blue Dye: 1,4-dialkylaminoanthraquinone and Red Dye: alkylazobenzene-4-azo-2-naphthol.

[0070] Further, the fuel Additive of any of the first, second or third aspects may comprise at least 10 ppm of calcium petroleum sulfonates in a liquid carrier (an C_7 to C_9 arene hydrocarbon), blended with any combination of specified detergents, anti-oxidants, anti-microbial agents and dyes and subsequently blended with any gasoline composition or aviation gasoline composition, which upon combustion prevents valve seat recession, intake coking, and reduces post-combustion deposits in the exhaust chamber.

[0071] In a fourth aspect, a method of treating VSR in a fuel formulation may comprise addition of a fuel Additive of the first, second or third aspects to yield a fuel formulation having the indicated amounts of calcium sulfonates in the final fuel.

[0072] In a fifth aspect, there is provided a fuel formulation comprising calcium sulfonates and other components, as disclosed herein, at amounts operative to limit, or eliminate, VSR for the engine in which the fuel formulation is used.

[0073] While the invention has been illustrated and described in detail in the foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiment has been shown and described and that all changes, equivalents, and modifications that come within the spirit of the inventions defined by following claims are desired to be protected. All publications, patents, and patent applications cited in this specification are herein incorporated by reference as if each individual publication, patent, or patent application were specifically and individually indicated to be incorporated by reference and set forth in its entirety herein.

Claims

1. A fuel additive for use in piston gasoline fuels comprising:
one or more calcium sulfonates in an amount of at least 10 ppm when added to the piston gasoline fuel to be effective to limit valve seat recession in a piston engine using the fuel; and
a liquid carrier, the one or more calcium sulfonates being in solution with the liquid carrier.

2. The fuel additive of claim 1 in which the calcium sulfonates comprise calcium petroleum sulfonates.

3. The fuel additive of claim 2 which further comprises:
one or more detergents present in an amount to provide enhanced limiting of the VSR over that achieved without the detergent, the calcium petroleum sulfonates and the one or more detergents being formulated for direct addition to a final fuel formulation.

4. The fuel additive of claim 3 in which the one or more detergents comprise from 50 to 200 ppm of the fuel additive.

5. The fuel formulation of claim 3 in which the combination of the calcium petroleum sulfonates and the one or more detergents provide enhanced limiting of VSR that is at least 50% better than use of the calcium petroleum sulfonates without the one or more detergents.

6. The fuel additive of claim 4 which further includes an antioxidant.

7. A piston gasoline fuel formulation comprising:

piston gasoline; and
one or more calcium sulfonates in an amount effective to limit valve seat recession in a piston engine using the piston gasoline fuel formulation.

8. The gasoline fuel formulation of claim 7 comprising at least 5 ppm of calcium petroleum sulfonates.

9. The gasoline fuel formulation of claim 8 including calcium petroleum sulfonates in a Ca^{2+} concentration of at least 10 ppm.

10. The gasoline fuel formulation of claim 9 and which further includes one or more detergents present in the gasoline fuel formulation at a concentration effective to provide enhanced limiting of the VSR over that achieved without the one or more detergents.

11. The gasoline fuel formulation of claim 10 which further includes an antioxidant.

12. The gasoline fuel formulation of claim 10 in which the gasoline is an unleaded gasoline blend comprised of aliphatic hydrocarbons or any combination of aliphatic hydrocarbons and oxygenates.

13. The fuel formulation of claim 10 in which the gasoline comprises greater than 80% ethyl tert-butyl ether (ETBE).

14. A method for treating VSR in a piston engine using piston engine gasoline, comprising:
blending with the piston engine gasoline an amount of calcium petroleum sulfonates to provide a concentration of at least 10 ppm in the piston engine gasoline; and
using the piston engine gasoline in the piston engine.

15. The method of claim 14 and further comprising:

blending an amount of the calcium petroleum sulfonates with the piston engine gasoline to produce a residue film in and around the combustion area of the cylinder, piston head, and intake and exhaust port areas of the piston engine, and
removing the residue film.

REFERENCES CITED IN THE DESCRIPTION

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Non-patent literature cited in the description

- Technical Committee on Petroleum Additive Manufacturers in Europe - (ATC) document 113. September 2013 **[0006]**