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(54) **Method and compositions for reducing wear in engines combusting ethanol-containing fuels**

(57) The present disclosure provides a method to reduce wear and prevent deposit formation in an internal combustion engine, said method comprising combusting in said engine a fuel composition comprising gasoline, ethanol and at least one fuel additive. There is also provided a composition to improve wear protection in an internal combustion engine combusting an ethanol-containing fuel, said composition comprising gasoline, ethanol, and one or more fuel additive materials.

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Description

FIELD

[0001] The present disclosure relates to the use of fuel additives in fuels containing ethanol. The additives improve the properties of the resulting fuel and also enhance the benefits to the consumer and to the environment of utilizing varying amounts of ethanol as a fuel in combustion engines. More particularly, the present disclosure provides compositions and methods for reducing engine deposits and improving engine wear in engines combusting ethanol-containing gasoline fuel blends.

BACKGROUND

[0002] Much has been said about the use of ethanol as a fuel by itself, and also as a blend component for use with gasoline, and even with diesel fuels. Ethanol can be produced from crops and thus provides a viable renewable fuel source.

[0003] A common blend of gasoline and ethanol being discussed is 15 % gasoline and 85 % ethanol, often commonly referred to as "E85" fuel (hereinafter "E85"). Other ethanol fuels can comprise, for example 10% ethanol (E10) and 100% ethanol (E100).

[0004] The use of ethanol alone or in gasoline blends can create new problems for fuel equipment designed to handle the more non-polar hydrocarbonaceous petroleum fractions commonly known as gasolines. The polarity, corrosivity, adhesiveness, friction properties, and perhaps conductivity of ethanol or ethanol-containing fuel can create new problems and new needs in the fuel industry.

[0005] E85, gasoline, and diesel are seasonally adjusted to ensure proper starting and performance in different geographic locations. For example, E85 sold during colder months often contain only 70% ethanol and then 30% petroleum additives to produce the necessary vapor pressure for starting in cold temperatures. During warmer months the petroleum additive content for E85 can often be, for example, 17% to about 20%. However, as the interest increases to other fuel blends and to possibly wider use of E100, the need for better cold start performance and reliability will increase.

[0006] So-called "driveability" of a vehicle is a function of the fuel combustion performance and poor driveability is manifested as slow starts, uneven combustion, and potential for misfires and stalling. Various techniques and fuel additives have been employed in the past to address this problem with gasoline fuels. Ethanol-containing fuels, from E100 to E5, and other gasoline-ethanol blends will produce additional problems with achieving improved driveability. A need exists to improve the driveability of vehicles combusting such gasoline-ethanol blends.

[0007] Similarly, engine wear can be a problem in engines combusting ethanol or ethanol-containing gasoline fuels, particularly in older engines designed and built before the introduction of ethanol-containing fuels. This engine wear can appear as corrosion or increased deposits. And will often result in decreased driveability, reduced fuel economy, or even catastrophic engine failure. A need exists for a method and fuel compositions to reduce the engine wear in engines combusting ethanol-containing fuels, such as gasoline.

[0008] Commercial ethanol is widely treated with additives designed to prevent human consumption. Such treated ethanol is called denatured alcohol, or denatured ethanol and common denaturants include gasoline, gasoline components, and kerosene. Other denaturants for rendering fuel alcohol unfit for beverage use are defined in 27 CFR 21.24.

[0009] Fuel delivery systems in vehicles combusting gasoline fuels have increasingly complicated componentry, some of which is, can be or will be highly sensitive to variations in certain fuel parameters. Physical and chemical properties of the fuel can negatively impact the performance or life of these fuel delivery systems. Thus, certain components designed for use in traditional gasolines might be susceptible to fatigue, reduce performance or complete failure upon prolonged exposure to fuels containing ethanol, particularly fuels containing high percentages of ethanol, like E85 and E100. Therefore, a need exists to protect such older engines and well as improve the reliability of newer engines when all are exposed to prolonged combustion of ethanol-containing fuels.

[0010] The use of varying degrees of ethanol in gasoline fuels can create problems with, for example, increased engine deposits, fuel stability, corrosion, fuel economy, fuel driveability, luminosity, fuel economy, fuel driveability, luminosity, fuel economy, demulse, ignition, driveability, driveability, antioxidancy, oil drain interval, achieving CARB standards, achieving Top-Tier auto-maker standards, achieving US EPA standards, solubility, component compatibility, fuel line plugging, engine durability, engine ear, and injector fouling, which will benefit from the inclusion in the fuel of certain fuel additives.

[0011] As currently offered to consumers by several automakers, flexible fuel vehicles (FFVs) are designed to operate on <u>any</u> mixture of gasoline and ethanol - with ethanol concentrations of up to 85% by volume (E85). There is one major difference between an FFV and a conventional gasoline-fueled vehicle - the FFV detects the ethanol/gasoline ratio and makes appropriate adjustments to the engine's ignition timing and air/fuel mixture ratios to account for the ethanol and optimize performance and maintain emissions control. The vehicle must be equipped with an air/fuel ratio map capable of handling the adjustments necessary for optimized performance on both gasoline and E85. Components of the fuel delivery systems on FFVs are also modified and upgraded to be resistant to the corrosive effects of alcohol in the fuel.

[0012] Much like gasoline, the volatility of E85 must be adjusted seasonally and by geographic region to assure adequate cold start and drive away performance. This is done by increasing the amount of gasoline (typically from 15% to 30% by volume) in blends sold during colder months.

[0013] Pure ethanol has broader flammability limits than gasoline and burns with lower flame luminosity. When blended with hydrocarbon fuels, the vapor space flammability limits of ethanol approach those of gasoline and luminosity is increased.

[0014] OGA-480, a polyetheramine available from Chevron Oronite, has been used in E100 fuel but has not been used in E85, nor have other amines been used in ethanol/gasoline blends, to the knowledge of the present inventors.

SUMMARY OF THE EMBODIMENTS

[0015] An embodiment presented herein provides fuel additive agents for use in reducing wear and deposits in engines combusting ethanol-containing fuels, including but not limited to E100, E85, E50, and the like down to E10 and trace blends of ethanol in gasoline.

[0016] Another embodiment provides a method to reduce wear and/or deposit formation in an internal combustion engine, said method comprising combusting in said engine a fuel composition comprising gasoline, ethanol and at least one fuel additive.

[0017] Accordingly, in one example herein is provided a composition to improve wear protection and/or to reduce deposit formation in an internal combustion engine combusting an ethanol-containing fuel, said composition comprising gasoline, ethanol, and one or more materials selected from the group consisting of succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, polyetheramine dispersants, p-phenylenediamine, dicyclohexylamine phenolics, hindered phenolics, aryl amines, diphenyl amines, monocarboxylic acids, dicarboxylic acids, polycarboxylic acids, methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl manganese tricarbonyl, azides, peroxides, alkyl nitrates, oxylated alkylphenolic resins, formaldehyde polymer with 4-(1,1-dimethylethyl)phenol, methyloxirane and oxirane, octane enhancer materials, monoesters, diesters, ethers, diethers, methyloxirane, oxiranes, peroxides, alkyl nitrates, C1-C8 aliphatic hydrocarbons (such as alkanes), ketones, butylene oxides, propylene oxides, ethylene oxides, epoxides, butane, pentane, nitrous oxide, nitromethane, xylene, diethyl ether, polyethers, glycols, phenates, salicylates, sulfonates, nonylphenol ethoxylates, alkali detergents and an alkaline earth metal-containing detergents.

[0018] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present disclosure, as claimed.

DETAILED DESCRIPTION OF EMBODIMENTS

[0019] By "ethanol" herein is meant ethyl alcohol, the chemical compound C_2H_5OH. This can arise in or be provided in many qualities or grades, such a commercial of fuel grade, as well as pure or reagent grade ethanol, and can be derived from any source such as but not limited to petroleum refinery streams, distillation cuts, and bio-derived (e.g. bioethanol from corn).

[0020] Fuels containing varying amounts of ethanol can, when evaporated or combusted, produce increased engine wear as well as increased engine deposits relative to deposits produced from evaporation or combustion of gasoline alone. By the present disclosure the engine wear and deposits can be reduced or prevented by combusting a fuel composition containing the gasoline, ethanol and one or more fuel additive as described herein.

[0021] By the present disclosure is provided in one embodiment a method to reduce wear and/or deposits in an internal combustion engine combusting an ethanol-containing fuel, said method comprising combusting in said engine a fuel containing gasoline, ethanol, and one or more wear reducing agents selected from the group consisting of succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, polyetheramine dispersants, p-phenylenediamine, dicyclohexylamine, phenolics, hindered phenolics, aryl amines, diphenyl amines, monocarboxylic acids, dicarboxylic acids, polycarboxylic acids, methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl manganese tricarbonyl, azides, peroxides, alkyl nitrates, oxylated alkylphenolic resins, formaldehyde polymer with 4-(1,1-dimethylethyl) phenol, methyloxirane and oxirane, octane enhancer materials, monoesters, diesters, ethers, diethers, methyloxirane, oxiranes, peroxides, alkyl nitrates, C1-C8 aliphatic hydrocarbons (such as alkanes), ketones, butylene oxides, propylene oxides, ethylene oxides, epoxides, butane, pentane, nitrous oxide, nitromethane, xylene, diethyl ether, polyethers, glycols, phenates, salicylates, sulfonates, nonylphenol ethoxylates, alkali detergents and an alkaline earth metal-containing detergents.

[0022] The compositions herein can further comprise a fuel additive selected from the group consisting of lubricity additives, combustion improvers, detergents, dispersants, cold flow improvers, dehazers, demulsifiers, cetane improvers, antioxidants, scavengers, and pollution suppressants.

[0023] Also provided herein is a deposit reducer fuel additive concentrate for gasoline engines combusting an ethanol-containing fuel, said concentrate comprising one or more deposit reducing agents and a diluent selected from the group consisting of an oil, a fuel, gasoline, ethanol, solvent, carrier fluid, and other liquid materials combustible in a gasoline engine.

[0024] Further provided herein is a wear reducer fuel additive concentrate for gasoline engines combusting an ethanol-containing fuel, said concentrate comprising one or more wear reducing agents and a diluent selected from the group consisting of an oil, a fuel, gasoline, ethanol, solvent, carrier fluid, and other liquid materials combustible in a gasoline engine.

[0025] In another embodiment the wear or deposit reducer is selected from the group consisting of methyloxirane, oxiranes, peroxides, alkyl nitrates, C1-C8 aliphatic hydrocarbons, ketones, butylene oxides, propylene oxides, ethylene oxides, epoxides, butane, pentane, nitrous oxide, nitromethane, xylene, and diethyl ether.

[0026] Particularly useful wear and/or deposit reducers herein are tall oil fatty acids, dodecenyl succinic acid, and oleic acid plus N,N dimethylcyclohexylamine.

[0027] Also provided herein is a method to reduce deposit formation in an internal combustion engine combusting an ethanol-containing fuel, said method comprising, or in another embodiment, consisting essentially of, combusting in said engine a fuel containing gasoline, ethanol, and one or more materials selected from the group consisting of succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, polyetheramine dispersants, p-phenylene-diamine, dicyclohexylamine, phenolics, hindered phenolics, aryl amines, diphenyl amines, monocarboxylic acids, dicarboxylic acids, polycarboxylic acids, methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl manganese tricarbonyl, azides, peroxides, alkyl nitrates, oxylated alkylphenolic resins, formaldehyde polymer with 4-(1,1-dimethylethyl) phenol, methyloxirane and oxirane, octane enhancer materials, monoesters, diesters, ethers, methyloxirane, oxiranes, peroxides, alkyl nitrates, C1-C8 aliphatic hydrocarbons, ketones, butylene oxides, propylene oxides, ethylene oxides, epoxides, butane, pentane, nitrous oxide, nitromethane, xylene, diethyl ether, diethers, polyethers, glycols, phenates, salicylates, sulfonates, nonylphenol ethoxylates, alkali detergents and an alkaline earth metal-containing detergents.

	Vapor Pressure
Ethanol Blend	**at 77 F mmHg**
E100	59.02
E75	250.60
+4% pentane	256.60
+8% pentane	262.60
+10% pentane	265.60
E85	188.14
+0.1% Pentane	188.25
+0.5% Pentane	188.68
+1% Pentane	189.23
+4% Pentane	192.47
+8% Pentane	196.77
+10% Pentane	198.90
+0.1% Butane	188.87
+0.5% Butane	191.77
+1% Butane	195.38
+4% Butane	217.00
+8% Butane	245.70

(continued)

Ethanol Blend	Vapor Pressure at 77 F mmHg
+10% Butane	260.00
+4% diethyl ether	188.05
+8% diethyl ether	187.95
+10% diethyl ether	187.89
+0.1% dimethyl ether	189.13
+0.5% dimethyl ether	193.07
+1% dimethyl ether	197.99
+4% dimethyl ether	227,40
+8% dimethyl ether	266.30
+10% dimethyl ether	285.70

EXAMPLES:

[0028]

Table 1 IVD Rig Test Deposits From E85 Fuels

Ethanol Source	Deposit, mg.
New Energy Ethanol	1.6
ADM Ethanol	10.8
New Energy Ethanol is a commercial ethanol with a denaturant ADM Ethanol is ethanol with a corrosion inhibitor (DCI-11, from Innospec) and a denaturant	

[0029] Table 1 shows the intake valve deposits generated on an Intake Valve Deposit simulator rig test using E85 fuels containing the ethanols indicated. In this rig test, the fuel blend is sprayed onto a hot surface and the resulting residue weighed. The base gasoline was Citgo RUL and without any additives the Intake Valve Deposit rating for the base gasoline in the rig test was 12.4 mg. As can be seen, the two different ethanol sources (New Energy and ADM) yielded significant differences, indicating a need for additives and a problem of non-uniformity across ethanol suppliers. While both ethanol products contain a denaturant, the ADM Ethanol is further believed to have 32 PTB of a corrosion inhibitor known commercially as DCI-11 from Innospec. As can be seen by comparing the rig test deposits from these two ethanols when used in E85 gasoline-ethanol fuel blend, the ADM Ethanol generated a 10-fold increase in deposits relative to the deposits produced by the New Energy Ethanol in the rig test. Such an E85 fuel will therefore need more detergents, dispersants and other additives than E85 fuels utilizing other ethanol sources.

Table 2 IVD Rig Test Deposits on E85 Fuel Containing Additives

Additive	Dosage, in ptb	Deposit, mg
H-4733	10	1.4
H-3000	25	0.9
H-4142	50	1.0

(continued)

Additive	Dosage, in ptb	Deposit, mg
H-4848A	50	12.7
H-4247	38	15.6
DDSA 50%	25	0.5
H-6560	100	4.0
AP-5000	100	2.1
H-4705	20	1.5
GAR515A01	100	2.7
H-6457	50	2.7
H-4858	50	18.9
H-6400	100	6.6
H-4103	5000ppmv	0.4

H-4733 is 2,6-di t-butyl phenol antioxidant
H-3000 is methylcyclopentadienyl manganese tricarbonyl
H-4142 is oleic acid plus N,N dimethylcyclohexylamine
H-4848A is diethanol amide, demulsifier, aromatic solvent
H-4247 is succinimide dispersant and aromatic solvent
DDSA 50% is dodecenyl succinic acid in A150 solvent
H-6560 is Mannich base dispersant from dibutyl amine
AP-5000 is BASF polyisobutylene amine dispersant
H-4705 is 1,2 propane diamine salicylaldehyde metal deactivator
GARS15A01 is a cresol Mannich dispersant from dibutyl amine; and polyol
H-6457 is diethanol amide of isostearic acid friction modifier
H-4858 is ethylene glycol ester-based lubricity additive
H-6400 is polyetheramine and DDS corrosion inhibitor, Tolad demulsifier, aromatic solvent
H-4103 is 2-ethyl hexyl nitrate combustion improver
Ptb is pounds per thousand barrels

[0030] Table 1 shows the intake valve deposits generated on the Intake Valve Deposit simulator rig test using E85 fuels containing the New Energy Ethanol. The dosage reported is the treat rate of the additive in the gasoline-ethanol fuel blend. As can be seen by comparing the rig test deposits from these additives when used in the E85 gasoline-ethanol fuel blend, the deposits varied. However, it must be noted that (a) this table used the ethanol contributing the lowest deposit level (New Energy Ethanol), so other ethanol sources, such as ADM Ethanol, will clearly have significantly more need for detergents, dispersants and other fuel additives, and (b) the deposits shown in Table 2 will include about 1.6 mg of deposits from the New Energy Ethanol in the E85 fuel. Thus, for at least those additives that generated deposits of about 2.7 mg or less, the total effective deposit not coming from the ethanol is essentially zero, that is, the present disclosure shows in at least these embodiments virtually complete prevention of deposits and the resulting wear on the engine. These additives include 2,6-di t-butyl phenol antioxidant, methylcyclopentadienyl manganese tricarbonyl combustion improver and octane enhancer, oleic acid plus N,N dimethylcyclohexylamine, dodecenyl succinic acid, polyisobutylene amine dispersant, 1,2 propane diamine salicylaldehyde metal deactivator, cresol Mannich dispersant, diethanol amide of isostearic acid friction modifier, and 2-ethyl hexyl nitrate combustion improver. The alkyl nitrate, 2-ethyl hexyl nitrate, was particularly effective in reducing deposits and hence improving wear in the engine combusting the E85 fuel blend.

[0031] Thus, there is provided herein a method of reducing deposits formed in an internal combustion engine combusting an ethanol-gasoline blend, said method comprising combining the blend with at least one additive selected from the group consisting of 2,6-di t-butyl phenol antioxidant, methylcyclopentadienyl manganese tricarbonyl combustion improver and octane enhancer, oleic acid plus N,N dimethylcyclohexylamine, dodecenyl succinic acid, polyisobutylene amine dispersant, 1,2 propane diamine salicylaldehyde metal deactivator, cresol Mannich base dispersant, diethanol amide of isostearic acid friction modifier, and 2-ethyl hexyl nitrate combustion improver, whereby the deposits formed in said engine are less than the deposits formed in the engine when combusting the blend without the at least one additive.

[0032] In another example, a Keep Clean Test was performed by driving a Chevrolet Impala for 5,000 miles using fuel containing gasoline without ethanol, and fuel containing E85 blend. The Intake Valve Deposits (IVD) and the Combustion Chamber Deposits (CCD) were then measured and are reported in Table 3. The ethanol used in the E85 blend was ADM Ethanol except for Test No 6 where New Energy Ethanol was used.

Table 3 Keep Clean Test 5000 Miles

Test No.	Ethanol %	H-6560, PTB	IVD, mg	CCD, mg
1	0	0	429	1232
2	0	85	5	1438
3	84	30/5 (1)	191	299
4	74	85/22(1)	134	265
5	84	0	227	184
6	84	0	99	176
7	84	500 (2)	4	277

1 First number is treat rate in the gasoline, second number is treat rate in the finished blend.
2 H-6400 polyetheramine dispersant, not H-6560

[0033] Table 3 illustrates the effect on deposits of having no ethanol (Test No's 1 and 2) when used without and with (respectively) HiTEC® 6560, a Mannich dispersant with a polyol and polyisobutylene carriers. The use of the Mannich dispersant reduced the IVD deposits from 429 mg to 5 mg. In the E85 fuel blend of Test No. 3 at a 5 PTB treat rate of the Mannich dispersant in the finished fuel had a IVD deposit of 191 mg but when the dispersant was lacking from the E85 blend (Test No. 5), the IVD deposit went up to 227, due in part to the contribution from the ethanol. Comparing Test No. 3 and Test No. 4 also shows that reducing the ethanol content in the fuel blend from 84% to 74% reduced the deposits from 299 mg to 265 mg. This further illustrates that gasoline ethanol blends will need better dispersancy and detergency. Test No. 6 used the New Energy Ethanol which as shown in Table 1 contributes much less to deposits than does the ADM Ethanol, so the IVD in Table 3 correspondingly shows only 99 mg of deposit. Test No. 7 shows the result from a higher treat rate (500 PTB) of a polyetheramine dispersant instead of the Mannich dispersant and the result when combusting the E85 fuel was an amazingly low 4 mg of deposit, at least a major portion of which can be attributed to the ethanol by comparing to Test No. 6.

[0034] For the CCD results of Table 3, comparing Test No. 3 (E85 plus Mannich dispersant) and Test No. 5 (E85 without the Mannich dispersant) one sees an improvement in reducing Combustion Chamber Deposits from 299 mg to 184 mg and using the cleaner New Energy Ethanol of Test No. 6 reduced the Combustion Chamber Deposit even further to 176 mg.

[0035] In this manner it is clear that the present disclosure provides a method to reduce the Intake Valve Deposits and Combustion Chamber Deposits in an engine combusting an ethanol-containing fuel by adding to the fuel a polyetheramine dispersant or a Mannich dispersant. It is therefore expected that the combination thereof will have similar or even enhanced and synergistic results. The reduction of deposit formation is directly related to reduction in engine wear.

Table 4

Run	BLEND	Treat Rate, PTB	MWSD
1	E85	--	605
2	E85 + H4142	50	445
3	E85 + 50% DDSA	25	540

(continued)

Run	BLEND	Treat Rate, PTB	MWSD
4	E85 with ADM Ethanol	--	495
H-6560 is a Mannich dispersant containing a PIB carrier and a polyol carrier E85 with ADM Ethanol has the DCI-11 (@32PTB) corrosion ethanol MWSD is measured in microns.			

Table 4 shows the results of wear scar testing in which a median wear scar diameter MWSD) is reported. Run 1 was E85 using New Energy Ethanol and this baseline MWSD was 605. When HiTEC® 4142 (oleic acid plus N,N dimethylcyclohexylamine) was added as a corrosion inhibitor, the MWSD was reduced to 445. Changing the corrosion inhibitor in the E85 fuel to DDSA (50% in A150 solvent) gave a slightly higher value of 540 but still improved over the baseline for E85. Using ADM Ethanol in the E85 produced even further reduction in the wear scar, probably due to the corrosion inhibitor (DCI-11) in the ethanol. This Table shows the benefit in wear scar reduction and hence in reducing wear in an engine achieved by incorporation of dodecenyl succinic acid and/or oleic acid plus N,N dimethylcyclohexylamine into an ethanol-containing gasoline fuel blend.

[0036] Other embodiments of the present disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the disclosure disclosed herein. As used throughout the specification and claims, "a" and/or "an" may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent, ratio, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the disclosure are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the disclosure being indicated by the following claims.

Claims

1. A method to reduce wear in an internal combustion engine, said method comprising combusting in said engine a fuel composition comprising gasoline, ethanol and at least one fuel additive, said additive being selected from the group consisting succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, and polyetheramine dispersants, whereby the engine wear is reduced relative to the engine wear when combusting a fuel composition without ethanol.

2. The method of claim 1, wherein the fuel composition comprises at least one second fuel additive, said additive being selected from the group consisting of phenolics, hindered phenolics, aryl amines, and diphenyl amines.

3. The method of claim 1 or claim 2, wherein the fuel composition comprises at least one second fuel additive, said additive being selected from the group consisting of tall oil fatty acids, monocarboxylic acids, dicarboxylic acids, and polycarboxylic acids.

4. The method of any one of the preceding claims, wherein the fuel composition comprises at least one second fuel additive, said additive being selected from the group consisting of oxylated alkylphenolic resins, and formaldehyde polymer with 4-1(1,1-dimethylethyl) phenol, methyloxirane and oxirane.

5. The method of any one of the preceding claims, wherein the fuel composition comprises at least one second fuel additive, said additive being selected from the group consisting of methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl manganese tricarbonyl, azides, peroxides, and alkyl nitrates.

6. The method of any one of the preceding clams, wherein the fuel composition comprises at least one second fuel

additive, said additive being selected from the group consisting of monoesters, diesters, ethers, diethers, polyethers, and glycols.

7. The method of any one of the preceding claims, wherein the fuel composition comprises at least one second fuel additive, said additive being selected from the group consisting of p-phenylenediamine and dicyclohexylamine.

8. The method of any one of the preceding claims, wherein the fuel composition comprises at least one second fuel additive, said additive being selected from the group consisting of phenates, salicylates, sulfonates, nonylphenol ethoxylates, fuel-soluble alkali detergents and alkaline earth metal-containing detergents.

9. The method of any one of the preceding claims, wherein the fuel composition comprises at least one second fuel additive, said additive being selected from the group consisting of methyloxirane, oxiranes, peroxides, alkyl nitrates, C1-C8 aliphatic hydrocarbons, ketones, butylene oxides, propylene oxides, ethylene oxides, epoxides, butane, pentane, nitrous oxide, nitromethane, xylene, and diethyl ether.

10. The method of any one of the preceding claims, wherein the fuel composition comprises at least one second fuel additive, said additive being selected from the group consisting of tall oil fatty acids, dodecenyl succinic acid, and oleic acid plus N,N dimethylcyclohexylamine.

11. A composition to improve wear protection in an internal combustion engine combusting an ethanol-containing fuel, said composition comprising gasoline, ethanol, and one or more materials selected from the group consisting of succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, polyetheramine dispersants, p-phenylenediamine, dicyclohexylamine, phenolics, hindered phenolics, aryl amines, diphenyl amines, monocarboxylic acids, dicarboxlic acids, polycarboxylic acids, methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl manganese tricarbonyl, azides, peroxides, alkyl nitrates, oxylated alkylphenolic resins, formaldehyde polymer with 4-(1,1-dimethylethyl) phenol, methyloxirane and oxirane, octane enhancer materials, monoesters, diesters, ethers, diethers, methyloxirane, oxiranes, peroxides, alkyl nitrates, C1-C8 aliphatic hydrocarbons, ketones, butylene oxides, propylene oxides, ethylene oxides, epoxides, butane, pentane, nitrous oxide, nitromethane, xylene, diethyl ether, polyethers, glycols, alkali detergents, phenates, salicylates, sulfonates, nonylphenol ethoxylates, and an alkaline earth metal-containing detergents.

12. A method to reduce wear in an internal combustion engine combusting an ethanol-containing fuel, said method comprising combusting in said engine gasoline, ethanol, and one or more materials selected from the group consisting of succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, polyetheramine dispersants, p-phenylenediamine, dicyclohexylamine, phenolics, hindered phenolics, aryl amines, diphenyl amines, monocarboxylic acids, dicarboxylic acids, polycarboxylic acids, methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl manganese tricarbonyl, azides, peroxides, alkyl nitrates, oxylated alkylphenolic resins, formaldehyde polymer with 4-(1,1-dimethylethyl) phenol, methyloxirane and oxirane, octane enhancer materials, monoesters, diesters, ethers, diethers, methyloxirane, oxiranes, peroxides, alkyl nitrates, C1-C8 aliphatic hydrocarbons, ketones, butylene oxides, propylene oxides, ethylene oxides, epoxides, butane, pentane, nitrous oxide, nitromethane, xylene, diethyl ether, polyethers, glycols, alkali detergents phenates, salicylates, sulfonates, nonylphenol ethoxylates, and alkaline earth metal-containing detergents.

13. A method to reduce deposit formation in an internal combustion engine combusting an ethanol -containing fuel, said method comprising combusting in said engine gasoline, ethanol, and one or more materials selected from the group consisting of succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, polyetheramine dispersants, p-phenylenediamine, dicyclohexylamine, phenolics, hindered phenolicsa, aryl amines, diphenyl amines, monocarboxylic acids, dicarboxylic acids, polycarboxylic acids, methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl manganese tricarbonyl, azides, peroxides, alkyl nitrates, oxylated alkylphenolic resins, formaldehyde polymer with 4-(1,1-dimethylethyl) phenol, methyloxirane and oxirane, octane enhancer materials, monoesters, diesters, ethers, diethers, methyloxirane, oxiranes, peroxides, alkyl nitrates, C1-C8 aliphatic hydrocarbons, ketones, butylene oxides, propylene oxides, ethylene oxides, epoxides, butane, pentane, nitrous oxide, nitromethane, xylene, diethyl ether, polyethers, glycols, phenates, salicylates, sulfonates, nonylphenol ethoxylates, alkali detergents and alkaline earth metal-containing detergents.

14. The method of claim 12, wherein the additive comprises a polyetheramine dispersant.

15. A method to reduce wear in an internal combustion engine, said method comprising combusting in said engine a

fuel composition comprising gasoline, ethanol and at least one fuel additive, said additive being selected from the group consisting of tall oil fatty acids, dodecenyl succinic acid, and oleic acid plus N,N dimethylcyclohexylamine.

16. A method of reducing deposits formed in an internal combustion engine combusting an ethanol-gasoline blend, said method comprising combining the blend with at least one additive selected from the group consisting or 2,6-di t-butyl phenol, methylcyclopentadienyl manganese tricarbonyl, oleic acid plus N,N dimethylcyclohexylamine, dodecenyl succinic acid, polyisobutylene amine dispersant, 1,2 propane diamine salicylaldehyde, cresol Mannich base dispersant, diethanol amide of isostearic acid, and 2-ethyl hexyl nitrate, whereby the deposits formed in said engine are less than the deposits formed in the engine when combusting the blend without the at least one additive.

17. The composition of claim 11, wherein the composition further comprises an fuel additive selected from the group consisting of lubricity additives, combustion improvers, detergents, dispersants, cold flow improvers, dehazers, demulsifiers, cetane improvers, antioxidants, scavengers, and pollution suppressants.

18. A wear reducer fuel additive concentrate for gasoline engines combusting an ethanol-containing fuel, said concentrate comprising one or more wear reducing agents and a diluent selected from the group consisting of an oil, a fuel, gasoline, ethanol, solvent, carrier fluid, and other liquid materials combustible in gasoline engine.

19. A deposit reducer fuel additive concentrate for gasoline engines combusting an ethanol-containing fuel, said concentrate comprising one or more deposit reducing agents and a diluent selected from the group consisting of an oil, a fuel, gasoline, ethanol, solvent, carrier fluid, and other liquid materials combustible in a gasoline engine.

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Application Number
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Place of search	Date of completion of the search	Examiner
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