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(54) **Methods and Compositions for Reducing Corrosion and Increasing Engine Durability in Engines Combusting Alcohol-Containing Fuels**

(57) The present disclosure provides compositions and methods for reducing corrosion and improving durability in engines combusting a fuel containing ethanol and a corrosion inhibitor. The present disclosure also provides compositions and methods for reducing corrosion

and improving durability in engines combusting a fuel containing ethanol, a corrosion inhibitor, and a dispersant.

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Description**FIELD**

5 **[0001]** The present disclosure relates to the use of a dispersant fuel additive in fuels containing an alcohol and a corrosion inhibitor. The dispersant fuel 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. Further, the present disclosure relates to the use of a dodecenyl succinic acid (DDSA) corrosion inhibitor in fuels containing an alcohol. In particular, the present disclosure provides compositions and methods for reducing corrosion and increasing engine durability in engines combusting a fuel containing an alcohol, such as ethanol.

BACKGROUND

15 **[0002]** The use of ethanol alone or in gasoline blends can create new problems for fuel management and injection hardware 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.

20 **[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] 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.

25 **[0005]** The use of varying degrees of ethanol in gasoline fuels can create problems with, for example, increased engine deposits, fuel stability, corrosion, fuel economy, driveability, luminosity, demulsability, ignition, 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 wear, and injector fouling, which will benefit from the inclusion in the fuel of certain fuel additives.

30 **[0006]** Work by the auto manufacturers and others has indicated that low pHe ethanol (in both E-85 and E-10 blends) can contribute to accelerated corrosion of certain fuel system components. While ASTM Standard D 6423 currently limits total acidity as acetic acid to 0.007 mass percent (56 mg/L), this standard is not always sufficient to limit more aggressive sulfuric based acids. Ethanol meeting the ASTM acidity standard may still be of low pHe. This accelerated corrosion has prompted the use of corrosion inhibitors to buffer the ethanol and protect metal components of the fuel distribution system; however, these can cause the formation of undesirable engine deposits. Therefore, a buffer is often desired.

35 **[0007]** DCI-11 is a commercially available corrosion inhibitor and buffer sold by Innospec (formerly Associated Octel) and used in fuels. However, engine corrosion problems still arise from the combustion of ethanol-containing fuels containing this and other corrosion inhibitors. This corrosion can further lead to problems with engine durability.

40 **[0008]** A need therefore exists for a solution to the problem of engine corrosion of engines combusting ethanol-containing fuels having corrosion inhibitors or gasoline-ethanol-corrosion inhibitor mixtures. A need also exists to retain DCI-11 to buffer the acidic species such as acetic acid and/or sulfuric based acids, among others, present in ethanol-containing fuels, but overcome the engine corrosion.

SUMMARY OF THE EMBODIMENTS

45 **[0009]** An embodiment presented herein provides fuel additive agents for use in reducing or inhibiting corrosion in engines (or engine components) 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.

50 **[0010]** Another embodiment presented herein provides a dispersant fuel additive agent for use in reducing or inhibiting corrosion in engines (or engine components) combusting a corrosion inhibitor and ethanol-containing fuels, including but not limited to E100, E85, E50, and the like down to E10 and trace blends of ethanol in gasoline. Suitable dispersant fuel additives include succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, polyalkylene amine dispersants, and polyisobutylene amine dispersants.

55 **[0011]** In another embodiment, it has been observed that the dispersants or mixtures thereof are very effective in improving the engine durability of an engine combusting an ethanol-containing fuel that further contains combinations of at least one organic acid and at least one amine or their salts useful as corrosion inhibitors.

[0012] In one embodiment herein, the ethanol content of the fuel composition is from about 74 to about 8.5%. In another embodiment, the fuel is 100% ethanol and in yet another embodiment the ethanol content of the fuel composition is about 50%, or is from about 50% to about 74%.

[0013] Another embodiment provides a method to improve corrosion resistance and/or to reduce corrosion of an internal combustion engine, said method comprising combusting in said engine a fuel composition comprising gasoline, ethanol and at least one dispersant fuel additive. The dispersant fuel additives used herein are effective in preventing or minimizing corrosion of metal surfaces and certain plastic or synthetic parts or surfaces in combustion engines that come in contact with fuel containing ethanol and a corrosion inhibitor. Parts such as fuel pumps, valves, gaskets, float devices, relay or signaling devices, gauges, screens, filters, intake valves, pistons, engine bearings, ferrous metal parts, and others can all experience some degree of corrosion. The corrosion can vary depending on the type and duration of exposure, the chemical nature of the exposed surface, and the concentration of ethanol and corrosion inhibitor in the fuel, and the concentration of the fuel and corrosion inhibitor in the engine oil. By the present disclosure, a fuel additive package or concentrate for ethanol-containing fuel can be designed to reduce corrosion in these engines. The fuel additive concentrate herein can contain one or more corrosion inhibitors, a dispersant, and a diluent which can be an oil, a fuel, gasoline, ethanol, solvent, carrier fluid, or other material combustible in a gasoline-fueled engine.

[0014] In one embodiment herein is provided a fuel additive concentrate comprising ethanol and a dispersant, for use in a gasoline containing a corrosion inhibitor as defined herein, including but not limited to those materials having a product resulting from combining an organic acid or diacid and an amine, diamine, or polyamine.

[0015] Accordingly, in another example herein is provided a composition to reduce corrosion and/or improve engine durability of 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, polyalkylene amine dispersants, and polyisobutylene amine dispersants.

[0016] In another embodiment, a method for reducing corrosion and/or improving the durability of an internal combustion engine combusting an alcohol-containing fuel composition may comprise combining the fuel with a dodecenyl succinic acid (DDSA) corrosion inhibitor and combusting the fuel and the DDSA corrosion inhibitor in the engine. The corrosion may be reduced relative to the corrosion occurring when combusting the alcohol-containing fuel composition with a corrosion inhibitor substantially free of a DDSA corrosion inhibitor.

[0017] In another embodiment, a composition to reduce corrosion and/or improve engine durability of an internal combustion engine combusting an alcohol-containing fuel may comprise a DDSA corrosion inhibitor and an alcohol.

[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 "corrosion" herein is meant any degradation, rusting, weakening, deterioration, softening, and the like of an engine surface or a part or component of an engine or an engine component or part due to exposure to, or combustion of, an ethanol-containing fuel.

[0020] By "PEA" and "polyetheramine" herein is meant organic compounds having one or more aminic nitrogen atoms, and one or more oxygen-containing ether bonds. Thus, the prefix "poly-" is not a limitation here requiring two or more but rather is the common term of art and can, in one embodiment, encompass an organic compound having one aminic nitrogen, and one oxygen-containing ether bond if the molecular weight and solubility reduce corrosion. The ether portions can be derived from, for example, ethylene oxide, propylene oxide, butylene oxide and mixtures thereof. In a particular embodiment, the PEA can be a diamine, and/or can have a molecular weight of greater than 700. In another embodiment, the molecular weight of the polyetheramine can be 700 to 3000 and particularly 900 to 1500. More specifically, PEA's useful in the present disclosure can also include carbamates, amino carbamates, mono- and di- thiocarbamates, amino alkyls, and amido alkanolamines, all of which are known to those skilled in the art. A key to the performance in the present disclosure is the need for solubility of the detergent in the ethanol-containing fuel requires more polarity than present with conventional (non-polar) polyisobutylene detergents.

[0021] By "corrosion inhibition" or "reducing corrosion" herein is meant any improvement in minimizing, reducing, eliminating, or preventing corrosion. By "engine durability" herein is meant the accumulation of metals in the lubricating oil indicative of wear and/or adverse stress on the engine or moving parts thereof. Enhanced engine durability enables longer and longer oil drain intervals. Engine durability is therefor a performance characteristic distinct from corrosion inhibition.

[0022] 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 as commercial or 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 or other crops). In some embodiments, ethanol may be present in an amount of from about 10 to about 100 wt% based on the total fuel composition. In another embodiment, the ethanol may be present in an amount of from about 15 to about 8.5 wt% based on the total fuel composition. In an even further embodiment, the ethanol may be present in an amount of from about 74 to about 85 wt% based on the total fuel composition.

[0023] By "New Energy ethanol" herein is meant ethanol produced by or for a company known as New Energy and

which ethanol is known to have about 0.9 PTB or less of Innospec DCI-11 corrosion inhibitor.

[0024] By "ADM ethanol" herein is meant ethanol produced by or for Archer Daniels Midland Corporation and which is known to have about 32 PTB of Innospec DCI-11 corrosion inhibitor.

[0025] By "corrosion inhibitor" herein is meant at least the following: low molecular weight (i.e., <700) amines (mono-, di-, tri, and poly), amines, etheramines, imines, imidazolines, thiadiazoles, monocarboxylic acids, dicarboxylic acids, p-phenylenediamine and dicyclohexylamine, alkyl substituted succinic anhydrides and acids and mixtures thereof and salts thereof. Corrosion inhibitors useful herein can also include or comprise tetrapropenylsuccinic acid or anhydride and polymers thereof, and dodecenyl succinic acid (DDSA) or anhydride and polymers thereof. These can include the commercial products, for example, those known as Petrolite Tolad 3222 and Petrolite Tolad 3224 which are believed to be generally of a structure $\text{NH}_2(\text{CH}_2)_n\text{-NH}(\text{CH}_2)_m\text{O-C}_{8-10}$ where n and m are independently 1 to about 10. Also included herein as "corrosion inhibitor" is the Innospec (formerly Associated Octel) product DCI-11™, which is believed to contain the reaction product of an organic acid and an amine or a diamine, such as Duomine™ having the structure $\text{NH}_2(\text{CH}_2)_n\text{-NH-C}_{8-10}$ where n is 1 to about 10. The DCI-11 product is believed to be the low molecular weight (<500) amine salt of a carboxylic acid. Another suitable corrosion inhibitor is dodecenyl succinic acid (DDSA), commercially available from Afton Chemical Corporation as HiTEC® 6455 Fuel Additive.

[0026] By "dispersant," "dispersant additive," or "dispersant fuel additive" herein is meant a dispersant, a dispersant-detergent, or a dispersant composition that contains two or more dispersants of the same or different type. Suitable dispersants include, but are not limited to succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, polyalkylene amine dispersants, and polyisobutylene amine dispersants.

[0027] A fuel additive suitable for use in compositions disclosed herein may also comprise one or more of a phenolic; a hindered phenolic; a polyolefin amine; an aryl amine; a diphenyl amine; a monocarboxylic acid; a dicarboxylic acid; a polycarboxylic acid; an oxylated alkylphenolic resin; a formaldehyde polymer with 4-(1,1-dimethylethyl)phenol, a methyloxirane, and oxirane; an octane enhancer material selected from the group consisting of tetraethyl lead, methylcyclopentadienyl manganese tricarbonyl, an azide, a peroxide, and an alkyl nitrate; a monoester; a diester; an ether; a ketone; a diether; a polyether; a glyme; a glycol; an oxirane; a C1-C8 aliphatic hydrocarbon; a butylene oxide; a propylene oxide; an ethylene oxide; an epoxide; a butane; a pentane; a xylene; a nitrous oxide; a nitromethane; a phenate; a salicylate; a sulfonate; a nonylphenol ethoxylate; a fuel-soluble alkali detergent; and an alkaline earth metal-containing detergent.

[0028] Petrolite Tolad 357 is a corrosion inhibitor useful herein and believed to be a composition having a molecular weight of about 700 or less comprising (1) an alkenyl succinic acid or anhydride (ASAA), and (2) the reaction product of ASAA and a trialkanol amine such as triethanolamine (TEA) where ASAA (3 moles) is reacted with TEA (1 mole) to yield an amide and/or an amine salt.

[0029] In another embodiment the corrosion inhibitor is the product of combining an organic acid or diacid and an amine, diamine, or polyamine in a ratio of about 5:1

[0030] In another embodiment herein is provided a fuel composition that can be, or can comprise, 1.0 to 100 volume percent of one or more alcohols, and 0 to 99% gasoline, and a corrosion inhibitor, said inhibitor comprising, by weight, (a) about 35% to 70% of at least one mono- or di-alkenyl succinic acid in which the alkenyl group has 8 to 18 carbons; and (b) about 30% to 65% of an aliphatic or cycloaliphatic amine, diamine or polyamine containing 2 to 12 carbon atoms. In one embodiment, the corrosion inhibitor can be dissolved in a hydrocarbon solvent consisting of an aromatic hydrocarbon, an alcohol containing 1 to 4 carbon atoms, or mixture thereof, the ratio of the hydrocarbon solvent to the total of (a) and (b) being about 1.5:85 to 50:50, wherein the corrosion inhibitor is present in the fuel composition at less than about 1000 ppm.

[0031] In another embodiment herein the corrosion inhibitor can be or comprise a composition having by weight (a) about 75% to 95% of at least one polymerized unsaturated aliphatic monocarboxylic acid, said unsaturated acid having 16 to 18 carbons per molecule, and (b) about 5% to 25% of at least one monoalkenylsuccinic acid in which the alkenyl group has 8 to 18 carbons.

[0032] In another embodiment the corrosion inhibitor may comprise a dodecenyl succinic acid (DDSA).

[0033] The corrosion inhibitor can be blended into or with the ethanol, or the gasoline, or the ethanol/gasoline blend.

[0034] Corrosion inhibitors herein can include, but are not limited to, the following commercial products and their derivatives and chemically equivalent products:

Octel DCI-11 often used in fuel ethanol at, for example, about 20 PTB

Petrolite Tolad 3222 often used in fuel ethanol at, for example, about 20 PTB

Petrolite Tolad 3224 often used in fuel ethanol at, for example, about 13 PTB

Petrolite Tolad 357 often used in fuel ethanol at, for example, about 15 PTB

Nalco 5403 often used in fuel ethanol at, for example, about 30 PTB

ENDCOR FE-9730 (formerly Betz® ACN 13) often used in fuel ethanol at, for example, about 20 PTB

MidContinental MCC5011E often used in fuel ethanol at, for example, about 20 PTB

MidContinental MCC5011EW often used in fuel ethanol at, for example, about 27 PTB
 CorrPro 6.54 often used in fuel ethanol at, for example, about 13 PTB
 Afton Chemical's HiTEC® 645.5 at, for example, about 32 PTB

[0035] By "PTB" herein is meant "pounds per thousand barrels" a common term of art in the fuel additive industry. A PTB is roughly equivalent to about 4 ppm.

[0036] Thus, there is provided herein in one embodiment a method to reduce corrosion and/or improve engine durability of an internal combustion engine, said method comprising combusting in said engine a fuel composition comprising gasoline, alcohol, a corrosion inhibitor and at least one dispersant fuel additive, whereby corrosion of the engine is reduced and/or the durability of the engine is improved relative to the corrosion and/or durability of the engine when combusting an alcohol-containing fuel composition containing a corrosion inhibitor but without at least one dispersant fuel additive. In one embodiment herein the alcohol is ethanol and in another it is methanol, propanol, butanol, and/or mixtures comprising any combination thereof.

[0037] As a result of the improved engine durability recited above, the present disclosure enables extended oil drain intervals and longer mileage without changing the oil and/or damage to the engine, when the engine is combusting an alcohol-containing fuel composition containing a corrosion inhibitor. Thus is provided a method to improve the lubricating oil drain interval in a vehicle lubricated with an oil when the engine of the vehicle is combusting an alcohol-containing fuel composition containing a corrosion inhibitor.

[0038] It has also been discovered that excess acidic components, such as acetic acid and sulfuric acid species, contribute to wear and deposit accumulation in the engines and/or on the valves or other engine parts. The use herein of a dispersant helps to raise the pH slightly by buffering the acetic and/or sulfuric acid components, thereby reducing or preventing the formation of deposit-contributing reaction products. The use of dispersant herein is also useful in buffering the acid corrosion inhibitor. Thus, the present disclosure provides a corrosion inhibitor buffer in the form of a dispersant used in ethanol-containing fuels.

[0039] Also provided herein is a fuel comprising (a) an alcohol selected from the group consisting of methanol, ethanol, propanol, and butanol, and mixtures thereof, (b) gasoline, (c) the product of combining an organic carboxylic acid or diacid and an amine, diamine, or polyamine and (d) a dispersant comprising one or more of a succinimide dispersant, a succinamide dispersant, an amide, a Mannich base dispersant, a polyalkylene amine dispersant, and a polyisobutylene amine dispersant.

[0040] It has also been found that utilizing a dodecenyl succinic acid (DDSA) corrosion inhibitor decreases the corrosion and/or improves the durability of an internal combustion engine susceptible to corrosion and/or loss of durability. In one embodiment, DDSA is suitable for use in lieu of the conventional DCI-11 corrosion inhibitor. Further, in another embodiment, the DDSA corrosion inhibitor may be used with or without a dispersant fuel additive.

[0041] The following examples further illustrate aspects of the present disclosure but do not limit the present disclosure.

EXAMPLES

[0042] Samples of fuels, as defined in Table I below, were prepared and aged (or "used") by combusting them in a 2006 3.5 liter 6-cylinder Flexible Fuel Vehicle (FFV) Chevrolet Impala operated for 5000 miles. FFV refers to vehicles capable of operating on blends of up to 85% ethanol and 15% hydrocarbon such as unleaded gasoline. The test consisted of multistage 100 minute cycles made up of a mix of accelerations and steady driving at 25 MPH, 40 MPH and 65 MPH. Original Equipment Manufacturers (OEM's) use the "severe service" maintenance table when using E8.5, which specifies oil changes at 3500 miles. Thus, the present aging process is more severe than industry standards and the present embodiments both meet and exceed the recommended service interval by greater than about 40%.

[0043] The aged engine oils were then tested to determine corrosion properties using the ASTM D6557 Ball Rust Test, herein incorporated by reference. Results are given as Average Gray Value (AGV). The API Engine Oil Classifications for 2004 requires that a new oil have minimum AGV of 100. The International Lubricant Standardization and Approval Committee (ILSAC) GF-4 Standard for Passenger Car Engine Oils also requires that a new oil have a minimum AGV of 100. The AGV results shown in Table I are based on aged (or used) oil samples. A result of greater than 100 for a new oil is considered within the petroleum additive industry to be a passing result. A result of less than 100 for a new oil is a failing result. In the present examples, the aged samples based on embodiments described herein provide passing results based on the API and ILSAC standards for new oils. Such exceptional results indicate a preservation of the corrosion protection properties of the oil even after aging.

[0044] Each of the samples was also tested for iron concentration using standard analytical test procedures. This is shown in Table I. Iron content of the aged, or used, oil is indicative of the rusting of, or corrosion of, the engine parts. A value of less than 50 ppm is desirable; however, a value of less than 30 ppm in a used oil is ideal.

Table I

5,000 Mile Chevrolet Impala FFV Ball Rust Test Results								
Examples	Ethanol Source	Ethanol, %	RUL gasoline, %	H-6560, Mannich Dispersant, PTB	H-6455, DDSA PTB	DCI-11, PTB	AGV	Iron Content After Aging, ppm
1	A	84	16			32	88	36
2	B	84	16				70	26
3	A	84	16	85		32	115	21
4	B	84	16		32		124	18

[0045] In the Table, Ethanol Source A refers to ADM Denatured Ethanol containing 4 ppm sulfates and 32 PTB Innospec DCI-11 corrosion inhibitor. The 32 PTB Innospec DCI-11 is indicated in the table. No additional DCI-11 is added to Ethanol Source A in any of the examples. Ethanol Source B refers to New Energy Denatured Ethanol containing less than 1 ppm sulfates and 0.9 PTB corrosion inhibitor.

[0046] Example 1 - A fuel was prepared by blending 84% Ethanol Source A with 16% conventional regular unleaded gasoline. The Ethanol Source A contained 32 PTB of Innospec DCI-11 corrosion inhibitor as supplied. This is indicated in Table I. No additional DCI-11 was added to the mixture. When the used engine oil was tested in the Ball Rust Test, Example 1 gave an AGV of 88 and contained 36 ppm of iron. The AGV results indicated a deterioration in the corrosion protection properties of the oil after usage even though Example 1 contained a commercial corrosion inhibitor.

[0047] Example 2 - A fuel was prepared from 84% Ethanol Sample B which contained no detectable amount of corrosion inhibitor. No other additives were added. When the used engine oil was tested in the Ball Rust Test, Example 2 gave an AGV of 70 and contained 26 ppm of iron. The AGV results indicated an even greater deterioration in the corrosion protection properties of the oil after aging compared to Example 1. This is as expected since Example 2 did not contain a corrosion inhibitor.

[0048] Example 3 - This fuel was prepared by blending 84% Ethanol Sample A, which contains 32 PTB of Innospec DCI-11 corrosion inhibitor as supplied, with 16% regular unleaded gasoline and 85 PTB of HiTEC® 6560 which contains a Mannich dispersant. When the used engine oil was tested in the Ball Rust Test, Example 3 gave an AGV of 115 and contained 21 ppm of iron, which were both very good results. The AGV results indicated little to no deterioration in the corrosion protection properties of the oil after aging compared to Example 1.

[0049] Example 4 - This fuel was prepared by blending 84% Ethanol Sample B with 16% regular unleaded gasoline and 32 PTB HiTEC® 6455 DDSA corrosion inhibitor. When the used engine oil was tested in the Ball Rust Test, Example 4 gave an AGV of 124 and contained 18 ppm of iron, which were both very good results. The AGV results indicated little to no deterioration in the corrosion protection properties of the oil after aging compared to Example 2.

[0050] These examples show surprising and significant improvements in corrosion reduction when either adding a dispersant to a corrosion inhibitor-containing alcohol-containing fuel or using a DDSA instead of commercially available corrosion inhibitors. Further, such improved reduction in or prevention of corrosion is indicative of improved engine durability.

[0051] Table II below provides illustrations of some desired additive combinations for various ethanol-containing fuels whereby corrosion might be controlled or reduced in an engine combusting the ethanol-containing fuel.

Table II

Fuel	A	B	C	D	E	F	G	H	I	J
E85	40-200	120								
E85	40-200		80							
E85	40-200			100						
E85	40-200				120					
E85	40-200					140				
E85	40-200						160			
E85	40-200							100		
E85	40-200								120	

(continued)

Fuel	A	B	C	D	E	F	G	H	I	J
E85	40-200									100

Where amounts are in ppm of the finished fuel:

A = HITEC® 6400 PEA, HiTEC® 6.560 Additive Package including a Mannich Dispersant, or other suitable dispersants such as a succinimide, a succinamide, a polyalkylene amine, polyisobutylene amine, and an amide

B = DCI-11 corrosion inhibitor

C = Petrolite Tolad 3222 corrosion inhibitor

D = Petrolite Tolad 3224 corrosion inhibitor

E = Petrolite Tolad 357 corrosion inhibitor

F = MidContinental MCC5011E corrosion inhibitor

G = MidContinental MCC5011EW corrosion inhibitor

H = CorrPro 654 corrosion inhibitor

I = Nalco 5403 corrosion inhibitor

J = ENDCOR FE 9730 corrosion inhibitor

[0052] Table II illustrates examples of how the corrosion inhibitors can be combined with one or more dispersant fuel additives, whereby the result will be reduction in or prevention of corrosion and/or improvement in durability of an engine combusting the E85 fuel.

[0053] Thus, in one embodiment herein is provided a fuel comprising ethanol, gasoline, at least one corrosion inhibitor selected from the group consisting of HiTEC® 6455 corrosion inhibitor, Octel DCI-11 corrosion inhibitor, Petrolite Tolad 3222 corrosion inhibitor, Petrolite Tolad 3224 corrosion inhibitor, Nalco 5403 corrosion inhibitor, ENDCOR FE-9730 corrosion inhibitor, MidContinental MCC5011E corrosion inhibitor, MidContinental MCC5011EW corrosion inhibitor, CorrPro 654 corrosion inhibitor, NALCO 5403 corrosion inhibitor, ENDCOR FE 9730 corrosion inhibitor, and Betz ® ACN 13 corrosion inhibitor, or chemical equivalents thereof, and optionally one or more dispersant fuel additives. In one embodiment, the fuel is an E85 gasoline-ethanol blend.

[0054] In one embodiment herein the ratio of corrosion inhibitor to dispersant fuel additive can be from about 1:20 to about 20:1. In another embodiment, the ratio of corrosion inhibitor to dispersant fuel additive can be from about 1:10 to about 10:1. In yet another embodiment the ratio of corrosion inhibitor to dispersant fuel additive can be from about 1:5 to about 5:1.

[0055] In yet another embodiment herein the minimum amount of corrosion inhibitor, such as DCI-11 or DDSA, is about 5 PTB and in another the amount is from about 10 PTB to about 50 PTB in the finished fuel. In addition, the fuel can in one embodiment contain from 30-100 PTB of the dispersant fuel additive.

[0056] 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 for reducing corrosion in an internal combustion engine susceptible to corrosion, increasing the engine oil drain interval in an engine or improving the durability of an engine combusting an alcohol-containing fuel composition comprising a corrosion inhibitor, said method comprising:

- (a) combining the fuel with a corrosion inhibitor,
 (b) optionally, combining the fuel and corrosion inhibitor with at least one dispersant fuel additive selected from the group consisting of a succinimide dispersant, a succinamide dispersant, an amide dispersant, a Mannich base dispersant, and a polyalkylene amine dispersant, and
 (c) combusting the fuel in the engine,

wherein either:

(A) when the corrosion inhibitor is dodecenyl succinic acid one of:

- (i) the corrosion in the engine is reduced relative to the corrosion occurring in the engine when combusting the alcohol-containing fuel with a corrosion inhibitor substantially free of a dodecenyl succinic acid corrosion inhibitor, and
 (ii) the durability of the engine is improved relative to the durability of an engine combusting the alcohol-containing fuel with a corrosion inhibitor but without the at least one dispersant fuel additive; or

(B) when the optional dispersant fuel additive is present, one of:

- (iii) the corrosion in the engine is reduced relative to the corrosion in an engine occurring when combusting the alcohol-containing fuel with a corrosion inhibitor but without the at least one dispersant fuel additive,
 (iv) the engine oil drain interval is increased relative to the engine oil drain interval in an engine combusting the alcohol-containing fuel with a corrosion inhibitor but without the at least one dispersant fuel additive, and
 (v) the durability of the engine is improved relative to the durability of an engine combusting the alcohol-containing fuel with a corrosion inhibitor but without the at least one dispersant fuel additive.

2. The method of claim 1, wherein the fuel further comprises gasoline.
3. The method of any one of claims 1-2, wherein the alcohol is selected from the group consisting of methanol, ethanol, propanol, butanol, and mixtures of any combination thereof.
4. The method of any one of claims 1-2, wherein the alcohol is ethanol.
5. The method of claim 4, wherein the ethanol content of the fuel composition is from about 10 wt.% to about 100 wt.%.
6. The method of claim 4, wherein the ethanol content of the fuel composition is from about 15 wt.% to about 85 wt.%.
7. The method of claim 4, wherein the ethanol content of the fuel composition is from about 74 wt.% to about 85 wt.%.
8. The method of any one of claims 1-7, wherein the corrosion inhibitor comprises a dodecenyl succinic acid.
9. The method of any one of claims 1-7, wherein the corrosion inhibitor is selected from the group consisting of those materials having a structure $\text{NH}_2(\text{CH}_2)_n\text{-NH-(CH}_2)_m\text{O-C}_{8-10}$ where n and m are independently 1 to about 10.
10. The method of any one of claims 1-7, wherein the corrosion inhibitor is selected from the group consisting of those materials having a structure $\text{NH}_2(\text{CH}_2)_n\text{-NH-C}_{8-10}$ where n is 1 to about 10.
11. The method of any one of claims 1-7, wherein the corrosion inhibitor comprises the result of combining a carboxylic acid or diacid and an amine, diamine or polyamine.
12. The method of any one of claims 1-7, wherein the corrosion inhibitor has a molecular weight of less than 700 and is selected from the group consisting of monoamines, diamines, triamines, polyamines, etheramines, imines, imidazolines, thiadiazoles, monocarboxylic acids, dicarboxylic acids, p-phenylenediamine, dicyclohexylamine, alkyl substituted succinic anhydrides and acids, mixtures and reaction products thereof and salts thereof.
13. The method of any one of claims 1-12, wherein the fuel additive comprises a polyisobutylene amine dispersant.
14. The method of any one of claims 1-13, wherein the method further comprises the step of:

combining the fuel with at least one fuel additive selected from the group consisting of a phenolic; a hindered phenolic; a polyolefin amine; an aryl amine; a diphenyl amine; a monocarboxylic acid; a dicarboxylic acid; a polycarboxylic acid; an oxylated alkylphenolic resin; a formaldehyde polymer with 4-(1,1-dimethylethyl)phenol, a methyloxirane, and oxirane; an octane enhancer materials selected from the group consisting of tetraethyl lead, methylcyclopentadienyl manganese tricarbonyl, an azide, a peroxide, and an alkyl nitrates; a monoester, a diester, an ether, a ketone, a diether, a polyether, a glyme, a glycol, an oxirane, a C1-C8 aliphatic hydrocarbon, a butylene oxide, a propylene oxide, an ethylene oxide, an epoxide, a butane, a pentane, a xylene, a nitrous oxide, a nitromethane, a phenate, a salicylate, a sulfonate, a nonylphenol ethoxylate, a fuel-soluble alkali detergent, and an alkaline earth metal-containing detergent.

15. A method as claimed in any one of claims 1-14, wherein the fuel is combined with the optional dispersant fuel additive and durability of the engine is improved relative to the durability of an engine combusting the alcohol-containing fuel with a corrosion inhibitor but without the at least one dispersant fuel additive.

16. A method as claimed in any one of claims 1-7 and 13-14, wherein the corrosion inhibitor is a dodecenyl succinic acid and the corrosion in the engine is reduced relative to the corrosion occurring in the engine when combusting the alcohol-containing fuel with a corrosion inhibitor substantially free of a dodecenyl succinic acid corrosion inhibitor.

17. A method as claimed in any one of claims 1-7 and 13-14, wherein the corrosion inhibitor is a dodecenyl succinic acid corrosion inhibitor and the durability of the engine is improved relative to the durability of an engine combusting the alcohol-containing fuel with a corrosion inhibitor substantially free of a dodecenyl succinic acid corrosion inhibitor.

18. A method as claimed in any one of claims 1-14, wherein the fuel is combined with the optional dispersant fuel additive and the engine oil drain interval is increased relative to the engine oil drain interval in an engine combusting the alcohol-containing fuel with a corrosion inhibitor but without the at least one dispersant fuel additive.

19. A method as claimed in any one of claims 1-14, wherein the fuel is combined with the optional dispersant fuel additive and the corrosion in the engine is reduced relative to the corrosion in an engine occurring when combusting the alcohol-containing fuel with a corrosion inhibitor but without the at least one dispersant fuel additive.

20. A composition to reduce corrosion in an internal combustion engine combusting an alcohol-containing fuel, said composition comprising:

- (a) a corrosion inhibitor,
- (b) an alcohol, and
- (c) optionally, at least one of a succinimide dispersant, a succinamide dispersant, an amide dispersant, a Mannich base dispersant, and a polyalkylene amine dispersant, with the proviso that for compositions not containing element (c), the corrosion inhibitor is a dodecenyl succinic acid corrosion inhibitor.

21. The composition of claim 20, wherein the corrosion inhibitor comprises a dodecenyl succinic acid.

22. The composition of any one of claims 20-21, wherein the alcohol is selected from the group consisting of methanol, ethanol, propanol, butanol, and mixtures of any combination thereof.

23. The composition of any one of claims 20-21, wherein the alcohol comprises ethanol.

24. The composition of claim 23, wherein the ethanol content of the fuel composition is from about 10 wt.% to about 100 wt.%.

25. The composition of claim 23, wherein the ethanol content of the fuel composition is from about 15 wt.% to about 85 wt.%.

26. The composition of claim 23, wherein the ethanol content of the fuel composition is from about 74 wt.% to about 85 wt.%.

27. The composition of any one of claims 20-26, wherein the dispersant of (c) comprises a polyisobutylene amine dispersant.

28. The composition of any one of claims 20-27, wherein the fuel further comprises gasoline.

29. The composition of claim 20, wherein the composition consists of:

- 5 (a) a dodecenyl succinic acid corrosion inhibitor, and
 (b) an alcohol.

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EUROPEAN SEARCH REPORT

Application Number
EP 07 12 0792

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EPO FORM 1503 03/82 (F04C01)



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EPO FORM 1503 03 82 (P04C01)



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