

FUEL LUBRICITY ADDITIVES

DESCRIPTION OF THE INVENTION

Field of the Invention

[001] The present disclosure relates to a fuel lubricity additive comprising an imidazoline. The fuel lubricity additive may be useful for improving the lubricity of fuels and reducing wear in internal combustion engines.

Background of the Invention

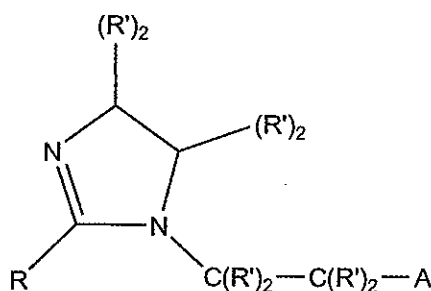
[002] In order to reduce pollution and conserve energy, automobiles are constantly being engineered to give improved gasoline mileage. This effort is a result, at least in part, of governmental regulation enacted to compel auto manufacturers to achieve prescribed gasoline mileage. In an effort to achieve the required mileage, a number of cars are being down-sized. However, there are limits in this approach beyond which the cars will not accommodate a typical family. Another way to improve fuel mileage is to reduce engine wear attributable in part to engine friction. The present disclosure relates to fuel lubricity additives for gasoline and diesel fuels, as well as methods for reducing engine wear.

[003] It is known to use imidazoline derivatives in fuels to modify engine performance, e.g., as detergents, anti-corrosive agents, and to minimize fuel vaporization. U.S. Patent No. 3,036,902 discloses certain imidazoline derivatives as being useful for reducing the incidence of carburetor icing. The derivatives are combined with an alkanol to form a deicing composition. There is no disclosure of, *inter alia*, lubricity additives.

U.S. Patent No. 6,562,086 discloses a diesel fuel and spark ignition fuel lubricity aid containing an alkanolamide of a fatty acid, an alkanolamide of a modified fatty acid or a mixture thereof. The preparation of alkanolamides as lubricity additives is known. Such alkanolamides, however, may not be as effective in reducing engine wear as the fuel lubricity additives of the present disclosure.

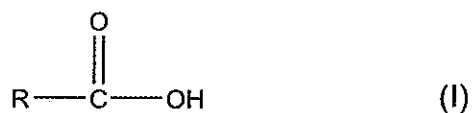
SUMMARY OF THE INVENTION

[004] In accordance with the present disclosure, there is provided a fuel lubricity additive comprising an imidazoline of the following formula:

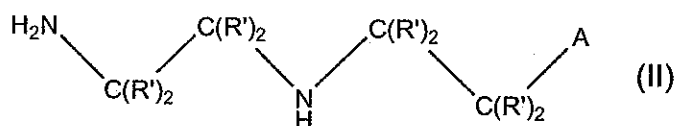


wherein R may be chosen from saturated and unsaturated, linear, aromatic, branched, and cyclic hydrocarbyl groups, which may be unsubstituted or substituted with at least one of hydroxyl, nitro, amino, and cyano groups; R' may be independently chosen from hydrogen, hydroxyl, nitro, amino, cyano, and saturated and unsaturated, linear, aromatic, branched and cyclic hydrocarbyl groups; A may be chosen from SH, OH, and NY₂ groups; and Y may be independently chosen from hydrogen and saturated and unsaturated, linear, aromatic, branched and cyclic hydrocarbyl groups, each of which may be unsubstituted or substituted with at least one of hydroxyl, nitro, amino, and cyano groups. By "amino" herein is meant any mono-, di-, tri- and polyamines, and mixtures thereof.

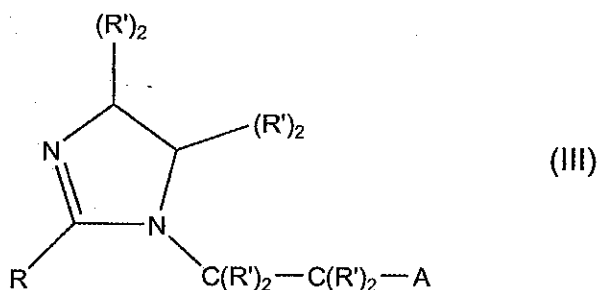
[005] According to another aspect of the present disclosure, there is provided a fuel lubricity additive comprising an imidazoline, wherein said imidazoline may be prepared by a process comprising reacting a compound of formula (I):



with a compound of formula (II):



to yield an imidazoline of formula (III):



wherein R may be chosen from saturated and unsaturated, linear, aromatic, branched, and cyclic hydrocarbyl groups, which may be unsubstituted or substituted with at least one of hydroxyl, nitro, amino, and cyano groups; R' may be independently chosen from hydrogen, hydroxyl, nitro, amino, cyano, and saturated and unsaturated, linear, aromatic, branched and cyclic hydrocarbyl groups; A may be chosen from SH, OH and NY₂ groups; and Y may be independently chosen from hydrogen and saturated and unsaturated, linear, aromatic, branched and

cyclic hydrocarbyl groups, each of which may be unsubstituted or substituted with at least one of hydroxyl, nitro, amino, and cyano groups.

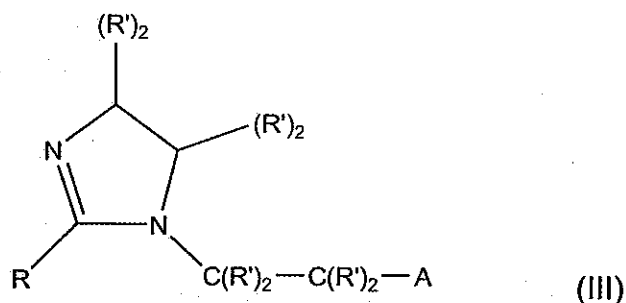
[006] It is to be understood that both the foregoing and following description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

[007] The tables herein illustrate aspects of the invention and together with the description, serve to explain the principles of the invention.

DESCRIPTION OF THE EMBODIMENTS

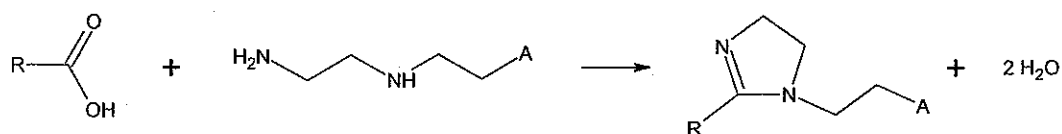
[008] Interest in lubricity additives for both gasoline and diesel fuel has been increasing. This has been driven by the new requirements on diesel fuel lubricity (ASTM maximum 520 μm wear scar diameter using High Frequency Reciprocating Rig (HFRR)) and the desire for gasoline additives that improve fuel economy. The imidazoline compounds described herein may be effective in reducing friction and wear resulting from the combustion of fuels, including gasoline, diesel, and biodiesel fuels.

[009] The imidazolines useful as fuel lubricity additives may be represented by the following general formula:

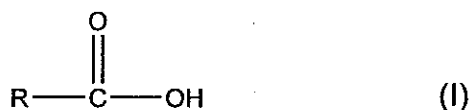


wherein R may be chosen from saturated and unsaturated, linear, aromatic, branched, and cyclic hydrocarbyl groups, which may be further substituted with at least one of hydroxyl, nitro, amino, and cyano groups; R' may be independently chosen from hydrogen, hydroxyl, nitro, amino, cyano, and saturated and unsaturated, linear, aromatic, branched and cyclic hydrocarbyl groups; A may be chosen from SH, OH and NY_2 groups; and Y may be independently chosen from hydrogen and saturated and unsaturated, linear, aromatic, branched and cyclic hydrocarbyl groups, each or which may be unsubstituted or substituted with at least one of hydroxyl, nitro, amino, and cyano groups.

[010] The imidazolines of formula (III) may be obtained by reacting a suitable organic acid with a polyamine, such as a diamine or a triamine, each of which may be substituted with other groups such as, for example, hydroxyl groups. The reaction may involve the elimination of two molecules of water between the acid and the amine. The reaction may be represented by the following equation:

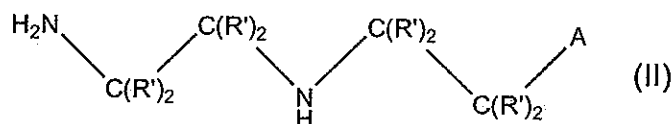


[011] Acids which are useful in preparing the imidazolines include those that are capable of reacting with a polyamine to form an imidazoline, such as those represented by the following formula (I):



wherein R is chosen from saturated and unsaturated, linear, aromatic, branched, and cyclic hydrocarbyl groups, each of which is unsubstituted or substituted with at

[012] Suitable polyamines include those that form an imidazoline upon reaction with an organic acid. According to certain aspects of the present disclosure, the polyamines may be represented by the formula (II):



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[013] The fuel lubricity additives disclosed herein comprise at least one imidazoline compound and optionally at least one solvent or co-solvent for the purposes of, e.g., facilitating handling and blending of the compound. Suitable solvents include alcohols (e.g., methanol, ethanol, isopropanol), 2-ethylhexanol, ketones (acetone, methyl ethyl ketone), esters (tert-butyl acetate), and ethers (e.g., methyl tert-butyl ether). Aromatic hydrocarbons may also be useful solvents, such as Aromatic 100-150. Suitable non-limiting examples of aromatic hydrocarbons comprise benzene, toluene, and/or xylene, and higher molecular weight aromatic solvents.

[014] According to one aspect of the disclosure, the solvent is a commercial blend of aromatics. The molar ratio of acid to amine is generally from 1:2 to 3:1 in one embodiment, and 1:2 to 2:1 in another embodiment. Especially useful are acid to amine ratios of 1:1 to 2:1.

[015] The present disclosure also relates to fuel compositions comprising fuel in a major amount, and the fuel lubricity additive disclosed herein in a minor amount. Suitable fuels include, by way of non-limiting example, diesel fuel, biodiesel fuel, gasoline emulsions, diesel emulsions, gasoline-alcohol blends, diesel-alcohol blends, gasoline, and mixtures thereof. The fuel lubricity additive may be used at a concentration providing the desired amount of lubricity to the fuel. A useful range may be, for example, about 1 to about 5000 pounds per thousand barrels (ptb), for example 5 to 2000 ptb, or 5 to 500 ptb. The fuel lubricity additive may be added to the gasoline or diesel fuel at the refinery or at any stage of subsequent storage, shipment (such as pipeline), or delivery (such as pump

stations). It may be manufactured as an after-market gasoline or diesel additive and sold over the counter in a package to a consumer, who then adds it directly to a fuel tank.

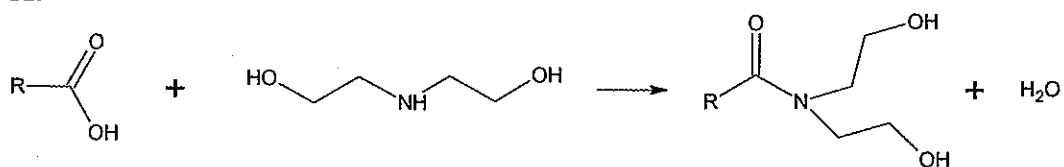
[016] Diesel fuel may include any of the various mixtures of hydrocarbons which can be used as diesel fuels and thus include distillate and residual fuel oils, blends of residual fuel oils with distillates, gas oils, recycled stock from cracking operations and blends of straight run and cracked distillates. Biodiesel has long been known as an alternative diesel fuel and may be obtained by, for example, subjecting oil obtained from oleaginous seeds to various filtration and extraction techniques well-known to those of ordinary skill in the art.

[017] The fuel compositions disclosed herein may contain at least one additional ingredient besides fuel and the fuel lubricity additive. For example, the fuel compositions may comprise at least one of dispersants, detergents, oxygenates, antioxidants, carrier fluids, metal deactivators, dyes, markers, pour-point depressants, corrosion inhibitors, biocides, cetane improvers, antistatic additives, stabilizers, anti-foam agents, drag-reducing agents, demulsifiers, dehazers, anti-icing additives, anti-knock additives, anti-valve-seat recession additives, additional lubricity additives, and combustion improvers. Oxygenates herein can include for example and without limitation methanol, ethanol, esters, ethers, combustion improvers, and antiknock materials. Particularly useful herein is the additional antiknock ingredient methyl cyclopentadienyl manganese tricarbonyl, at for example a level of 20-200 milligrams per liter of fuel.

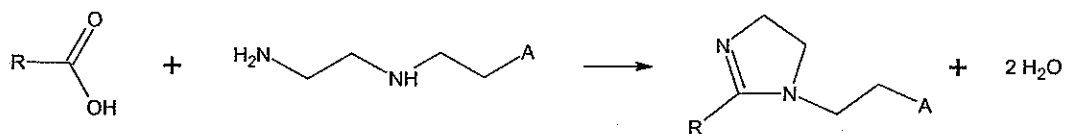
Examples

[018] Several compounds were made with different starting materials using the following reaction schemes:

A:



B:



wherein R was a saturated or unsaturated, aromatic, branched or linear, alkyl group and A was either OH or NH₂. Compounds produced according to reaction scheme A are known to be additives suitable for modifying the lubricity of gasoline and diesel fuel, and were thus compared against inventive fuel lubricity additives produced according to scheme B.

[019] The synthesized materials were tested in the High Frequency Reciprocating Rig (HFRR) for their ability to reduce friction and wear in both gasoline and diesel fuel. The HFRR apparatus and the procedure used are described as follows: a steel ball is attached to an oscillating arm assembly and is mated to a steel disk specimen in the HFRR sample cell. The sample cell contains

2 ml of the fuel being tested and the sample is maintained in a bath at a temperature of 60° C for diesel but 25° C for gasoline. A load of 200 grams is applied to the ball/disk interface by dead weights. The ball assembly is oscillated over a 1 mm path at a rate of 50 Hertz. These conditions ensure that a fluid film does not build up between the ball and disk. After a prescribed period of time (for example, 75 minutes), the steel ball assembly is removed. Wear, and hence the lubricity of the fuel, is assessed by measuring the mean wear scar diameter on the ball, resulting from oscillating contact with the disk. The smaller the wear scar obtained, the greater the lubricity of the fuel. A low coefficient of friction and a low wear scar are evidence of a good lubricating effect.

[020] Table 1 compares the HFRR performance in gasoline of a number of additives produced using both reaction schemes. Materials produced from the identical starting acids using inventive scheme B consistently outperformed the comparative fuel lubricity additives produced using scheme A. The friction coefficient values given in Tables 1 and 2 are an average over the entire 75-minute test.

Table 1

HFRR of Experimental Lubricity Additives in Gasoline					
Fuel	Additive Chemistry	Reaction Scheme	Treat Rate (PTB)	Friction Coefficient*	Wear Scar (um)
G1	--	--	--	0.299	485
G1	Isostearic Acid/DEA	A	50	0.219	365
G1	Iso-oleic Acid/DEA	A	50	0.237	445
G1	Iso-oleic Acid/DEA	A	50	0.235	430
G1	Naphthenic Acid/DEA	A	50	0.276	515
G1	Iso-oleic Acid/DEA	A	100	0.200	342.5
G1	Isostearic Acid/AEEA	B	50	0.216	370

G1	Naphthenic Acid/AEEA	B	50	0.235	370
G1	Isostearic Acid/DETA	B	50	0.213	325
G2	--	--	--	0.434	780
G2	Isostearic Acid/DEA	A	100	0.236	438
G2	Isostearic Acid/AEEA	B	100	0.223	325
G2	Isostearic Acid/AEEA	B	50	0.254	400

* Friction Coefficient = F/P where F is the measured friction force and P is the applied load

Iso-oleic Acid = Century 1164 Isooleic Acid from Arizona Chemical Company

Isostearic Acid = Century 1105 Isostearic Acid from Arizona Chemical Company

Nap Acid = Naphthenic Acid from Merrichem Company

DEA = Diethanolamine

AEEA = Aminoethyl ethanolamine

DETA = Diethylenetriamine

G1 = Unadditized gasoline from Sunoco

G2 = Unadditized gasoline from Citgo

[021] Fuels 1 and 2 are typical U.S. unadditized gasolines.

[022] The results in Table 1 demonstrate that the inventive fuel lubricity additives may substantially improve the lubricity of a fuel as compared to the fuel lubricity additives prepared by scheme A.

[023] The HFRR test was again conducted using an ultra low sulfur diesel fuel obtained from a U.S. refinery instead of gasoline. Table 2 shows that the superior performance from scheme B fuel lubricity additives extends to diesel fuel.

[024] **Table 2**

HFRR of Experimental Lubricity Additives in Diesel Fuel					
Fuel	Additive Chemistry	Reaction Scheme	Treat Rate (ppm)	Friction Coefficient*	Wear Scar (um)
ULSD1	Base Fuel - No Additive	--	--	0.391	637.5
ULSD1	TOFA	--	100	0.230	435

ULSD1	TOFA/DEA	A	100	0.213	380
ULSD1	Isostearic Acid/AEEA	B	100	0.230	417
ULSD1	TOFA/DETA	B	100	0.253	480
ULSD1	TOFA/AEEA	B	100	0.244	460

* Friction Coefficient = F/P where F is the measured friction force and P is the applied load

ULSD1 = Ultra Low Sulfur Diesel Fuel from Conoco Phillips

Isostearic Acid = Century 1105 Isostearic Acid from Arizona Chemical Company

TOFA = Tall Oil Fatty Acid from Arizona Chemical Company

DEA = Diethanolamine

AEEA = Aminoethyl ethanolamine

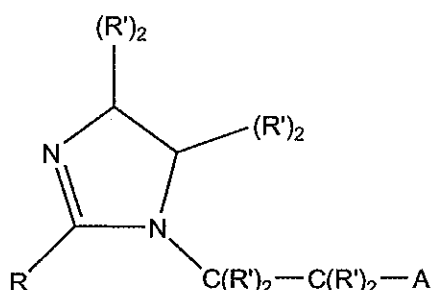
DETA = Diethylenetriamine

[025] Table 2 demonstrates the wear scar diameters obtained from the incorporation into the diesel fuel of the noninventive samples 1-3 and contain embodiments of the present invention samples 4-7.

[026] Other aspects of the disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

WHAT IS CLAIMED IS:

1. A fuel lubricity additive comprising an imidazoline of the following formula:



wherein:

R is chosen from saturated and unsaturated, linear, aromatic, branched, and cyclic hydrocarbyl groups, which are unsubstituted or substituted with at least one of hydroxyl, nitro, amino, and cyano groups;

R' is independently chosen from hydrogen, hydroxyl, nitro, amino, cyano, and saturated and unsaturated, linear, aromatic, branched and cyclic hydrocarbyl groups;

A is chosen from SH , OH and NY_2 groups; and

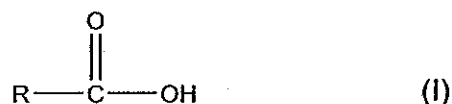
Y is independently chosen from hydrogen and saturated and unsaturated, linear, aromatic, branched and cyclic hydrocarbyl groups, which are unsubstituted or substituted with at least one of hydroxyl, nitro, amino, and cyano groups.

2. The fuel lubricity additive according to Claim 1, wherein R is chosen from hydrocarbyl groups having from 10 to 20 carbon atoms, and A is an amino group.

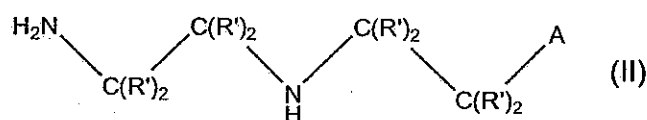
3. The fuel lubricity additive according to Claim 1, wherein R' is hydrogen, and A is NH₂.

4. The fuel lubricity additive according to Claim 1, wherein A is chosen from -SH, -OH and -NY₂ groups.

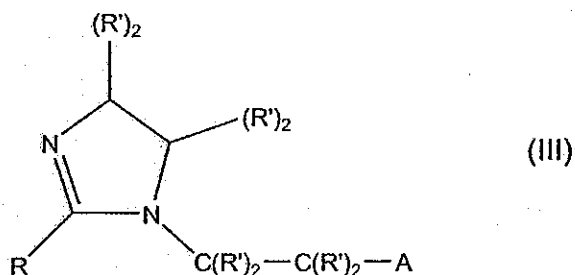
5. A fuel lubricity additive comprising an imidazoline, wherein said imidazoline is prepared by a process comprising reacting a compound of formula (I):



with a compound of formula (II):



to yield an imidazoline of formula (III):



wherein:

R is chosen from saturated and unsaturated, linear, aromatic, branched, and cyclic hydrocarbyl groups, and is unsubstituted or substituted with at least one of hydroxyl, nitro, amino, and cyano groups;

R' is independently chosen from hydrogen, hydroxyl, nitro, amino, cyano, and saturated and unsaturated, linear, aromatic, branched and cyclic hydrocarbyl groups;

A is chosen from -SH, OH and NY₂ groups; and

Y is independently chosen from hydrogen and saturated and unsaturated, linear, aromatic, branched and cyclic hydrocarbyl groups, each of which is unsubstituted or substituted with at least one of hydroxyl, nitro, amino, and cyano groups.

6. The fuel lubricity additive according to Claim 5, wherein R is chosen from hydrocarbyl groups having from 10 to 20 carbon atoms.
7. The fuel lubricity additive according to Claim 5, wherein R' is hydrogen.
8. The fuel lubricity additive according to Claim 5, wherein A is chosen from -SH, -OH and -NH₂ groups.
9. The fuel lubricity additive according to Claim 5, wherein compounds (I) and (II) are reacted together in a molar ratio ranging from 1:2 to 2:1.
10. The fuel lubricity additive according to Claim 5, wherein compounds (I) and (II) are reacted together in a molar ratio ranging from 0.8:1 to 1:0.8.
11. The fuel lubricity additive according to Claim 5, wherein the fuel is a diesel fuel.
12. The fuel lubricity additive according to Claim 5, wherein the fuel is a biodiesel fuel.
13. The fuel lubricity additive according to Claim 5, wherein the fuel is gasoline.

14. The fuel lubricity additive according to Claim 5, wherein the R is chosen from linear alkenyl groups.

15. The fuel lubricity additive according to Claim 5, wherein the compound of formula (I) is chosen from 9,10-decylenic acid, octenoic acid, linoleic acid, naphthenic acid, and a tall oil fatty acid.

16. The fuel lubricity additive according to Claim 5, wherein the compound of formula (II) is chosen from ethylene diamine, aminoethyl ethanolamine, and diethylenetriamine.

17. The fuel lubricity additive according to Claim 5, wherein the compound of formula (I) is isostearic acid and the compound of formula (II) is aminoethyl ethanolamine.

18. The fuel lubricity additive according to Claim 5, wherein the compound of formula (I) is naphthenic acid and the compound of formula (II) is aminoethyl ethanolamine.

19. The fuel lubricity additive according to Claim 5, wherein the compound of formula (I) is isostearic acid and the compound of formula (II) is diethylenetriamine.

20. The fuel lubricity additive according to Claim 5, wherein the compound of formula (I) is a tall oil fatty acid and the compound of formula (II) is diethylenetriamine.

21. The fuel lubricity additive according to Claim 5, wherein the compound of formula (I) is isostearic acid and the compound of formula (II) is diethylenetriamine.

22. The fuel lubricity additive according to Claim 5, wherein the compound of formula (I) is a tall oil fatty acid and the compound of formula (II) is aminoethyl ethanolamine.

23. The fuel lubricity additive according to Claim 5, wherein said imidazoline is prepared under batch process conditions.

24. The fuel lubricity additive according to Claim 5, wherein said imidazoline is prepared under continuous process conditions.

25. A fuel composition comprising:

(A) a fuel in major amount; and

(B) a fuel lubricity additive according to Claim 1 in a minor amount.

26. The fuel composition according to Claim 25, wherein the fuel is gasoline, or a gasoline-alcohol blend.

27. The fuel composition according to Claim 25, wherein the fuel is a diesel fuel, or diesel fuel-alcohol blend.

28. The fuel composition according to Claim 25, wherein the fuel is a biodiesel fuel.

29. The fuel composition according to Claim 25, wherein the fuel comprises an emulsion of diesel fuel and water or ethanol.

30. The fuel composition according to Claim 25, further comprising at least one of dispersants, detergents, oxygenates, antioxidants, carrier fluids, metal deactivators, dyes, markers, pour-point depressants, corrosion inhibitors, biocides, cetane improvers, antistatic additives, stabilizers, anti-foam agents, drag-reducing agents, demulsifiers, dehazers, anti-icing additives, anti-knock additives, anti-

valve-seat recession additives, additional lubricity additives, and combustion improvers.

31. An anti-wear composition comprising the fuel lubricity additive according to Claim 1, wherein said fuel lubricity additive is present in an amount sufficient to reduce the wear in an internal combustion engine.

32. A friction modifying composition comprising the fuel lubricity additive according to Claim 1, wherein said fuel lubricity additive is present in a fuel in an amount sufficient to modify the friction of the fuel.

33. A process for improving the lubricity of a fuel composition in an engine, comprising operating said engine with a fuel comprising a fuel lubricity additive according to Claim 1.

34. A process for improving the lubricity of a fuel composition in an engine, comprising operating said engine with a fuel composition according to Claim 25.

35. The process according to Claim 34, wherein said fuel composition comprises gasoline.

36. The process according to Claim 34, wherein said fuel composition comprises a diesel fuel.

37. The process according to Claim 34, wherein said fuel composition comprises a biodiesel fuel.

38. A process for improving the fuel economy of an internal combustion engine comprising using as a fuel in the internal combustion engine the fuel composition according to Claim 25, wherein the fuel lubricity

additive is present in an amount sufficient to improve the fuel economy of the internal combustion engine using the fuel composition, as compared to the engine operated in the same manner and using the same fuel except that the fuel is devoid of the fuel lubricity additive.

39. The process according to Claim 38, wherein the fuel lubricity additive is present in the fuel composition in an amount ranging from 25 to 150 ptb.

40. The process according to Claim 38, wherein the fuel lubricity additive is present in the fuel composition in an amount ranging from 40 to 60 ptb.

41. A process for reducing wear in an internal combustion engine comprising using as a fuel for the internal combustion engine the fuel composition of Claim 25, wherein the fuel lubricity additive is present in an amount sufficient to reduce the wear in an internal combustion engine operated using the fuel composition, as compared to the wear in the engine operated in the same manner and using the same fuel except that the fuel is devoid of the fuel lubricity additive.

42. The process according to Claim 41, wherein the fuel lubricity additive is present in the fuel composition in an amount ranging from 25 to 150 ptb.

43. The process according to Claim 41, wherein the fuel lubricity additive is present in the fuel composition in an amount ranging from 40 to 60 ptb.

44. A process for providing friction modification in an internal combustion engine comprising using as a fuel for the internal combustion engine the fuel composition of Claim 25, wherein the fuel lubricity additive is present in an amount sufficient to reduce the wear in an internal combustion engine operated using the fuel composition, as compared to the wear in the engine operated in the same manner and using the same fuel except that the fuel is devoid of the fuel lubricity additive.

45. The process according to Claim 44, wherein the fuel lubricity additive is present in the fuel composition in an amount ranging from 25 to 150 ptb.

46. The process according to Claim 44, wherein the fuel lubricity additive is present in the fuel composition in an amount ranging from 40 to 60 ptb.