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(54) Lubricant additive for alcohol fuel burning engines

(57) A lubricant additive for use in internal combustion engines burning alcohol or alcohol-containing fuels comprises a major amount of an organic amine selected from aromatic primary or secondary amines, aliphatic primary or secondary amines, cycloaliphatic primary amines, and mixtures thereof, and a minor amount of a phosphoric or phosphonic acid ester. A preferred composition comprises about 68.75 wt. % to 75.0 wt. % of said amine, and about 25.0 to 31.25 wt. % of said ester.

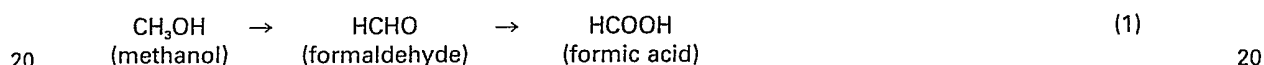
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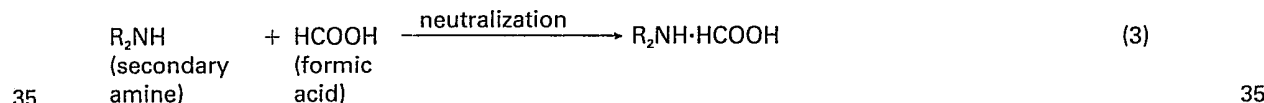
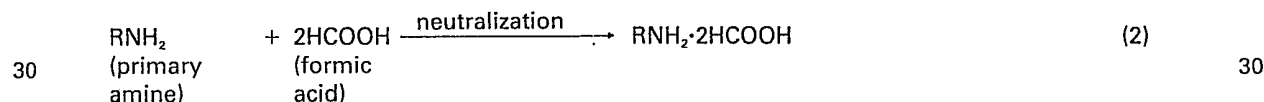
Lubricant additive for alcohol fuel burning engines

5 The present invention is directed to a high detergent/dispersant content additive formulation for use with 5
conventional internal combustion engine lubricants to provide a lubricant suitable for use in internal
combustion engines burning alcohol or alcohol-containing fuels, such as methanol or ethanol fuels. The
present invention is also directed to a lubricant composition containing said lubricant additive, a method
of making said lubricant composition, and a method of inhibiting corrosion and excessive engine wear
10 using said lubricant composition. 10

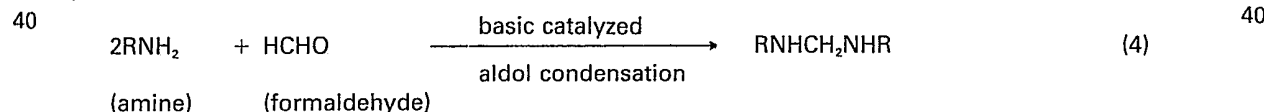
Commonly used automotive lubricants are not effective in alcohol burning engines as evidenced by
excessive engine wear and progressively increasing rates of lubricant consumption. One reason for this
is the large difference in chemical reactivity of the combustion products from gasoline and alcohol auto-
motive fuel systems. In an alcohol fuel system, a number of lubricant degradation reactions occur which
15 are not encountered in the gasoline fuel system. These chemical reactions cause the increased corrosive- 15
ness of alcohol fuels. For instance, methanol readily oxidizes to form formaldehyde and formic acid. This
reaction is represented by Equation 1.



Most vehicles using methanol fuel suffer from excessive upper-cylinder corrosion and bearing wear
resulting from the formic acid produced by methanol combustion. Formic acid reacts with the conven-
tional automotive lubricant's organic amine additives which function as antioxidants, corrosion inhibitors,
25 and anti-wear agents. The amine additives neutralize the formic acid. However, the conventional additi- 25
ves seem unable to adequately neutralize the amount of formic acid formed in methanol combustion.
These reactions are represented in Equations 2 and 3.

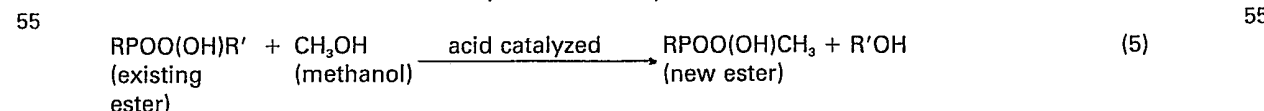


Formaldehyde is highly reactive with amine additives. Formaldehyde reacts with the amines which are
used as antioxidants, antiacids and ashless dispersants. These formaldehyde reactions, represented by
Equation (4), contribute significantly to oil degradation in a methanol fuel system.



45 There is a need for a lubricant additive which minimizes the oxidation of methanol to formaldehyde 45
and formic acid and minimizes excessive formaldehyde and formic acid reactions in order to prolong the
life of lubricant additives which are depleted rapidly by reaction with formaldehyde and formic acid. Sim-
ilarly, there is a need for a lubricant additive which minimizes the oxidation of ethanol to acetaldehyde
and acetic acid and minimizes excessive reactions of those components.

50 Another significant problem in an alcohol fuel system is that zinc dialkyldithiophosphate, a major multi- 50
functional additive in most conventional lubricants, readily transesterifies and thereby loses many of its
anti-wear properties. The transesterification reaction involves the interchange of an alcohol alkyl group,
such as methanol or ethanol, with an existing ester, such as zinc dialkyldithiophosphate, to form a new
ester. A transesterification reaction is represented in Equation 5.



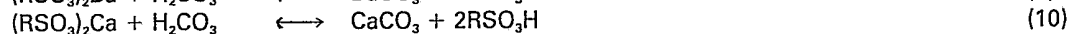
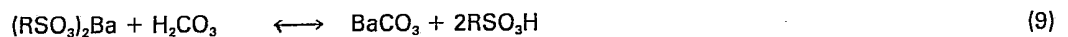
60 The transesterification reaction is acid catalyzed and therefore occurs after the amine base additives in 60
the lubricant are depleted by reaction with aldehydes and acids formed in the combustion process. Tran-
sesterification is not a major mechanism of oil degradation in hydrocarbon fuel systems but is a primary
mechanism of oil degradation in methanol and other alcohol fuel systems. For instance, when methanol
and ethanol are blended with gasoline, the magnitude of the transesterification reaction is proportional to
65 the amount of alcohol in the mixture. 65

Another cause of increased corrosiveness in an alcohol burning engine is the increased solubility of carbon dioxide in the alcohol. For instance, carbon dioxide is much more soluble in methanol than in water. Both water and methanol are usually present in the cooler parts of the crankcase as products of combustion. The water reacts with the fuel combustion products, such as SO_3 , NO_2 , and CO_2 to form the corresponding acids, sulfuric acid, nitric acid, and carbonic acid, as represented in Equations 6, 7 and 8.



These acids reacting with metals in the engine are one of the major causes of corrosion in an internal combustion engine. The lubricants commonly used in a hydrocarbon fuel system effectively neutralize these acids with basic additives such as organic amines and alkaline metal compounds. However, carbonic acid levels are significantly higher in a methanol or other alcohol fuel system than in a gasoline fuel system due to the increased solubility of CO_2 in alcohols. The same may be true of nitric acid formed from NO_2 combustion products. Absorption of carbon dioxide appears to be an important reason for the unexpectedly high corrosiveness of alcohol fuels.

Lubricant analysis indicates that corrosion inhibitors composed of sulfonates, naphthenates or other alkaline metal salts are extensively depleted by reaction with carbonic acid, resulting in the precipitation of insoluble carbonates of the alkaline metals. The precipitation reaction is represented in Equations 9 and 10.



This precipitation reaction competes with the neutralization of carbonic acid by organic amines. Although the neutralization is faster and more likely to occur, the reaction with alkaline metal salts increases as the organic amines are depleted. Thus, there is a need for a lubricant additive wherein depletion of the organic amine additives due to neutralization of formic acid or acetic acid and carbonic acid occurs less rapidly, thus decreasing the likelihood that alkaline metal salts will be depleted by the precipitation reactions represented in Equations 9 and 10.

The present invention aims to provide a lubricant additive for use in an alcohol fuel burning internal combustion engine which provides protection against corrosive and engine wear effects caused by alcohol and, more particularly, to provide a lubricant additive with a high detergent/dispersant content to emulsify liquid alcohol droplets, such as methanol or ethanol, introduced into the lubricant by blow-by gases during combustion, and thereby reduce engine wear.

The present invention provides a lubricant additive for use in internal combustion engines burning alcohol or alcohol-containing fuels, comprising a major amount of an organic amine component selected from the group consisting of aromatic primary amines, aromatic secondary amines, aliphatic primary amines, aliphatic secondary amines, cycloaliphatic primary amines, and mixtures thereof, and a minor amount of a phosphoric acid ester or phosphonic acid ester. Preferably, the amine content is about 68.75 to 75 wt. % and the ester content is about 25 to 31.25 wt. %.

More particularly, the present invention provides a lubricant additive which can be added to conventional automatic lubricants which meet the minimum requirements of the American Petroleum Institute (API) for heavy duty service grade oils (SF/CD) or the Committee of Common Market Automobile Constructors (CCMC) for 2.2 service grade oils, and other internal combustion engine lubricants selected from the group consisting of single viscosity and multiple viscosity grade mineral and synthetic oils with an SAE of 5 to 50, to produce a lubricant suitable for use in alcohol or alcohol-containing fuel burning engines.

The amine component of the lubricant additive of the present invention can be an aliphatic amine, a cycloaliphatic amine, an aromatic primary amine, an aromatic secondary amine or any mixture thereof. Preferably, the amine component is an aliphatic primary or secondary amine; a cycloaliphatic primary amine; a mixture of an aliphatic primary or secondary amine or a cycloaliphatic primary amine with an aromatic primary amine, an aromatic secondary amine, or both; a mixture of an aliphatic primary or secondary amine and a cycloaliphatic primary amine; or a mixture of an aromatic primary amine and an aromatic secondary amine. An aliphatic primary or secondary amine alone is the more preferred amine component.

Preferred aromatic primary amines include ortho-, meta-, and para-phenylenediamine, ortho- meta- and para-toluidine, aniline, xylylidine, naphthylamine, benzylamine, toluenediamine, and naphthalenediamine. A more preferred primary aromatic amine is ortho-phenylenediamine. Preferred aromatic secondary amines include N-phenyl-2-naphthylamine, phenyl- α -naphthylamine, phenyl- β -naphthylamine, tolylnaphthylamine, diphenylamine, ditolylamine, phenyltolylamine, 4,4'-diamino-diphenylamine, and N-methylaniline. A

more preferred aromatic secondary amine is N-phenyl-2-naphthylamine. Preferred aliphatic amines are aliphatic amines having 10 to 30 carbon atoms. A more preferred aliphatic amine has 12 to 30 carbon atoms. The most preferred aliphatic amine is octadecylamine. Preferred cycloaliphatic amines include cyclohexylamine and methylcyclohexylamine.

5 Preferred phosphoric acid esters include ortho, meta-, or para-tricresylphosphate, dibutylphenylphosphate, tributylphosphate, tri-2-ethyl-hexylphosphate and trioctylphosphate. Preferred phosphonic acid esters include diphenyl ortho-phosphonate, dicresyl ortho-phosphonate, trilauryl ortho-phosphonate, and tristearyl ortho-phosphonate. A more preferred phosphoric acid ester is para-tricresylphosphate.

10 A preferred composition of the lubricant additive of the present invention comprises about 68.75 to 75 wt. % of octadecylamine and about 31.25 to 25 wt. % of para-tricresylphosphate.

Another preferred composition of the lubricant additive of the present invention comprises about 68.75 to 75 wt. % of octadecylamine and about 31.25 to 25 wt. % of the mixed isomers of the tricresylphosphate.

15 All of the above chemicals are commercially available. The lubricant additive of the present invention is made by blending together a minor amount of a lubricant additive comprising a major amount of an organic amine selected from the group consisting of aliphatic primary amines, aliphatic secondary amines, cycloaliphatic primary amines, aromatic primary amines, aromatic secondary amines, and mixtures thereof, and a minor amount of a phosphoric acid ester or a phosphonic acid ester, and a major amount of a lubricant blend stock which meets the minimum requirements of the API for SF/CD grade oils or the CCMC for 2.2 service grade oils, or any other lubricant blend stock selected from the group consisting of single and multiple viscosity grade mineral and synthetic oils with an SAE of about 5 to 50. Preferably the lubricant additive of the present invention is prepared by blending together about 1 to 8 wt. % of the amine, about 0.25 to 2.5 wt. % of the phosphoric acid ester or phosphonic acid ester, and about 89.5 to 98.75 wt. % of the lubricant blend stock.

25 The lubricant additive of the present invention can be used by adding approximately one quart of the lubricant additive to a 5 quart oil change. The lubricant additive of the present invention may provide effective protection against corrosive and engine wear effects caused by methanol, ethanol, or other alcohol or alcohol-containing fuels for oil change intervals of more than 4000 miles and in some cases up to 6000 miles (6437 and 9656 km).

30 The phosphoric acid ester, preferably para-tricresylphosphate or the mixed isomers of tricresylphosphate, or the phosphonic acid ester functions as a methanol or ethanol solubilizer and a non-ash detergent/dispersant for alcohol droplets, such as methanol or ethanol, in the lubricant. A solubilizer of this type is required to dissolve or disperse the relatively large amounts of alcohol, such as methanol or ethanol, introduced into the lubricant during the combustion process in an alcohol fuel burning combustion engine. The phosphoric acid ester or phosphonic acid ester solubilizes and disperses the alcohol droplets of methanol or ethanol thereby preventing dry spots on the moving parts of the internal combustion engine. In the absence of phosphoric acid ester or phosphonic acid ester, methanol or ethanol is insoluble in hydrocarbon lubricants and dry spots can occur which result in excessive engine wear.

35 The phosphoric acid ester or phosphonic acid ester also functions as an anti-wear agent and when used with methanol or ethanol fuel it is superior to the conventional anti-wear agent, zinc dialkyldithiophosphate. Zinc dialkyldithiophosphate is almost universally used in automotive lubricants for gasoline burning engines but loses its anti-wear properties rapidly in methanol or ethanol burning engines because it readily transesterifies with the alcohols.

40 The amine component functions as a base number additive to neutralize formic or acetic and carbonic acids formed by the oxidation of methanol or ethanol and by the reaction of water and carbon dioxide, respectively. The amine component also functions as an antioxidant, minimizing the oxidation of methanol or ethanol to their respective aldehydes and acids.

45 The presence of larger amounts (about 68.75 to 75 wt. %) of organic amines in the lubricant additive of the present invention permits preparation of a lubricant containing about 1 to 8 wt. % of organic amines, as compared to about 0.25 wt. % organic amines in lubricants containing conventional lubricant additives, minimizes depletion of alkaline metal salts, such as naphthenates and sulfonates. The alkaline metal salts are depleted when they react with carbonic acid to form insoluble carbonates, competing with the neutralization of carbonic acid. The neutralization reaction is faster and more likely to occur, but the precipitation reaction becomes a problem when the organic amines become depleted. With more organic amines present, more carbonic acid is neutralized and there is less carbonic acid available to react with the alkaline metal salts.

55 Analysis of the lubricant after use in the automobile engine provides a convenient and reliable indication of engine wear during an oil change interval as short as a few thousand miles.

60 A lubricant additive can be evaluated based on the amounts of wear elements, such as iron, lead, copper, chromium, nickel, tin, aluminum and molybdenum, detected in an oil sample by spectrochemical analysis after the engine has been driven a certain number of miles after an oil change. These metals or wear elements show up in the lubricant as a result of excessive corrosion of or failure of certain engine components made of that metal as well as normal mechanical wear.

65 Since the materials of construction of automobiles vary widely, it is not technically feasible to determine exactly what wear element content in a used oil analysis indicates excessive engine wear. However,

generalized criteria for evaluation of lubricant wear element data are available and are set forth in Table 1. The primary and secondary source in the engine of each wear element is given as well as the average amount in ppm's of each wear element which would be found in the oil at the "break-in" point and at the "post break-in" point. Engine wear levels during the break-in period tend to be relatively high. After the engine has been broken in, the wear levels reach a plateau, remaining stable for about 50,000 (80,467 km), depending on the particular vehicle and degree of maintenance. The "break-in" point for an average engine is generally in the 0 to 10,000 mill (16,093 km) range. The evaluation criteria found in Table 1 will be used to evaluate the data set forth in Examples 1 through 13.

The most useful indication of excessive engine wear is obtained from sudden deviations in a given wear element content in a used-oil analysis pattern which has been previously established for a given engine in a given service using a specific oil.

Base number is a measure of the oil detergent action and its ability to inhibit corrosion. New automotive oils commonly have a base number of 4 to 5. For any oil, a reading of 1 or less indicates a dangerous depletion of additive reserves. A base number of 2 is generally considered to provide an adequate margin of protection in a gasoline burning engine.

TABLE 1
Criteria for Evaluation of Lubricant Wear Element Data

Evaluation Criteria, ppm						Source	
5	Break-In			Post Break-In		Primary cylinder wall	Secondary block, crank- shaft, wrist pins, rings, valves, oil pump, fuel tank
	Wear Element	Average 200-400	Excessive 400	Average 10-100	Excessive 200		
10	Iron (Fe)						10
15							15
20	Molybdenum (Mo)	2-4	5	0-2	3	cylinder wall	block, crank- shaft wrist pins, rings, valves, oil pump, fuel tank
25							25
30	Lead (Pb)	100-300	300	5-100	150	bearings	flashing, TEL in fuel
35	Copper (Cu)	50-150	150	5-75	100	bearings	bushings, wrist pins, cam, valve train, thrust washers, oil pump
40							40
45	Tin (Sn)	20-50	50	1-10	15	bearings	flashing
45	Chromium (Cr)	2-10	10	1-5	5	rings	crank- shaft, exhaust valves
50	Nickel (Ni)	3-5	5	1-2	4	valves, crankshaft	rings
55	Aluminum (Al)	30-100	100	1-15	30	pistons, aluminum blocks	

Example 1

An oil sample comprising about 98.68 wt. % of Kendall 40 wt. automotive lubricant and about 1.32 wt. % of the lubricant additive of the present invention comprising about 75.0 wt. % octadecylamine and about 25.0 wt. % para-tricresylphosphate, was taken from the crankcase of a methanol-fueled 1981 Chevrolet Citation engine which had been driven 91,298 miles (146,930 km) with an oil change at about 4,009 miles prior thereto. The methanol fuel used was an 88.0% methanol/12.0% unleaded regular gasoline (Octane No. 87) blend.

The oil sample had a base number of 3.14 which is well above the acceptable base number value of 2,

indicating that the octadecylamine had not been depleted and was still available for neutralizing acids and preventing oxidation of methanol of formic acid and formaldehyde.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 25 ppm iron; 49 ppm lead; 83 ppm copper; 1 ppm chromium; 3 ppm aluminum; 1 ppm nickel; 15 ppm tin; and 2 ppm molybdenum. Because the engine had been driven 91,298 miles (146,930 km), the "post break-in" criteria from Table 1 were used to evaluate the wear element content.

Referring to Table 1, the iron, lead, chromium, aluminum, nickel and molybdenum content were within the average wear element content range for these wear elements at post break-in mileage. The copper content was above average but not excessive. According to Table 1, the tin content was considered excessive, however the tin content in the oil sample taken from the crankcase during the oil change at 4,009 miles (6452 km) prior to the present oil change was 14 ppm which indicates no significant change in the tin content, and thus no excessive engine wear. As mentioned previously, a sudden deviation of wear element content in a used-oil analysis pattern is more indicative of excessive engine wear, than the generalized criteria in Table 1.

Example 2

An oil sample comprising 98.68 wt. % of the lubricant used in Example 1 and 1.32 wt. % of the lubricant additive used in Example 1 was taken from the crankcase of the same methanol-fueled engine as in Example 1. The engine had been driven 95,152 miles (153,132 km), thus the previous oil change occurred 3,854 miles (6202 km) previously.

The oil sample had a base number of 2.8 which is well above the acceptable base number value of 2, indicating that the octadecylamine had not been depleted.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 34 ppm iron; 72 ppm lead; 95 ppm copper; 0 ppm chromium; 4 ppm aluminum; 1 ppm nickel; 19 ppm tin; and 3 ppm molybdenum. The "post break-in" mileage criteria from Table 1 were applied.

Referring to Table 1, the iron, lead, chromium, aluminum, and nickel contents were within the average wear element range for these wear elements at "post break-in" mileage. The copper content was above average but not excessive and had not significantly deviated from the prior copper content described in Example 1. The tin and molybdenum content were considered excessive according to Table 1 but there was not a significant deviation from the prior tin and molybdenum content described in Example 1, thus indicating no excessive engine wear.

Example 3

An oil sample comprising about 98.68 wt. % of the lubricant used in Examples 1 and 2 and about 1.32 wt. % of the lubricant additive used in Examples 1 and 2 was taken from the crankcase of the same methanol-fueled engine used in Examples 1 and 2 which had been driven 98,978 miles (159,290 km). Thus, the prior oil change occurred at about 3,826 miles (6157 km) prior to the present oil change.

The sample had a base number of 3.02 indicating that the octadecylamine had not been depleted.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 20 ppm iron; 49 ppm lead; 97 ppm copper; 1 ppm chromium; 2 ppm aluminum; 2 ppm nickel; 19 ppm tin; and 2 ppm molybdenum. The sample was evaluated using "post break-in" criteria from Table 1.

Referring to Table 1, the iron, lead, chromium, aluminum, nickel, and molybdenum content were within the average wear element content range for these wear elements at "post break-in" mileage. The copper content was above average but not excessive. The tin content was considered excessive according to Table 1, however there was no change at all from the prior oil change and thus there is no indication of excessive engine wear.

Example 4

An oil sample comprising about 98.68 wt. % of Kendall 30 wt. automotive lubricant and about 1.32 wt. % of the lubricant additive of the present invention comprising about 75.0 wt. % octadecylamine and 25.0 wt. % paratricsylphosphate, was taken from the crankcase of a methanol-fueled 1982 Chevrolet S-10 engine which had been driven about 79,760 miles (128,361 km) with an oil change at about 4,042 miles (6504 km) prior thereto. The methanol fuel used was an 88.0% methanol/12.0% unleaded regular gasoline (Octane No. 87) blend.

The base number of the sample was 2.52 which indicates that the octadecylamine had not been depleted.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 96 ppm iron; 27 ppm lead; 49 ppm copper; 3 ppm chromium; 14 ppm aluminum; 2 ppm nickel; 5 ppm tin; and 7 ppm molybdenum. The "post break-in" criteria from Table 1 were used because 79,760 miles (128,361 km) represents post break-in mileage.

Referring to Table 1, the iron, lead, copper, chromium, aluminum, nickel, and tin content were within the average wear element content for these wear elements at post break-in mileage. The molybdenum content was considered excessive according to Table 1, but as shown in Examples 5 and 6 below, there was never a sudden deviation in the molybdenum content at the various oil changes, thus there was no

indication of excessive engine wear.

Example 5

An oil sample comprising about 98.68 wt. % of the lubricant used in Example 4 and about 1.32 wt. % of the lubricant additive used in Example 4 was taken from the crankcase of the same methanol-fueled engine used in Example 4 which had been driven 83,977 miles (135,148 km). Thus, the prior oil change occurred about 4,217 miles (6787 km) prior to the current oil change.

The oil sample had a base number of 1.93 which is very close to the acceptable base number value of 2, thus indicating sufficient amounts of octadecylamine to neutralize acids and minimize methanol oxidation.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 57 ppm iron; 26 ppm lead; 42 ppm copper; 2 ppm chromium; 16 ppm aluminum; 2 ppm nickel; 0 ppm tin; and 18 ppm molybdenum. The post break-in mileage criteria from Table 1 were applied.

Referring to Table 1, the iron, lead, copper, chromium, nickel, and tin contents were within the average wear element content range for these wear elements at post break-in mileage. The aluminum content was slightly above average but not excessive. The molybdenum content is considered excessive according to Table 1 but had not significantly changed from the content at the last oil change, indicating no excessive engine wear.

Example 6

An oil sample comprising about 98.68 wt. % of the lubricant used in Examples 4 and 5 and about 1.32 wt. % of the lubricant additive used in Examples 4 and 5 was taken from the crankcase of the methanol-fueled engine used in Examples 4 and 5 which had been driven the equivalent of 88,491 miles (142,412 km). Thus, the previous oil change occurred about 4,514 miles (7265 km) prior to the current oil change.

The base number of the sample was about 1.62 which is slightly lower than the more acceptable base number value of 2 but is still greater than 1.0, thus indicating that sufficient amounts of octadecylamine were present.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 71 ppm iron; 22 ppm lead; 41 ppm copper; 1 ppm chromium; 16 ppm aluminum; 1 ppm nickel; 0 ppm tin; and 34 ppm molybdenum. The post break-in criteria from Table 1 should be used to evaluate the oil sample because 88,491 miles (142,412 km) is considered post break-in mileage.

Referring to Table 1, the iron, lead, copper, chromium, nickel and tin wear element contents were within the average wear element content range for post break-in mileage. The aluminum content was above average but not excessive. The molybdenum content was considered excessive according to Table 1, however the molybdenum content had not significantly changed from the content at both of the prior oil changes, indicating no excessive engine wear.

Example 7

An oil sample comprising about 98.68 wt. % of Kendall™ 30 wt. automotive lubricant and about 1.32 wt. % of the lubricant additive of the present invention comprising about 75.0 wt. % octadecylamine and about 25.0 wt. % para-tricresylphosphate, was taken from the crankcase of a methanol-fueled 1982 Chevrolet S-10 engine which had been driven 76,636 miles (123,334 km) with an oil change at about 3,241 miles (5216 km) prior thereto. The methanol fuel used was 88.0% methanol/12.0% unleaded regular gasoline (Octane No. 87) blend.

The oil sample had a base number of 3.3 which is well above the acceptable base number of value 2, indicating that the octadecylamine had not been depleted and was still available for neutralizing acids and minimizing methanol oxidation.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 50 ppm iron; 10 ppm lead; 56 ppm copper; 2 ppm chromium; 9 ppm aluminum; 0 ppm nickel; 0 ppm tin; and 3 ppm molybdenum. The "post break-in" criteria from Table 1 were used to evaluate the oil sample because 76,636 miles (123,334 km) represents post break-in mileage.

Referring to Table 1, the iron, lead, copper, chromium, aluminum, nickel and tin contents were within the average wear element content range for these wear elements at post break-in mileage. The molybdenum content was considered excessive according to Table 1, but as shown in Examples 8 and 9 below, there was no sudden deviation in the molybdenum content at the various oil changes, thus indicating no excessive engine wear.

Example 8

An oil sample comprising about 98.68 wt. % of the lubricant used in Example 7 and about 1.32 wt. % of the lubricant additive used in Example 7 was taken from the crankcase of the same methanol-fueled engine used in Example 7 which had been driven 81,197 miles (130,674 km). Thus, the prior oil change occurred at about 4,561 (7340 km) prior to the present oil change.

The base number of the oil sample was 3.64 which is well above the acceptable base number of value 2, indicating that the octadecylamine had not been depleted.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil

sample: 39 ppm iron; 9 ppm lead; 27 ppm copper; 2 ppm chromium; 7 ppm aluminum; 0 ppm nickel; 0 ppm tin; and 11 ppm molybdenum.

The iron, lead, copper, chromium, aluminum, nickel, and tin contents were within the average wear element content range for these wear elements at post break-in mileage. The molybdenum content was considered excessive according to Table 1, but there was not a sudden deviation from the content at the prior oil change described in Example 7 and thus does not indicate excessive engine wear.

Example 9

An oil sample comprising about 98.68 wt. % of the automotive lubricant used in Examples 7 and 8 and about 1.32 wt. % of the lubricant additive used in Examples 7 and 8 was taken from the crankcase of the same methanol-fueled engine used in Examples 7 and 8 which had been driven 85,351 miles (137,359 km). Thus, the prior oil change occurred at about 4,154 miles (6685 km) prior to the current oil change.

The base number of the oil sample was 3.36 which is well above the acceptable base number value of 2, indicating that the octadecylamine had not been depleted.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 39 ppm iron; 9 ppm lead; 94 ppm copper; 2 ppm chromium; 7 ppm aluminum; 1 ppm nickel; 0 ppm tin; and 12 ppm molybdenum. The sample was evaluated using post break-in mileage criteria from Table 1.

Referring to Table 1, the iron, lead, chromium, aluminum, nickel and tin contents were within the average wear element content range for these wear elements at post break-in mileage. The copper content was above average but not excessive. The molybdenum content was considered excessive according to Table 1 but increased only 1 ppm from the prior oil change described in Example 8, thus indicating no excessive engine wear.

Example 10

An oil sample comprising about 98.68 wt. % of Kendall 30 wt. automotive lubricant and about 1.32 wt. % of the lubricant additive of the present invention comprising about 75.0 wt. % octadecylamine and about 25.0 wt. % paratricresylphosphate, was taken from the crankcase of a methanol-fueled 1982 Chevrolet S-10 engine which had been driven the equivalent of about 78,612 miles (126,514 km) with a prior oil change at about 4,256 miles (6849 km) prior thereto. The methanol fuel used was an 88.0 % methanol/12.0% unleaded regular gasoline (Octane No. 87) blend.

The base number of the oil sample was about 3.02 which is well above the acceptable base number value of 2, indicating that the octadecylamine had not been depleted.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 130 ppm iron; 15 ppm lead; 69 ppm copper; 4 ppm chromium; 14 ppm aluminum; 2 ppm nickel; 5 ppm tin; and 11 ppm molybdenum. The oil sample was evaluated using "post break-in" mileage criteria in Table 1 because 78,612 miles (126,514 km) represents post break-in mileage.

Referring to Table 1, the lead, copper, chromium, aluminum, nickel, and tin contents were within the average wear element content range for these wear elements at post break-in mileage. The iron content was above average but not excessive. The molybdenum content was excessive according to Table 1, however as shown in Examples 11 and 12, the molybdenum content did not suddenly deviate from the pre-established pattern at any of the various oil changes, thus indicating no excessive engine wear.

Example 11

An oil sample comprising about 98.68 wt. % of the lubricant used in Example 10 and about 1.32 wt. % of the lubricant additive used in Example 10 was taken from the crankcase of the same methanol-fueled engine used in Example 10 which had been driven 81,959 miles (131,900 km). Thus, the prior oil change occurred at about 3,347 miles (5386 km) prior to the present oil change.

The base number of the oil sample was 3.36 which is well above the acceptable base number value of 2, indicating that the octadecylamine had not been depleted.

Spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 63 ppm iron; 10 ppm lead; 83 ppm copper; 3 ppm chromium; 9 ppm aluminum; 2 ppm nickel; 0 ppm tin; and 31 ppm molybdenum. The post break-in criteria of Table 1 was used to evaluate the oil sample.

Referring to Table 1, the iron, lead, chromium, aluminum, nickel, and tin contents were within the average wear element content ranges for these wear elements at post break-in mileage. The copper content was above average but not excessive. The molybdenum content was considered excessive according to Table 1, but did not significantly deviate from the prior molybdenum content at the prior oil change as described in Example 10. Thus, the molybdenum content does not indicate excessive engine wear. Further, the iron, lead, chromium, aluminum, and tin content decreased from Example 10 to Example 11, indicating that the lubricant additive of the present invention is effectively inhibiting corrosion and engine wear.

Example 12

An oil sample comprising about 98.68 wt. % of the lubricant used in Examples 10 and 11 and about 1.32 wt. % of the lubricant additive used in Examples 10 and 11 was taken from the crankcase of the same methanol-fueled engine used in Examples 10 and 11 which had been driven 86,253 miles (138,811 km). Thus, the prior oil change occurred at about 4,294 miles (6911 km) prior to the present oil change.

The base number of the oil sample was about 2.91 which is well above the acceptable base number value of 2, indicating that the octadecylamine had not been depleted and was still available for neutralizing acids and preventing oxidation of methanol to formaldehyde and formic acid.

The spectrochemical analysis revealed that the following amounts of wear elements were present in the oil sample: 70 ppm iron; 8 ppm lead; 22 ppm copper; 1 ppm chromium; 12 ppm aluminum; 0 ppm nickel; 0 ppm tin; and 17 ppm molybdenum. The oil sample was evaluated using the post break-in criteria from Table 1.

Referring to Table 1, the iron, lead, copper, chromium, aluminum, nickel, and tin contents were within the average wear element content range for these wear elements at post break-in mileage. The molybdenum content was considered excessive according to Table 1, but had decreased since the prior oil change described in Example 11 thus indicating that the lubricant additive is effectively inhibiting corrosion and excessive engine wear. Further, the lead, copper, chromium, and nickel contents decreased from the prior oil change evaluation described in Example 11 and the iron, lead, copper, chromium, nickel, and tin contents decreased from the prior oil change described in Example 10, indicating that the lubricant additive of the present invention effectively inhibits corrosion and excessive engine wear in a methanol-fuel burning engine.

Example 13

The average base number in the oil sample evaluations described in Examples 1 through 12 was 3.15 which is well above the acceptable base number value of 2.

The average wear element content of the oil sample evaluations described in Examples 1 through 12 are as follows: 57.8 ppm iron; 25.5 ppm lead; 63.2 ppm copper; 1.8 ppm chromium; 9.4 ppm aluminum; 1.2 ppm nickel; 5.25 ppm tin; and 12.5 ppm molybdenum.

All of the above wear element content data representing the average data from the previous twelve examples was within the average wear element content range set out in Table 1 for post break-in mileage, except molybdenum. However, the excessive amounts of molybdenum as described in the preceding twelve examples did not indicate excessive engine wear because there was never a sudden deviation from a pre-established used oil evaluation pattern.

The average values for the base number and wear element contents described herein illustrate that the lubricant additive of the present invention effectively inhibits corrosion and excessive engine wear in internal combustion engines burning alcohol or alcohol-containing fuels.

CLAIMS

1. A lubricant additive for use in internal combustion engines burning alcohol or alcohol-containing fuels, comprising a major amount of an organic amine component selected from the group consisting of aromatic primary amines, aromatic secondary amines, aliphatic primary amines, aliphatic secondary amines, cycloaliphatic primary amines, and mixtures thereof, and a minor amount of a phosphoric acid ester or phosphonic acid ester.
2. A lubricant additive according to claim 1, wherein the amine content is 68.75 to 75 wt. % and the ester content is 25 to 31.25 wt. %.
3. A lubricant additive according to claim 1 or claim 2, wherein the aromatic primary amine is ortho-phenylenediamine, meta-phenylenediamine, para-phenylenediamine, ortho-toluidine, meta-toluidine, para-toluidine, aniline, xylidine, naphthylamine, benzylamine, toluenediamine or naphthalenediamine.
4. A lubricant additive according to claim 3, wherein the aromatic primary amine is ortho-phenylenediamine.
5. A lubricant additive according to any one of the preceding claims, wherein the aromatic secondary amine is selected from the group consisting of N-phenyl-2-naphthylamine, phenyl- α -naphthylamine, phenyl- β -naphthylamine, tolynaphthylamine, diphenylamine, ditolylamine, phenyltolylamine, 4,4'-diaminodiphenylamine, and N-methylaniline.
6. A lubricant additive according to claim 5, wherein the aromatic secondary amine is N-phenyl-2-methylamine.
7. A lubricant additive according to any one of the preceding claims, wherein the aliphatic amine is an aliphatic amine having 10 to 30 carbon atoms.
8. A lubricant additive according to claim 7, wherein the aliphatic amine is octadecylamine.
9. A lubricant additive according to any one of the preceding claims, wherein the cycloaliphatic amine is cyclohexylamine or methylcyclohexylamine.
10. A lubricant additive according to any one of claims 1 to 8, wherein the amine component is a mixture comprising an aliphatic primary amine and an amine selected from the group consisting of aromatic primary amines, aromatic secondary amines, and mixtures thereof.

11. A lubricant additive according to any one of claims 1 to 7, wherein the amine component is a mixture comprising an aliphatic secondary amine and an amine selected from the group consisting of aromatic primary amines, aromatic secondary amines, and mixtures thereof.
12. A lubricant additive according to any one of claims 1 to 6 or 9, wherein the amine component is a mixture comprising a cycloaliphatic primary amine and an amine selected from the group consisting of aromatic primary amines, aromatic secondary amines, and mixtures thereof.
13. A lubricant additive according to any one of claims 1, 2, 7 or 8, wherein the amine component is an aliphatic primary amine.
14. A lubricant additive according to any one of claims 1, 2 or 7, wherein the amine component is an aliphatic secondary amine.
15. A lubricant additive according to any one of claims 1, 2 or 7 to 9, wherein the amine component is a mixture comprising an aliphatic primary amine and a cycloaliphatic primary amine.
16. A lubricant additive according to any one of claims 1, 2, 7 or 9, wherein the amine component is a mixture comprising an aliphatic secondary amine and a cycloaliphatic primary amine.
17. A lubricant additive according to any one of claims 1, 2 or 9, wherein the amine component comprises a cycloaliphatic primary amine.
18. A lubricant additive according to any one of claims 1 to 6, wherein the amine component is a mixture comprising an aromatic primary amine and an aromatic secondary amine.
19. A lubricant additive according to any one of the preceding claims, wherein the ester is ortho-tri-cresylphosphate, meta-tricresylphosphate, para-tricresylphosphate, dibutylphenylphosphate, tributylphosphate, tri-2-ethylhexylphosphate, trioctylphosphate, diphenyl ortho-phosphonate, dicresyl orthophosphonate, trilauryl ortho-phosphonate or tristearyl ortho-phosphonate.
20. A lubricant additive according to claim 19, wherein the ester is para-tricresylphosphate.
21. A lubricant additive substantially as hereinbefore described in any one of the Examples.
22. A method for inhibiting corrosion and excessive engine wear in an internal combustion engine burning alcohol or alcohol-containing fuel, comprising the step of adding to the engine an internal combustion engine lubricant selected from the group consisting of single viscosity and multiple viscosity grade mineral and synthetic oils with an SAE of about 5 to 50, the lubricant containing a lubricant additive as defined in any one of the preceding claims.
23. A method according to claim 22, wherein the lubricant contains 1.25 to 10.5 wt. % of the lubricant additive.
24. A method of making an internal combustion engine lubricant which inhibits corrosion and excessive engine wear in an internal combustion engine burning alcohol or alcohol-containing fuel, comprising the step of blending together a major amount of an internal combustion engine lubricant selected from the group consisting of single viscosity and multiple viscosity grade mineral and synthetic oils with an SAE of about 5 to 50, and a minor amount of a lubricant additive as defined in any one of claims 1 to 21.
25. A method according to claim 24, wherein 89.5 to 98.75 wt. % of the lubricant and 1.25 to 10.5 wt. % of the lubricant additive are blended together.
26. A lubricant composition which inhibits corrosion and excessive engine wear in an internal combustion engine burning alcohol-containing fuel, comprising a major amount of an internal combustion engine lubricant selected from the group consisting of single viscosity and multiple viscosity grade mineral and synthetic oils with an SAE of about 5 to 50, and a minor amount of a lubricant additive as defined in any one of claims 1 to 21.
27. A lubricant composition according to claim 26, wherein the lubricant content is 89.5 to 98.75 wt. % and the lubricant additive content is 1.25 to 10.5 wt. %.