



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 773 278 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
02.08.2006 Bulletin 2006/31

(51) Int Cl.:
C10L 1/18 (2006.01) C10L 1/22 (2006.01)

(21) Application number: **96308195.5**

(22) Date of filing: **13.11.1996**

(54) **Fuel additive**

Kraftstoffzusatz

Additif pour combustible

(84) Designated Contracting States:
BE FR

(30) Priority: **13.11.1995 GB 9523202**

(43) Date of publication of application:
14.05.1997 Bulletin 1997/20

(73) Proprietor: **Afton Chemical Limited**
Bracknell,
Berkshire RG12 2UW (GB)

(72) Inventor: **Quigley, Robert**
Bracknell,
Berkshire RG12 7WF (GB)

(74) Representative: **Cresswell, Thomas Anthony**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5JJ (GB)

(56) References cited:
FR-A- 511 487 FR-A- 1 399 466
FR-A- 1 405 551 US-A- 2 632 695
US-A- 2 854 324 US-A- 3 088 815
US-A- 4 244 829 US-A- 4 375 360
US-A- 4 512 903 US-A- 4 551 152
US-A- 5 338 470

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

[0001] The present invention relates to the use of certain compounds to improve the lubricating properties of low sulfur-content fuels and to fuels comprising the compounds.

[0002] Sulfur contained in fuel, for example middle distillate fuels such as diesel fuel and jet fuel, is said to constitute a serious environmental hazard. Hence, strict regulations limiting the amount of sulfur which may be present in such fuels have been introduced. Unfortunately, fuels having a suitably low sulfur content exhibit very poor inherent lubricity and this can lead to problems when the fuel is used. For example, the use of low sulfur fuel in diesel engines frequently results in damage to the fuel injector pump which relies on the natural lubricating properties of the fuel to prevent component failure. There is therefore a need to improve the lubricating properties of low sulphur fuels.

[0003] FR 1405551 discloses certain polycarboxylic acids or esters thereof for improving the lubricity of aviation turbo jet fuels. The only hydroxy substituted acid to which FR 1405551 refers is tartaric acid. US-A-4512903 relates to short chain amides as friction reducing agents in lubricants.

[0004] It has now been found that the lubricating properties of low sulfur fuels can be improved by the use of certain additive compounds as described in detail below. This enables mechanical failure, for example fuel injector pump failure, caused by inadequate fuel lubricity to be avoided while retaining the environmental benefit of using a low sulfur fuel.

[0005] Accordingly, the present invention provides the use of a carboxylic acid having from 10-60 carbon atoms and being substituted by at least one hydroxy group, or a derivative of this hydroxy-substituted acid, as an additive for improving the lubricity of a fuel having a sulfur content of 0.2% by weight or less, wherein said fuel is a diesel fuel, jet fuel or bio-diesel fuel.

[0006] In the present context the term "low sulfur-content fuel" is intended to mean fuels typically having a sulfur content of, 0.2 % by weight or less, for example 0.05% by weight or less and, more especially, 0.005% by weight or less. Fuels in which the additive compounds may be used are diesel and jet fuels and bio-diesel fuel. The latter is derived from a petroleum or vegetable source or mixture thereof and typically contains vegetable oils or their derivatives, such as esters produced by saponification and re-esterification or trans-esterification. Middle distillate fuels are usually characterised as having a boiling range of 100 to 500°C, more typically from 150 to 400°C.

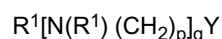
[0007] The said derivative of the hydroxy-substituted acid may be an ester formed by reaction of the acid with a polyhydric alcohol or alkanolamine, or an amide.

[0008] The hydroxy-substituted carboxylic acid or acid derivative may be used alone or in combination with any other hydroxy-substituted acid and/or acid derivative. Typically, the acid is an aliphatic fatty acid substituted by up to four hydroxyl groups. The hydroxy-substituted acid used in the present invention contains from 10 to 60 carbon atoms. The hydroxy-substituted acid may be a mono- or poly-carboxylic acid or a dimerized acid. When hydroxy-substituted mono-carboxylic acids are used they typically contain 10 to 40 carbon atoms, more commonly 10 to 30 and especially 12 to 24 carbon atoms. The preferred acid of this type is the fatty acid, ricinoleic acid. When hydroxy-substituted poly-carboxylic acids are used, such as di- or tri-carboxylic acids, they typically contain 3 to 40 carbon atoms, more commonly 3 to 30 and especially 3 to 24 carbon atoms. Examples of this kind of hydroxy-substituted poly-carboxylic acid include malic, tartaric and citric acids.

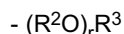
[0009] It is also possible to use as the hydroxy-substituted acid, dimerized acids. Herein such compounds are referred to as dimer and trimer acids. When used the dimerized acid typically contains 10 to 60, preferably 20 to 60 and most preferably 30 to 60, carbon atoms. Such acids are prepared by dimerizing unsaturated acids and introducing a hydroxyl functionality. Such acids typically consist of a mixture of monomer, dimer and trimer acid. According to a preferred embodiment of the invention the acid is a hydroxy-substituted dimerized fatty acid, for example of oleic and linoleic acids. Typically this dimer exists as a mixture of 2% by weight monomer, 83% by weight dimer and 15% by weight of trimer and possibly higher acids. The preferred dimer acid, as well as the other acids described above, are commercially available or may be prepared by the application or adaption of known techniques.

[0010] As described above, the additive compound(s) used may be in the form of a carboxylic acid derivative. One kind of derivative which may be used is an ester of the acid with a polyhydric alcohol. The polyhydric alcohol from which the ester may be derived typically contains from 2 to 7 carbon atoms. Examples of suitable alcohols include alkylene glycols such as ethylene glycol, diethylene glycol, triethylene glycol and dipropylene glycol, glycerol, arabitol, sorbitol, mannitol, pentaerythritol, sorbitan, 1,2-butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol and 1,2-cyclohexanediol. These alcohols are readily available. Of the alcohols mentioned it is preferred to use glycerol or sorbitan. In a preferred embodiment the ester has at least one free hydroxyl group in the moiety derived from the polyhydric alcohol, i.e. not all of the hydroxyl groups of the polyhydric alcohol are esterified. The use of glycerol monoricinoleate is particularly preferred.

[0011] Another kind of fatty acid derivative which may be used is the ester of the hydroxy-substituted acid with an alkanolamine of formula:



in which p is 2 to 10, q is 0 to 10, Y is $-N(R^1)_2$, 4-morpholinyl or 1-piperazinyl N-substituted by a group R^1 or a group $-[(CH_2)_pN(R^1)]_qR^1$ in which p and q are as defined above and each substituent R^1 is independently selected from alkyl groups having from 1 to 6 carbon atoms and a group of formula:



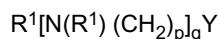
in which r is 0 to 10, R^2 is an alkylene group having 2 to 6 carbon atoms and R^3 is an hydroxyalkyl group having 2 to 6 carbon atoms, provided at least one group R^1 is $-(R^2O)_rR^3$. Thus, the alkanolamine is one which does not contain any hydrogen-bearing nitrogen atoms. The presence of free hydrogen atoms would be expected to lead to the formation of an amide on reaction with the acid. The alkanolamines which may be used are commercially available or may be made by the application or adaptation of known methods.

[0012] According to a preferred embodiment, in the alkanolamine of the above formula Y is $-N(R^1)_2$, p is 2 and q is 0 to 3. It is further preferred that each R^1 is a C_{2-4} hydroxyalkyl group, C_2 or C_3 hydroxyalkyl being particularly preferred. Specific examples of such compounds include triethanolamine, triisopropanolamine and ethylene diamine and diethylene triamine in which each nitrogen atom is substituted by hydroxyethyl or hydroxypropyl groups.

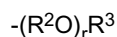
[0013] In another preferred embodiment, in the alkanolamine Y is 4-morpholinyl or substituted 1-piperazinyl, q is 0 or 1 and p is from 2 to 6. Examples of such alkanolamines include aminoethylpiperazine, bis-(aminoethyl)piperazine and morpholine, N-substituted by an hydroxypropyl group.

[0014] The alkanolamines are commercially available or may be made by the application or adaptation of known techniques.

[0015] It is also possible to use as the hydroxy-substituted acid derivative, an amide such as that formed by reaction of the substituted fatty acid with ammonia or a nitrogen-containing compound of formula:



in which p is 2 to 10, q is 0 to 10, Y is $-N(R^1)_2$, 4-morpholinyl or 1-piperazinyl optionally N-substituted by a group R^1 or a group $-[(CH_2)_qN(R^1)]_qR^1$ in which p and q are as defined above and each substituent R^1 is independently selected from hydrogen and alkyl groups having 1 to 6 carbon atoms and a group of formula:



in which r is 0 to 10, R^2 is an alkylene group having 2 to 6 carbon atoms and R^3 is an hydroxyalkyl group having 2 to 6 carbon atoms, provided that at least one group R^1 is hydrogen.

[0016] According to a preferred embodiment, in the nitrogen-containing compound Y is $-N(R^1)_2$, p is 2 and q is 0 to 3. Examples of such compounds include diethanolamine, tris(hydroxymethyl)aminomethane, triethylene tetramine or diethylene triamine optionally N-substituted by two hydroxypropyl groups.

[0017] In another embodiment, in the nitrogen-containing compound Y is 4-morpholinyl or optionally N-substituted 1-piperazinyl, p is 2 to 6, q is 0 or 1 and each R^1 is hydrogen. Examples of such compounds include aminoethylpiperazine, bis-(aminoethyl)piperazine or morpholine.

[0018] The compounds used to form the acid amides are commercially available or may be made by the application or adaptation of known techniques.

[0019] The alkanolamines and nitrogen-containing compounds of the above formulae in which r is 1 or more, i.e. those containing an ether or polyether linkage, can be prepared by reaction of a suitable amine, morpholine or piperazine compound with a molar excess of one or more alkylene oxides. When the same kind of alkylene oxide is used R^2 and R^3 contain the same alkylene moiety. When different kinds of alkylene oxides are used R^2 and R^3 may contain the same or different alkylene groups.

[0020] In the formulae for the alkanolamine compound p is 2 to 10, preferably 2 or 3, q is 0 to 10, preferably 0 to 5 and r is 0 to 15, preferably 0 to 10. When R^1 is alkyl the moiety contains from 1 to 6 carbon atoms, preferably 2 to 4 carbon atoms. R^2 is an alkylene group having 2 to 6 carbon atoms, preferably 2 to 4 carbon atoms. R^3 is an hydroxyalkyl group having 2 to 6 carbon atoms, preferably 2 to 4 carbon atoms. The hydroxyalkyl group typically contains 1 to 3 hydroxy groups. When r is greater than zero R^3 is typically a mono-hydroxyalkyl group, for example hydroxyethyl or hydroxypropyl. When r is zero R^3 is typically a mono- or poly-hydroxyalkyl group having up to 4 hydroxyl groups, for example hydroxyethyl, hydroxypropyl or a 1-hydroxy-2,2-bis(hydroxymethyl)ethyl group. The values p, q and r take are selected independently. This means for example that when q is greater than zero, p may take different values in each repeat unit. Also, when r is greater than zero, R^2 may be the same or different in each ether repeat unit.

[0021] Each of the acid derivatives described are commercially available or may be made by the application or adaptation of known techniques. When used in the form of a derivative it is preferred that the derivative is one derived from ricinoleic acid.

[0022] According to one aspect of the present invention, the lubricity enhancing additive compound is a derivative of the hydroxy-substituted acid and contains at least one free carboxylic group in the acid-derived moiety. This kind of compound may be formed using as the starting hydroxy-substituted acid a polycarboxylic acid, for example a dicarboxylic acid or a dimer or trimer acid. Suitably, the number of moles of the acid and compound used to form the acid derivative which are reacted is controlled such that the resulting compound contains at least one free carboxylic functional group in the acid-derived moiety. For example, if an acid having two carboxylic functions is used, such as a dicarboxylic or dimer acid, the mole ratio should be about 1:1.

[0023] In the case that the acid derivative contains at least one free carboxylic group in the acid moiety, it may be used as is or it may be derivatised further to enhance its properties. The kind of compound used to do this usually depends upon the kind of acid used initially and the properties of the acid derivative it is desired to influence. For example, it is possible to increase the fuel solubility of the acid derivative by introducing into its molecule a fuel-solubilizing species. As an example of such, long-chain alkyl or alkenyl may be mentioned. To this end the acid derivative may be reacted with an alcohol, ROH or an amine, RNH₂ in which R is alkyl or alkenyl having up to 30 carbon atoms, for example 4 to 30 carbon atoms. The number of carbon atoms in the alkyl or alkenyl group may depend upon the number of carbon atoms in the acid derivative itself. These compounds react with the free carboxylic functional group(s) of the acid derivative to form a further ester linkage or an amide linkage. Examples of particular alcohols and amides which may be used include oleyl amine and oleyl alcohols. Alternatively, it is possible to further react the acid derivative to introduce into its molecule one or more polar head groups. This has the result of increasing the lubricity enhancing effect which the acid derivative exhibits. This is believed to be due to the polar head group increasing the affinity of the acid derivative to metal surfaces. Examples of compounds which may be used to introduce one or more polar head groups include polyamines (e.g. ethylene diamine and diethylene triamine), and alkanolamines and polyhydric alcohols such as those described above.

[0024] Typically, unless the fatty acid derivative is one derived from a dimer or trimer acid, the derivative is further reacted to introduce fuel-solubilising species. Dimer and trimer acid derivatives tend already to contain in the acid backbone long chain alkyl-or alkenyl moieties sufficient to provide adequate fuel-solubility.

[0025] While it has been described above that it is the acid derivative which is reacted further, it is quite possible that the same final species can be formed by first reacting free carboxylic functional group(s) of a polycarboxylic acid to introduce fuel-solubilising or polar head groups and then reacting the resultant product to form the acid derivative. Of course, this assumes that the product formed after the initial reaction contains at least one free carboxylic group in the acid-derived moiety such that acid derivative formation is still possible.

[0026] Typically, the concentration of the lubricity enhancing additive in the fuel falls in the range 10 to 1000 ppm, preferably 50 to 500 ppm, more preferably still from 100 to 400 ppm. When mixtures of additives are used the overall additive concentration falls within the typical range quoted. The present invention further provides a diesel fuel, jet fuel, or bio-diesel fuel having a sulfur content of 0.2% by weight or less, comprising a lubricity enhancing additive as herein-before described. Such fuel can be formulated by simple mixing of the base fuel and the additive in the desired proportions. The base fuel may be a middle distillate fuel or a bio-diesel fuel as described above. For the sake of convenience, the additive may be provided as a concentrate for dilution with fuel. Such a concentrate typically comprises from 99 to 1% by weight additive and from 1 to 99% by weight of solvent or diluent for the additive which solvent or diluent is miscible and/or capable of dissolving in the fuel in which the concentrate is to be used. The solvent or diluent may, of course, be the low sulfur fuel itself. However, examples of other solvents or diluents include white spirit, kerosene, alcohols (e.g. 2-ethyl hexanol, isopropanol and isodecanol), high boiling point aromatic solvents (e.g. toluene and xylene) and cetane improvers (e.g. 2-ethyl hexylnitrate). Of course, these may be used alone or as mixtures.

[0027] The concentrate or fuel may also contain other fuel additives in the appropriate proportions thereby providing a multifunctional fuel additive package. Examples of conventional fuel additives which may be used include fuel stabilisers, dispersants, detergents, antifoams, cold flow improvers, cetane number improvers, antioxidants, corrosion inhibitors, antistatic additives, biocides, dyes, smoke reducers, catalyst life enhancers and demulsifiers. The total treat rate for multifunctional formulations containing the lubricity enhancing additive compounds described is typically 200 to 2000 ppm, more usually 300 to 1200 ppm.

[0028] The invention also provides a method of reducing fuel pump wear in an engine which operates on a fuel having a sulfur content of 0.2 % by weight or less, which comprises using a fuel described herein. The fuel may be used to reduce wear in rotary and in-line fuel pumps, for example as found in diesel engines, or in fuel transfer pumps. The latter are positioned between the fuel tank and the high pressure pump. The fuel is particularly well suited for reducing wear in fuel injector pumps. The fuel may also be used in the latest unit injectors which combine pump and injector mechanisms. The invention is particularly well-suited to the operation of diesel and jet engines.

[0029] The present invention is illustrated in the following Example.

Example

[0030] The efficacy of a number of diesel fuels was assessed using the Scuffing BOCLE (ball-on-cylinder lubricity evaluator) test. This test is a modification of the standard aviation BOCLE test (ASTM method D5001: "Standard Test Method for Measurement of Lubricity of Aviation Turbine Fuels by the Ball-on-Cylinder Lubricity Evaluator (BOCLE)", ASTM Standards, Section 5, Vol 3, 1993) in which a load of 1 kg is applied to a fixed ball in contact with a rotating cylinder lubricated by the test fuel. In this standard test fuel lubricity is assessed by measuring the size of the wear scar on the fixed ball resulting from the constant load contact with the cylinder. However, the standard BOCLE test suffers the disadvantage that the applied load is not high enough to model the type of severe wear failure that occurs in the field, for example in fuel injector pumps.

[0031] The Scuffing BOCLE test offers the advantage over the standard test of allowing discrimination and ranking of fuels of differing lubricity. The Scuffing test also simulates more closely the severe modes of wear failure encountered in fuel pumps than other fuel lubricity tests which run under mild wear conditions. The Scuffing BOCLE test therefore provides results which are more representative of how the fuel would behave in service.

[0032] In the Scuffing BOCLE test a load (0.25-8.0 kg) is applied to a fixed ball in contact with a rotating cylinder. The ball and cylinder are made of a standard grade steel. The cylinder rotates at 290 rpm. Since the temperature of the lubricating fuel can have a marked effect on the scuffing load, this is carefully controlled at 25°C. A nitrogen atmosphere is used to blanket the ball on cylinder assembly. Following a one minute run-in period the load is applied to the ball for two minutes. After this run, the ball is removed from the assembly and the type and size of wear scar examined by microscope. Further runs are then carried using increased applied loads in a stepwise manner until scuffing wear failure occurs. The load at which wear failure occurs is referred to as the scuffing load and is a measure of the inherent lubricity of the fuel. The scuffing load is primarily identified by the size and appearance of the wear scar on the ball, which is considerably different in appearance to that found under milder non-scuffing conditions. Fuels giving a high scuffing load on failure have better lubricating properties than fuels giving a low scuffing load on failure.

[0033] The base fuel used was a Class 2 Scandinavian diesel fuel. This is a diesel fuel having a sulfur content of 0.005% by weight. The composition and distillation profile of this fuel are shown below.

Density at 15°C (IP.160), g/ml	0.8160
Paraffins, %vol	89.6
Olefins, %vol	0.7
Aromatics, %vol	9.7
Distillation Characteristics (IP 123)	
Initial B.P., °C	184
5%	200
10%	204
20%	212
30%	217
40%	223
50%	228
60%	235
70%	243
80%	251
90%	263
95%	269
Final B.P., °C	290
Recovered, %	99
Residue, %	1
Loss, %	0

[0034] The table below shows the Scuffing BOCLE test results for a number of diesel fuels. Samples C, E-G, I and K-N are fuels in accordance with the present invention. Samples A, B, D, H and J are included for comparison.

Additive	Concentration (ppm)	Scuffing load (kg)
A. None	-	2.7
B. Oleic acid	200	3.1
C. Ricinoleic acid	200	4.2
D. Glycerol monooleate	200	3.4
E. Glycerol monoricinoleate	100	3.8
F. Glycerol monoricinoleate	200	4.1
G. Glycerol monoricinoleate	400	5.0
H. Amide: Oleic acid + DETA	200	3.1
I. Amide: Ricinoleic acid + DETA	200	4.6
J. Amide: Oleic acid + DETA.2PO	200	2.8
K. Amide: Ricinoleic acid + DETA.2PO	200	4.0
L. Amide: Ricinoleic acid + DEA	200	4.2
M. Amide: Ricinoleic acid + TETA	200	4.7
N. Amide: Ricinoleic acid + THAM	200	4.4

[0035] In the table above:

DEA stands for diethanolamine;

THAM stands for tris(hydroxymethyl)aminomethane;

DETA stands for diethylene triamine;

DETA.2PO indicates that the DETA is N-substituted by two hydroxypropyl groups; and

TETA stands for triethylene tetramine.

[0036] In runs D-N the mole ratio of fatty acid: derivatising species was in each case 1:1.

[0037] These results clearly demonstrate the improvement in lubricity of diesel fuels in accordance with the present invention. The base fuel used has a very low inherent lubricity giving a low scuffing load result of 2.7kg. The addition of 200 ppm of oleic acid, i.e. a C₁₈ unsubstituted fatty acid, leads to a slight improvement in lubricity performance exhibited as a higher scuffing load on failure of 3.1kg. Formulations of base fuel and the corresponding hydroxy-substituted C₁₈ acid (ricinoleic acid) leads to significantly improved scuffing performance of 4.2kg (run C). The free hydroxyl group in the 12-position of the ricinoleic acid tail is believed to be responsible for this. Good results are also obtained for the fuels of runs L, M and N which are in accordance with the present invention.

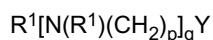
Claims

1. Use of a carboxylic acid having from 10 to 60 carbon atoms and being substituted by at least one hydroxy group, or a derivative of this hydroxy-substituted acid, as an additive for improving the lubricity of a fuel having a sulfur content of 0.2% by weight or less, wherein said fuel is a diesel fuel, jet fuel or bio-diesel fuel.
2. Use according to claim 1, wherein the acid is an aliphatic fatty acid substituted by up to 4 hydroxyl groups.
3. Use according to claim 2, wherein the fatty acid is ricinoleic acid.
4. Use according to claim 1, wherein the acid is a hydroxy-substituted dimer acid of oleic and linoleic acids.
5. Use according to any one of claims 1 to 4, wherein the acid derivative is an ester of a polyhydric alcohol selected from ethylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, glycerol, arabitol, sorbitol, mannitol,

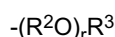
pentaerythritol, sorbitan, 1,2-butanediol, 2,3-hexanediol, 2,4-hexanediol, pinacol and 1,2-cyclohexanediol.

6. Use according to claim 5, wherein the polyhydric alcohol ester is glycerol monoricinoleate.

5 7. Use according to any one of claims 1 to 4, wherein the derivative is an ester of an alkanolamine of formula:



10 in which p is 2 to 10, q is 0 to 10, Y is -N(R¹)₂, 4-morpholinyl or 1-piperazinyl N-substituted by a group R¹ or a group -[(CH₂)_pN(R¹)]_qR¹ in which p and q are as defined above and each substituent R¹ is independently selected from alkyl groups having from 1 to 6 carbon atoms and a group of formula:

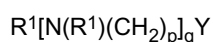


15 in which r is 0 to 10, R² is an alkylene group having 2 to 6 carbon atoms and R³ is a hydroxyalkyl group having 2 to 6 carbon atoms, provided at least one group R¹ is -(R¹O)_rR³.

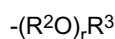
8. Use according to claim 7, wherein the alkanolamine is triethanolamine, triisopropanolamine or ethylene diamine or diethylene triamine in which each nitrogen atom is substituted by hydroxyethyl or hydroxypropyl groups.

20 9. Use according to claim 7, wherein the alkanolamine is (aminoethyl)piperazine, bis-(aminoethyl)piperazine or morpholine, each of which is N-substituted by a hydroxypropyl group.

25 10. Use according to any one of claims 1 to 4, wherein the acid derivative is an amide formed by reaction of the hydroxy-substituted carboxylic acid with ammonia or a nitrogen-containing compound of formula:



30 in which p is 2 to 10, q is 0 to 10, Y is -N(R¹)₂, 4-morpholinyl or 1-piperazinyl optionally N-substituted by a group R¹ or a group -[(CH₂)_pN(R¹)]_qR¹ in which p and q are as defined above and each substituent R¹ is independently selected from hydrogen and alkyl groups having 1 to 6 carbon atoms and a group of formula:



35 in which r is 0 to 10, R² is an alkylene group having 2 to 6 carbon atoms and R³ is a hydroxyalkyl group having 2 to 6 carbon atoms, provided that at least one group R¹ is hydrogen.

40 11. Use according to claim 10, wherein the nitrogen-containing compound is diethanolamine, tris(hydroxymethyl)aminomethane, triethylene tetramine or diethylene triamine optionally N-substituted by two hydroxypropyl groups.

12. Use according to claim 10, wherein the nitrogen-containing compound is aminoethylpiperazine, bis-(aminoethyl)piperazine or morpholine.

45 13. Use according to any one of claims 1 to 12, wherein the acid derivative contains at least one free carboxyl group in the acid-derived moiety.

14. Use according to claim 13, wherein the acid derivative is further derivatised by reaction with a compound which introduces a fuel-solubilising species into the acid derivative molecule or by reaction with a compound which introduces a polar head group into the acid derivative molecule.

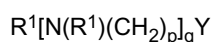
50 15. Use according to any one of claims 1 to 14, wherein the hydroxy-substituted carboxylic acid or derivative of the acid is present in the fuel at a concentration of from 10 to 1000 ppm.

55 16. A diesel fuel, jet fuel or bio-diesel fuel having a sulfur content of 0.2% by weight or less, comprising a hydroxy-substituted acid or derivative of the acid as defined in any one of claims 1 to 14.

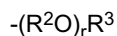
17. A method of reducing fuel pump wear in an engine which operates on a fuel having a sulfur content of 0.2% by weight or less, which comprises using a fuel as defined in claim 16.

Patentansprüche

1. Verwendung einer Carbonsäure mit 10 bis 60 Kohlenstoffatomen, die mit wenigstens einer Hydroxylgruppe substituiert ist, oder eines Derivates einer solchen hydroxylsubstituierten Säure als ein Additiv zur Verbesserung der Schmierfähigkeit eines Treibstoffs mit einem Schwefelgehalt von 0,2 Gew.-% oder weniger, wobei der Treibstoff ein Dieseltreibstoff, Kerosin oder Biodiesel-Treibstoff ist.
2. Verwendung nach Anspruch 1, wobei die Säure eine aliphatische Fettsäure ist, die mit bis zu vier Hydroxylgruppen substituiert ist.
3. Verwendung nach Anspruch 2, wobei die Fettsäure Retinolsäure ist.
4. Verwendung nach Anspruch 1, wobei die Säure eine hydroxylsubstituierte dimere Säure von Ölsäure und Linolsäure ist.
5. Verwendung nach einem der Ansprüche 1 bis 4, wobei das Säurederivat ein Ester eines mehrwertigen Alkohols, ausgewählt aus Ethylenglycol, Diethylenglycol, Triethylenglycol, Dipropylenglycol, Glycerin, Arabitol, Sorbitol, Mannitol, Pentaerythrit, Sorbitan, 1,2-Butandiol, 2,3-Hexandiol, 2,4-Hexandiol, Pinacol und 1,2-Cyclohexandiol ist.
6. Verwendung gemäß Anspruch 5, wobei der mehrwertige Alkoholester ein Glycerinmonorecinolsäureester ist.
7. Verwendung nach einem der Ansprüche 1 bis 4 wobei das Derivat ein Ester eines Alkanolamins der Formel:

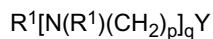


ist, indem p eine Zahl von 2 bis 10, q eine Zahl von 0 bis 10 ist, Y -N(R¹)₂, 4-Morpholinyl oder 1-Piperazinyl N-substituiert mit einer Gruppe R¹ oder einer Gruppe -[(CH₂)_pN(R¹)]_qR¹ wobei p und q wie oben definiert sind und jeder Substituent R¹ unabhängig voneinander ausgewählt ist aus Alkylgruppen, die 1 bis 6 Kohlenstoffatome aufweisen und eine Gruppe der Formel:

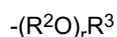


wobei r eine Zahl von 0 bis 10 ist, R² eine Alkylengruppe mit 2 bis 6 Kohlenstoffatomen und R³ eine Hydroxyalkylgruppe mit 2 bis 6 Kohlenstoffatomen ist, vorausgesetzt dass wenigstens eine Gruppe R¹ ist -(R²O)_rR³.

8. Verwendung nach Anspruch 7, wobei das Alkanolamin Triethanolamin, Triisopropanolamin oder Ethylendiamin oder Diethylentriamin ist, in dem jedes Stickstoffatom mit Hydroxyethyl- oder Hydroxypropylgruppen substituiert ist.
9. Verwendung nach Anspruch 7, wobei das Alkanolamin (Aminoethyl)piperazin, Bis-(aminoethyl)piperazin oder Morpholin ist, jeweils mit einer Hydroxypropylgruppe N-substituiert.
10. Verwendung nach einem der Ansprüche 1 bis 4, wobei das Säurederivat ein Amid ist, das durch die Reaktion einer hydroxylsubstituierten Carbonsäure mit Ammoniak oder einer stickstoffhaltigen Verbindung der folgenden Formel gebildet ist:



wobei p eine Zahl von 2 bis 10 ist; q eine Zahl von 0 bis 10 ist, Y ist -N(R¹)₂, 4-Morpholinyl oder 1-Piperazinyl, gegebenenfalls N-substituiert durch eine R¹-Gruppe oder eine -[(CH₂)_pN(R¹)]_qR¹-Gruppe, wobei p und q wie oben definiert sind und jeder Substituent R¹ unabhängig voneinander ausgewählt ist aus Wasserstoff und Alkylgruppen mit 1 bis 6 Kohlenstoffatomen und einer Gruppe der Formel:



Wobei r eine Zahl ist von 0 bis 10, R² eine Alkylengruppe mit 2 bis 6 Kohlenstoffatomen und R³ eine Hydroxyalkylgruppe mit 2 bis 6 Kohlenstoffatomen ist, vorausgesetzt dass wenigstens eine Gruppe R¹ Wasserstoff ist.

11. Verwendung nach Anspruch 10, wobei die stickstoffhaltige Verbindung Diethanolamin, Tris(hydroxymethyl)amino-

methan, triethylentetramin oder diethylentriamin ist, gegebenenfalls N-substituiert durch zwei Hydroxypropylgruppen.

12. Verwendung nach Anspruch 10, wobei die stickstoffhaltige Verbindung Aminoethylpiperazin, Bis-(aminoethyl)piperazin oder Morphinol ist.

13. Verwendung nach einem der Ansprüche 1 bis 12, wobei das Säurederivat wenigstens eine freie Carboxylgruppe im von der Säure abgeleiteten Bestandteil enthält.

14. Verwendung nach Anspruch 13, wobei das Säurederivat weiter derivatisiert ist durch Reaktion mit einer Verbindung, die eine Treibstoff-solubilisierende Spezies in das Molekül des Säurederivats einführt oder durch eine Reaktion mit einer Verbindung, die eine polare Kopfgruppe in das Säurederivatmolekül einführt.

15. Verwendung nach einem der Ansprüche 1 bis 14, wobei die hydroxysubstituierte Carbonsäure oder das Derivat der Säure im Treibstoff in einer Konzentration von 10 bis 1.000 ppm vorliegt.

16. Ein Dieseltreibstoff, Kerosin oder Biodieseltreibstoff mit einem Schwefelgehalt von 0,2 Gew.-% oder weniger, der eine hydroxysubstituierte Säure oder ein Derivat einer Säure enthält wie in einem der Ansprüche 1 bis 14 definiert.

17. Verfahren zur Verringerung des Verschleißes einer Treibstoffpumpe in einem Triebwerk, das mit einem Treibstoff arbeitet, der einen Schwefelgehalt von 0,2 Gew.-% oder weniger aufweist, wobei das Verfahren beinhaltet, dass ein Treibstoff wie in Anspruch 16 definiert verwendet wird.

Revendications

1. Utilisation d'un acide carboxylique ayant 10 à 60 atomes de carbone et qui est substitué avec au moins un groupe hydroxy, ou d'un dérivé de cet acide à substituant hydroxy, comme additif pour améliorer le pouvoir lubrifiant d'un carburant ayant une teneur en soufre égale ou inférieure à 0,2 % en poids, dans laquelle ledit carburant est un carburant Diesel, un carburéacteur ou un carburant biodiesel.

2. Utilisation suivant la revendication 1, dans laquelle l'acide est un acide gras aliphatique substitué avec jusqu'à 4 groupes hydroxyle.

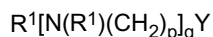
3. Utilisation suivant la revendication 2, dans laquelle l'acide gras est l'acide ricinoléique.

4. Utilisation suivant la revendication 1, dans laquelle l'acide est un acide dimère, à substituant hydroxy, d'acides oléique et linoléique.

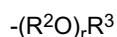
5. Utilisation suivant l'une quelconque des revendications 1 à 4, dans laquelle le dérivé d'acide est un ester d'un alcool polyhydroxylique choisi entre l'éthylèneglycol, le diéthylèneglycol, le triéthylèneglycol, le dipropylèneglycol, le glycérol, l'arabitol, le sorbitol, le mannitol, le pentaérythritol, le sorbitanne, le 1,2-butanediol, le 2,3-hexanediol, le 2,4-hexanediol, le pinacol et le 1,2-cyclohexanediol.

6. Utilisation suivant la revendication 5, dans laquelle l'ester d'alcool polyhydroxylique est le monoricinoléate de glycérol.

7. Utilisation suivant l'une quelconque des revendications 1 à 4, dans laquelle le dérivé est un ester d'une alcanolamine de formule :

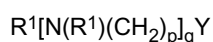


dans laquelle p a une valeur de 2 à 10, q a une valeur de 0 à 10, Y représente un groupe $-N(R^1)_2$, 4-morpholinyle ou 1-pipérazinyle N-substitué avec un groupe R^1 ou un groupe $-[CH_2]_pN(R^1)_qR^1$ dans lequel p et q répondent aux définitions précitées et chaque substituant R^1 est choisi indépendamment entre des groupes alkyle ayant 1 à 6 atomes de carbone et un groupe de formule :

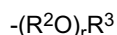


dans laquelle r a une valeur de 0 à 10, R² représente un groupe alkylène ayant 2 à 6 atomes de carbone et R³ représente un groupe hydroxyalkyle ayant 2 à 6 atomes de carbone, sous réserve qu'au moins un groupe R¹ soit un groupe - (R²O)_rR³.

8. Utilisation suivant la revendication 7, dans laquelle l'alcanolamine est la triéthanolamine, la triisopropanolamine ou l'éthylènediamine ou la diéthylènetriamine dans laquelle chaque atome d'azote est substitué avec des groupes hydroxyéthyle ou hydroxypropyle.
9. Utilisation suivant la revendication 7, dans laquelle l'alcanolamine est la (aminoéthyl)pipérazine, la bis-(aminoéthyl)pipérazine ou la morpholine, chacune étant N-substituée avec un groupe hydroxypropyle.
10. Utilisation suivant l'une quelconque des revendications 1 à 4, dans laquelle le dérivé d'acide est un amide formé par réaction d'un acide carboxylique à substituant hydroxy avec l'ammoniac ou un composé contenant de l'azote de formule :



dans laquelle p a une valeur de 2 à 10 ; q a une valeur de 0 à 10, Y représente un groupe -N(R¹)₂, 4-morpholinyne ou 1-pipérazinyne facultativement N-substitué avec un groupe R¹ ou un groupe -[(CH₂)_pN(R¹)_qR¹] dans lequel p et q répondent aux définitions précitées et chaque substituant est choisi indépendamment entre un atome d'hydrogène et des groupes alkyle ayant 1 à 6 atomes de carbone et un groupe de formule :



- dans laquelle r a une valeur de 0 à 10, R² représente un groupe alkylène ayant 2 à 6 atomes de carbone et R³ représente un groupe hydroxyalkyle ayant 2 à 6 atomes de carbone, sous réserve qu'au moins un groupe R¹ représente un atome d'hydrogène.
11. Utilisation suivant la revendication 10, dans laquelle le composé contenant de l'azote est la diéthanolamine, le tris(hydroxyméthyl)aminométhane, la triéthylènetétramine ou la diéthylènetriamine facultativement N-substituée avec deux groupes hydroxypropyle.
12. Utilisation suivant la revendication 10, dans laquelle le composé contenant de l'azote est l'aminoéthylpipérazine, la bis-(aminoéthyl)pipérazine ou la morpholine.
13. Utilisation suivant l'une quelconque des revendications 1 à 12, dans laquelle le dérivé d'acide contient au moins un groupe carboxyle libre dans le groupement dérivé d'un acide.
14. Utilisation suivant la revendication 13, dans laquelle le dérivé d'acide est en outre transformé en dérivé par réaction avec un composé qui introduit une entité de solubilisation dans les carburants dans la molécule du dérivé d'acide ou par réaction avec un composé qui introduit un groupe de tête polaire dans la molécule du dérivé d'acide.
15. Utilisation suivant l'une quelconque des revendications 1 à 14, dans laquelle l'acide carboxylique à substituant hydroxy ou le dérivé de l'acide est présent dans le carburant à une concentration de 10 à 1000 ppm.
16. Carburant Diesel, carburéacteur ou carburant biodiesel ayant une teneur en soufre égale ou inférieure à 0,2 % en poids, comprenant un acide à substituant hydroxy ou dérivé de l'acide tel que défini dans l'une quelconque des revendications 1 à 14.
17. Procédé pour réduire l'usure des pompes à carburant dans un moteur qui fonctionne avec un carburant ayant une teneur en soufre égale ou inférieure à 0,2 % en poids, qui comprend l'utilisation d'un carburant tel que défini dans la revendication 16.