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(71) Applicant: **ETHYL PETROLEUM ADDITIVES
LIMITED
Bracknell, Berkshire RG12 2UW (GB)**

(72) Inventor: **Jeffrey, Gareth Charles
Bracknell, Berkshire RG12 4DY (GB)**

(74) Representative: **Smaggasgale, Gillian Helen et al
Mathys & Squire,
100 Gray's Inn Road
London WC1X 8AL (GB)**

(54) The use of lubricity additives for reducing foam in fuels

(57) The present invention relates to fuel additives for improving the foam behavior of fuel compositions containing said additives. The objective of the invention is obtained by the addition of a lubricity additive to fuel

additive compositions containing colloiddally dispersed metals and conventional antifoam agents. The present invention further relates to fuel concentrates and fuel compositions containing the fuel additive.

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Description**BACKGROUND OF THE INVENTION**

5 Foam control is a highly important consideration in the preparation of additive compositions for use in fuels of the middle distillate boiling range, such as gas oils, diesel fuels, gas turbine fuels, burner fuels and the like. If a fuel foams during transfer from one tank to another, it becomes difficult to control flow rates and volumes. Similarly, foaming during the filling of fuel tanks can pose various other problems, such as delivery of inadequate amounts of fuel to the tanks or conversely, overflowing and spillage of fuel at the filling site.

10 To overcome these foaming problems, a variety of foam inhibitors such as polyacrylates and polysiloxanes have been proposed for use in diesel fuels and additive packages to be used in formulating finished diesel fuels.

When producing certain additive concentrates for use in improving the performance characteristics of middle distillate fuels it has been found necessary to include a fairly high amount of the foam inhibitor in the concentrates to ensure that the finished fuel will have a sufficient level of antifoam additive to effectively suppress or inhibit foam formation in the fuel during operations such as referred to above. In general, amounts of antifoam additive of at least 0.5% by weight in the additive concentrate are required. Indeed, amounts as high as 10% by weight or more of foam inhibitor in the concentrate may be required for effective utilization of some additive concentrates.

It has been discovered that when the additive concentrate contains both a high level of a silicone antifoam agent and an overbased detergent, a serious problem of incompatibility can arise. This problem is manifested in many ways. For one thing, insoluble sediments or particulate matter can be generated in the additive concentrate, especially during storage. Moreover, experimental results indicate that even if the interaction between the overbased detergent and the silicone antifoam agent does not result in visually perceptible amounts of solids, nevertheless this incompatibility can cause a significant loss of antifoam performance in the resultant finished fuel. Concurrent manifestation of both such adverse consequences is also possible. This incompatibility does not always occur in compositions containing an antifoam and an overbased detergent. Products, such as HiTEC® 4043L fuel additive commercially available from Ethyl Corporation, containing a polyether polysiloxane antifoam which is soluble in water at 25°C, such as TEGO-PREN® 5851 silicone surfactant commercially available from T.H. Goldschmidt AG, and an overbased calcium sulfonate detergent do not exhibit the above described incompatibility and are thus not within the purview of this invention.

A need has thus arisen for a way of effectively overcoming this problem of additive incompatibility as between overbased metal detergents and siloxane foam inhibitors especially when the latter are used at relatively high concentrations in additive packages and in resultant fuel compositions.

It has now been found that the addition of a lubricity additive can substantially improve the foam behavior of fuels containing colloiddally dispersed metal containing materials, such as overbased metal detergents or metal based emissions improving additives, in the presence of a wide range of antifoam agents.

SUMMARY OF THE INVENTION

According to the present invention there is provided a fuel additive composition which comprises as components thereof (i) a lubricity additive, (ii) at least one overbased metal detergent, and (iii) a foam inhibitor which is substantially insoluble in water at 25°C.

In one embodiment of the present invention there is provided a fuel additive composition as above which further comprises (iv) a dispersant and/or (v) a metal based emissions improving additive, the weight ratio of (iv) to (iii) on an active ingredient basis is normally in the range of about 0.25 to about 300 parts by weight of (iv) per part by weight of (iii).

Other components which may be, and preferably are, included in any of the foregoing concentrates include a liquid hydrocarbon diluent (especially a liquid highly aromatic hydrocarbon diluent) or a liquid alcohol diluent or a demulsifying agent or a corrosion inhibitor, or any mixture of any two or more of the foregoing.

Still other embodiments include liquid fuel compositions, such as fuels boiling in the middle distillate boiling range, containing the components in accordance with any of the foregoing additive concentrates.

In a further embodiment of the present invention there is provided a method of reducing foam in fuel compositions containing an overbased metal detergent and a silicone antifoam agent which is substantially insoluble in water at 25°C, wherein a lubricity additive is combined with said fuel compositions.

The above and other embodiments and advantages of this invention will become still further apparent from the ensuing description and appended claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

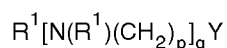
Component (i)

The lubricity additives of the present invention are preferably carboxylic acids, optionally substituted with at least one hydroxy group, or derivatives thereof. The preferred carboxylic acid derivatives are carboxylic acid amides and carboxylic acid esters.

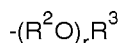
The hydroxy-substituted carboxylic acid or acid derivative may be used alone or in combination with any other hydroxy-substituted acid and/or acid derivative. The hydroxy-substituted acid used in the present invention typically contains up to 60 carbon atoms. The hydroxy-substituted acid may be a mono- 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 ricinoleic, malic, tartaric and citric acids. 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 one 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 adaptation of known techniques.

As described above, the lubricity 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.

Another carboxylic 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.

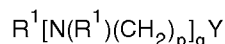
According to a preferred embodiment, in the alkanolamine of the above formula Y is $-N(R^1)_2$, p is 2 and q is 0 to 3. It is further preferred that each R^1 is a C_{2-4} hydroxyalkyl group, C_2 or C_3 hydroxyalkyl being particularly preferred. Specific examples of such compounds include triethanolamine,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

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.

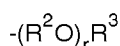
The alkanolamines are commercially available or may be made by the application or adaptation of known tech-

niques.

It is also possible to use as the carboxylic acid derivative, an amide such as that formed by reaction of a hydroxy substituted carboxylic 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 $-[(CH_2)_pN(R^1)]_qR^1$ 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 15, 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.

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.

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.

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

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.

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.

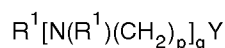
The preferred carboxylic acid amides are oleyl ethanolamide and oleyl diethanolamide.

The acid used in the present invention which does not contain any hydroxy-substitution in the acid backbone typically contains up to 60 carbon atoms. The acid may be a mono- or poly-carboxylic acid or a dimerized acid. When 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. Examples of such include aliphatic fatty acids such as lauric, myristic, heptadecanoic, palmitic, stearic, oleic, linoleic, linolenic, nonadecanoic, arachic or behenic acid. Of these the use of oleic acid, linoleic acid or mixtures of these is preferred. When 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 poly-carboxylic acid include dicarboxylic acids such as succinic, glutaric, adipic, suberic, azelaic or sebacic acid, and tricarboxylic acids such as 1,3,5-cyclohexane tricarboxylic acid and tetracarboxylic acids such as 1,2,3,4-butane tetracarboxylic acid.

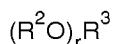
It is also possible to use as the acid containing no hydroxy substitution in the backbone, dimerized acids. Herein such compounds are referred to as dimer and trimer acids. When used the dimerized acid typically contains 10 to 60, preferably 20 to 60 and most preferably 30 to 60, carbon atoms. Such acids are prepared by dimerizing unsaturated acids and typically consist of a mixture of monomer, dimer and trimer acid. According to a preferred embodiment of the invention the acid is a 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 adaptation of known techniques.

The carboxylic acids containing no hydroxy substitution can be derivatized by reaction with an alkanolamine. The

alkanolamine is typically of formula:



in which p is 2 to 10, preferably 2 or 3, q is 0 to 10, preferably 0 to 5, 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, preferably 2 to 4 carbon atoms, and a group of formula:



in which r is 0 to 15, preferably 0 to 10, R^2 is an alkylene group having from 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, and provided at least one group R^1 is $(R^2O)_rR^3$. 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 hydroxy 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 other repeat unit. Thus, the alkanolamine is one which does not contain any hydrogen-bearing nitrogen atoms. The presence of such free hydrogen atoms on the nitrogen would be expected to lead to the formation of an amide on reaction with the fatty acid.

The alkanolamines which may be used to form the ester are commercially available or may be made by the application or adaptation of known techniques. For example, the alkanolamines 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 oxide are used R^2 and R^3 may contain the same or different alkylene groups.

According to a preferred embodiment, alkanolamines of the above formula are used in which Y is $-N(R^1)_2$, p is 2 and q is 0 to 3. Preferably the alkanolamine is triethanolamine or triisopropylamine or ethylene diamine or diethylene triamine in which each nitrogen atom is substituted by hydroxyethyl or hydroxypropyl groups.

According to an alternative preferred embodiment, in the formula shown above, Y is 4-morpholinyl or substituted 1-piperazinyl, p is 2 to 6 and q is 0 or 1. Examples of such alkanolamines include aminoethylpiperazine, bis-(aminoethyl) piperazine or morpholine, N-substituted by an hydroxypropyl group.

The esters described may be made by the application or adaptation of known techniques, or are commercially available ready for use.

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.

According to another aspect of the present invention, the ester contains at least one free carboxylic group in the acid-derived moiety and no hydroxy substitution in the acid backbone. This kind of compound may be formed using as the starting acid a polycarboxylic acid, for example a dicarboxylic acid or a dimer or trimer acid. Suitably, the number of moles of acid and alkanolamine which are reacted is controlled such that the resulting ester contains at least one free carboxylic functional group in the acid derived-moiety. For example, if an acid having two carboxyl functions is used, such as a dicarboxylic or dimer acid, the mole ratio could be about 1:1.

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, RNH_2 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 alcohols and oleyl amine. 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), monohydric alcohols (e.g., ethanol and propanol) and alkanolamines and polyhydric alcohols such as those described above.

Typically, unless the carboxylic 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.

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.

Component (ii)

The metal containing detergents are exemplified by oil-soluble overbased salts of alkali or alkaline earth metals with one or more of the following acidic substances (or mixtures thereof): (1) sulfonic acids, (2) carboxylic acids, (3) alkylphenols, (4) sulfurized alkylphenols, and (5) organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage. Such organic phosphorus acids include those prepared by the treatment of an olefin polymer (e.g., polyisobutylene) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of the above acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium.

The metal additives are preferably oil-soluble overbased salts of alkali or alkaline earth metals. The overbased salts are preferred as a means to add metals in a concentrated, hence cost effective, form but the metals need not be added in this form. The term "overbased" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. This includes low base detergents (i.e., those having a TBN of about 6 to 40), as well as high base (i.e., those having a TBN of about 250 to 500) materials. The commonly employed methods for preparing the overbased salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such metal oxide, hydroxide, carbonate, bicarbonate, or sulfide, carbonating the mixture in the presence of a promoter, and filtering the resulting mass. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthol, alkylphenol, thiophenol, sulfurized alkylphenol, and condensation products of formaldehyde with a phenolic substance; alcohols such as methanol, 2-propanol, octyl alcohol, cellosolve, carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; amines such as aniline, phenylenediamine, phenothiazine, phenyl- β -naphthylamine, and dodecylamine. A particularly effective method for preparing the overbased salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one suitable promoter, and carbonating the mixture at an elevated temperature such as 60°-200°C.

Examples of overbased sulfonates include overbased lithium sulfonates, sodium sulfonates, potassium sulfonates, calcium sulfonates, and magnesium sulfonates wherein each sulfonate moiety is attached to an aromatic nucleus which in turn usually contains one or more aliphatic substituents to impart hydrocarbon solubility.

The metal carboxylates may be derived from any organic carboxylic acid. The metal carboxylates are preferably those of a monocarboxylic acid such as that having from about 4 to 30 carbon atoms. Such acids can be hydrocarbon aliphatic, alicyclic, or aromatic carboxylic acids. Monocarboxylic acids such as those of aliphatic acids having about 4 to 18 carbon atoms are preferred, particularly those having an alkyl group of about 6 to 18 carbon atoms. The alicyclic acids may generally contain from 4 to 12 carbon atoms. The aromatic acids may generally contain one or two fused rings and contain from 7 to 14 carbon atoms wherein the carboxyl group may or may not be attached to the ring. The carboxylic acid can be a saturated or unsaturated fatty acid having from about 4 to 18 carbon atoms. Examples of some carboxylic acids that may be used to prepare the metal carboxylates include: butyric acid; valeric acid; caproic acid; heptanoic acid; cyclohexanecarboxylic acid; cyclodecanoic acid; naphthenic acid; phenyl acetic acid; 2-methylhexanoic acid; 2-ethylhexanoic acid; suberic acid; octanoic acid; nonanoic acid; decanoic acid; undecanoic acid; lauric acid; tridecanoic acid; myristic acid; pentadecanoic acid; palmitic acid; linolenic acid; heptadecanoic acid; stearic acid; oleic acid; nonadecanoic acid; eicosanoic acid; heneicosanoic acid; docosanoic acid; and erucic acid.

The most preferred carboxylic acids, for preparing the oil-soluble salts of the present invention, are salicylic acids. Overbased salicylate are exemplified by lithium salicylates, sodium salicylates, potassium salicylates, calcium salicylates, and magnesium salicylates wherein the aromatic moiety is usually substituted by one or more aliphatic sub-

stituents to impart hydrocarbon solubility.

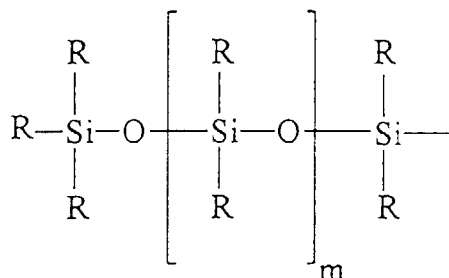
Examples of suitable overbased metal-containing phenate detergents include, but are not limited to, such substances as overbased lithium phenates, sodium phenates, potassium phenates, calcium phenates, magnesium phenates, sulfurized lithium phenates, sulfurized sodium phenates, sulfurized potassium phenates, sulfurized calcium phenates, and sulfurized magnesium phenates wherein each aromatic group has one or more aliphatic groups to impart hydrocarbon solubility. The foregoing overbased metal detergents are often referred to as "overbased phenates" or "overbased sulfurized phenates".

Also suitable, though less preferred, are (a) the overbased lithium, sodium, potassium, calcium, and magnesium salts of hydrolyzed phospho-sulfurized olefins having 10 to 2000 carbon atoms or of hydrolyzed phospho-sulfurized alcohols and/or aliphatic-substituted phenolic compounds having 10 to 2000 carbon atoms. Other similar overbased alkali and alkaline earth metal salts of oil-soluble organic acids are suitable, such as the overbased aliphatic sulfonate salts, often referred to as "petroleum sulfonates". Mixtures of salts of two or more different overbased alkali and/or alkaline earth metals can be used. Likewise, salts of mixtures of two or more different acids or two or more different types of acids (e.g., one or more overbased calcium phenates with one or more calcium sulfonates) can also be used. While rubidium, cesium and strontium salts are feasible, their expense renders them impractical for most uses. Likewise, while barium salts are effective, the status of barium as a heavy metal under a toxicological cloud renders barium salts less preferred for present day usage.

The metal containing detergent may be of the low base or high base type or mixtures thereof. Low base detergents have a total base number of greater than about 8, but less than about 200. Preferred metal containing detergents are high base calcium and magnesium sulfonates, sulfurized phenates and salicylates having a total base number (TBN) per ASTM D 2896-88 of at least 200, and preferably above 250.

Component (iii)

The foam inhibitors useful in the present invention include those antifoam additives conventionally used in fuel compositions, such as silicone antifoam agents. The advantages of the present invention are particularly evident when the antifoam used is one which exhibits a serious incompatibility with the overbased metal detergents. Incompatibility with the overbased metal detergents is evidenced by severe foaming upon combining the antifoam and the detergent. This incompatibility is most often seen where the antifoam agent is one that is largely insoluble in water at 25°C. This problem is solved by the addition of a lubricity additive of the type described above. Preferred antifoam agents are polyether polysiloxane copolymers of the formula



wherein R is independently selected from the group consisting of H, OH, C₁₋₃ alkyl, polyalkoxy, poly-(alkoxy)-X (wherein X is OH, methyl or an ester), and polyalkoxy derivatives, in which aromatic, phenolic or phenol derivatives are grafted to the alkoxy or polyether chain. Polyalkoxy chains typically contain ethoxy or propoxy units, or mixtures of the two. The polyether polysiloxane copolymers may be organosilicone terpolymers, such as those containing alkyl phenol or modified alkyl phenol derivatives and polyethers grafted onto a polysiloxane copolymer. Preferred are the antifoams which are substantially insoluble in water at 25°C.

Suitable polyether polysiloxane copolymers for use in the present invention include S911 antifoam, a polyether polydimethylsiloxane commercially available from Wacker Chemie GmbH; Dow Corning® Q2-2600 antifoam, a polyether polysiloxane copolymer commercially available from Dow Corning; and TP325 antifoam, an organosilicone terpolymer commercially available from OSi Specialties Inc.

Polyether polysiloxane copolymer antifoams which are not part of this invention include those which are water soluble at 25°C and do not exhibit serious incompatibility with overbased metal detergents. Examples of these types of copolymers include TEGOPREN® 5851 silicone surfactant commercially available from T.H. Goldschmidt AG, Essen, Germany. Antifoams of this specific class do not cause the foam stabilization effect for which the lubricity additives

of the present invention are required as a means of controlling.

Component (iv)

Among the preferred embodiments of this invention is inclusion in the compositions of at least one hydrocarbon-soluble dispersant. These dispersants comprise long chain succinimides, long chain succinic esters, long chain succinic ester-amides, long chain polyamines and long chain Mannich bases. The long chain of these detergent-dispersants contains an average of at least 20 carbon atoms, e.g., an average of 30 to 200 or more carbon atoms. Such long chain substituents are usually derived from polyolefin oligomers or polymers of suitable number average molecular weights such as about 800, 950, 1200, 1350, 1500, 1700, 2100 or 2300 which in turn are formed by polymerization or copolymerization of olefin monomers such as propylene, butylenes, isobutylene, amylenes, mixtures of ethylene and propylene, and the like.

Methods for the manufacture of such dispersant-detergents suitable for use, *inter alia*, as additives for fuel compositions are well known and reported in the literature. Thus, typical succinimides that can be used are described in published PCT Patent Application WO 93/06194 and published European Patent Application, Publication No. 0441014 (August 14, 1991). For exemplary disclosures of succinic esters or succinic ester-amides, one may refer for example to U.S. Pat. Nos. 3,184,474; 3,331,776; 3,381,022; 3,522,179; 3,576,743; 3,632,511; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,991,098; 4,071,548; and 4,173,540. Long chain polyamine dispersant-detergents are described for example in U.S. Pat. Nos. 3,275,554; 3,394,576; 3,438,757; 3,454,555; 3,565,804; 3,671,511; 3,821,302; and European Patent Publication No. 382,405. Suitable fuel-soluble Mannich base detergent-dispersants which can be used are disclosed for example in U.S. Patent Nos. 3,948,619; 3,994,698; and especially 4,231,759.

One preferred group of dispersant-detergents for use in this invention are succinimides formed by reaction of a polyisobutenyl succinic anhydride and a polyamine, especially an ethylene polyamine having an average of 2 to 6 nitrogen atoms per molecule such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and N-[2-hydroxyethyl]ethylene diamine. In these dispersants, the polyisobutenyl group preferably has a GPC number average molecular weight in the range of 750 to 2300, more preferably 800 to 1350.

Also preferred are the Mannich base dispersants formed by reaction of (i) an alkylphenol in which the alkyl group is derived from a olefin polymer that has a number average molecular weight in the range of 750 to 2300, preferably 800 to 1350 and most preferably 800 to 1100, (ii) polyalkylene polyamine and (iii) formaldehyde or a formaldehyde precursor. Most preferably, the alkyl group of the alkylphenol is derived from polypropene having a number average molecular weight in the range of 800 to 1100, and the polyalkylene polyamine is diethylene triamine. Other useful dispersants are referred to, for example, in EP 476,196 B1.

Component (v)

Additional materials which can be included in the compositions of this invention are metal based emissions improving additives such as cyclopentadienyl manganese tricarbonyl compounds. Such compounds, when present in the finished fuels, may contribute to reduction of exhaust emissions, particularly emission of particulates and smoke. In addition, use of the cyclopentadienyl manganese tricarbonyl compounds in the compositions of this invention results in further improvements in induction system cleanliness, particularly cleanliness of inlet valves. Cyclopentadienyl manganese tricarbonyl compounds which can be used in the practice of this invention include cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tert-butylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and the like, including mixtures of two or more such compounds. Preferred are the cyclopentadienyl manganese tricarbonyls which are liquid at room temperature such as methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, liquid mixtures of cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl, mixtures of methylcyclopentadienyl manganese tricarbonyl and ethylcyclopentadienyl manganese tricarbonyl, etc. Preparation of such compounds is described in the literature, for example, U.S. 2,818,417.

Although less preferred, other fuel-soluble or fuel-dispersible manganese compounds may be included in the compositions of this invention. These compounds are illustrated by manganese oleate, manganese naphthenates, manganese octylacetoacetate and manganese ethylene diamine tetracetate.

In principle, the advantages of this invention may be achieved in any liquid fuel derived from petroleum, biomass, coal, shale and/or tar sands. In most instances, at least under present circumstances, the base fuels will be derived

primarily, if not exclusively, from petroleum.

The invention is thus applicable to such fuels as kerosene, jet fuel, aviation fuel, diesel fuel, home heating oil, light cycle oil, heavy cycle oil, light gas oil, heavy gas oil, bunker fuels, residual fuel oils, ultra heavy fuel oils, and in general, any liquid (or flowable) product suitable for combustion either in an engine (e.g., diesel fuel, gas turbine fuels, etc.) or in a burner apparatus. Other suitable fuels include liquid fuels derived from biomass, such as vegetable oils (e.g., rapeseed oil, jojoba oil, cottonseed oil, etc.) or refuse-derived liquid fuels such as fuels derived from municipal and/or industrial wastes.

In general, the components of the additive compositions are employed in the fuels in minor amounts sufficient to improve the combustion characteristics and properties of the base fuel in which they are employed. The amounts will thus vary in accordance with such factors as base fuel type and service conditions for which the finished fuel is intended. However, generally speaking, the following concentrations (ppm) of the components (active ingredients) in the base fuels are illustrative:

	General Range	Preferred Range	Particularly Preferred Range
Component (i) Lubricity Additive	10 to 400	15 to 200	20 to 100
Component (ii) Metal Detergent	1 to 100 ppm of the metal component	5 to 50 ppm of the metal component	10 to 30 ppm of the metal component
Component (iii) Antifoam Agent	1 to 30	2 to 15	3 to 8

In the case of fuels additionally containing one or more of components (iv) and (v), the following concentrations (ppm) of active ingredients are typical:

	General Range	Preferred Range	Particularly Preferred Range
Component (iv) Dispersant	10 to 500	20 to 200	40 to 100
Component (v) Metal Based Emissions Improver	0.1 to 50 ppm of the metal	1 to 10 ppm of the metal	2 to 10 ppm of the metal

It will be appreciated that the individual components (i), (ii), and (iii), and also (iv) and/or (v), if used, can be separately blended into the fuel or can be blended therein in various subcombinations, if desired. Ordinarily, the particular sequence of such blending steps is not critical. Moreover, such components can be blended in the form of a solution or diluent. It is preferable, however, to blend the components used in the form of an additive concentrate of this invention, as this simplifies the blending operations, reduces the likelihood of blending errors, and takes advantage of the compatibility and solubility characteristics afforded by the overall concentrate. Such a concentrate forms part of the present invention and 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 fuel itself. However, examples of other solvents or diluents include white spirit, kerosene, alcohols (e.g., 2-ethyl hexanol, isopropanol and isodecanol), aromatic solvents (e.g., toluene and xylene) and cetane improvers (e.g., 2-ethyl hexylnitrate). These may be used alone or as mixtures.

The compositions of the present invention may further contain optional components conventionally used in fuel compositions such as fuel stabilizers, cetane number improvers, anti-icers, combustion modifiers, cold flow improvers, antistatic additives, biocides, antioxidants, corrosion inhibitors, wax antisetling additives and metal deactivators.

The various optional components that can be included in the fuel compositions of this invention are used in conventional amounts. Thus, the amounts of such optional components are not critical to the practice of the present invention. The amounts used in any particular case are sufficient to provide the desired functional property to the fuel composition, and such amounts are well known to those skilled in the art.

The invention is illustrated by the following examples.

EXAMPLES

The basic formulation for Examples 1 and 2, and Comparative Examples 1-4, excluding the antifoam and lubricity

additives listed in Table 2, is set forth below. The amounts are based on ml of additive per 1000 ml of fuel.

Table 1.

Basic Formulation	grams in mix	weight %
Solvent ¹	250.77	50.14
Demulsifier ²	4.62	0.92
Corrosion Inhibitor ³	4.12	0.82
Metal Detergent ⁴	149.02	29.8
Dispersant ⁵	71.02	14.2
MMT/LP62 ⁶	20.55	4.11

1: 2-ethyl hexanol.

2: OFRIC® D5021 demulsifier, commercially available from Baker Performance Chemical.

3: HiTEC® 536 corrosion inhibitor, low molecular weight succinimide/amide of polyalkylene polyamine commercially available from Ethyl Corporation.

4: HiTEC® 611 detergent, an overbased calcium alkyl benzene sulfonate having a nominal total base number of about 300, commercially available from Ethyl Corporation.

5: Ashless polyisobutylene succinimide dispersant based on 950 number average molecular weight polyisobutylene, succinic anhydride and tetra-ethylene pentamine.

6: Cyclopentadienyl manganese tricarbonyl compound in xylene/heptane solvent mix.

All treated fuels were treated with additive such that this basic formulation would be present at approximately 0.44 ml of formulation per 1000 ml of fuel.

To evaluate the various additives and their effects on fuel compositions, foam volume and time to first spot of fuel surface which was clear of foam were measured. Lower foam volumes and shorter times to first spot represent improved antifoam behavior. The base fuel used in the present examples is a low sulfur (< 0.05% by weight of sulfur) diesel fuel.

Measured quantities of the lubricity additive and different antifoam agents were added to separate portions of the basic formulation and the resultant additive concentrates were then blended into the base fuel to produce fuel compositions which in each case contained an amount of the additive concentrate equivalent to approximately 0.44 ml/1000 ml of fuel of the basic formulation along with a specified amount of the antifoam agent and lubricity additive which had been included in the package. The respective fuels were then promptly shaken under controlled conditions, and in each instance the time needed for the foam to dissipate was measured. The procedure involved use of graduated glass cylinders, as employed in ASTM D 1094, that had been cleaned in chromic acid for a minimum of one hour, rinsed with water followed by acetone and then dried. The cylinders were filled to the 100 mL mark with fuel. They were then stoppered and shaken for 1 minute at 2-3 strokes per second, each stroke being 15 to 30 cm long and in a vertical plane. The shaken cylinders were then placed on a level surface, free from vibration, and the maximum foam volume (ml of foam), and the time for the first clear point of fuel to form (time (sec) to first spot) were recorded.

The results in Table 2 indicate that the fuel additive compositions of the present invention (Examples 1 and 2) provide fuel compositions which exhibit significantly reduced foam volume and time to first spot compared to compositions containing only base fuel (Comparative Example 5), or fuel compositions containing additive mixtures outside the scope of the present invention (Comparative Examples 1-4) as is evidenced by the significantly lower values for the foam volume and time to first spot tests obtained in Examples 1 and 2.

Table 2.

	Antifoam System	Amount Antifoam ml/ 1000 ml fuel	Amount H2658 ⁷ present ml/1000 ml fuel	Foam Volume (ml)	Time to First Spot (sec)
Example 1	S911 ⁸	0.011	0.045	1.7	15.7
Comparative Example 1	S911	0.011	0	40	>900
Example 2	Q2-2600 ⁹	0.011	0.045	3	13

7: HiTEC® 2658 lubricity additive, oleyl diethanolamide commercially available from Ethyl Corporation.

8: S911 antifoam, a silicone antifoam agent commercially available from Wacker Chemie GmbH.

9: Q2-2600 antifoam, a silicone antifoam commercially available from Dow Corning.

Table 2. (continued)

	Antifoam System	Amount Antifoam ml/ 1000 ml fuel	Amount H2658 ⁷ present ml/1000 ml fuel	Foam Volume (ml)	Time to First Spot (sec)
Comparative Example 2	Q2-2600	0.011	0	40	>1560
Comparative Example 3	no antifoam	0	0.045	33.3	32.3
Comparative Example 4	no antifoam	0	0	33.3	34
Comparative Example 5	Base fuel Only	0	0	33	28

7: HiTEC® 2658 lubricity additive, oleyl diethanolamide commercially available from Ethyl Corporation.

Table 3 demonstrates the beneficial effects on foam properties obtained by the addition of a fatty acid lubricity additive to a system containing an antifoam and an overbased detergent.

The results in Table 3 indicate that the fuel additive compositions of the present invention (Example 3) provide fuel compositions which exhibit significantly reduced foam volume and time to first spot compared to compositions containing additive mixtures outside

Table 3.

Components	Example 3	Comparative Example 6
Solvent ¹	24.4g	20.83g
Metal Detergent ⁴	17.86g	20.3g
Antifoam ⁸	1.63g	1.87g
Lubricity Additive ¹⁰	6.09g	---
Treat rate: volume added to fuel	0.41 ml of formulation per 1000 ml of fuel	0.36 ml of formulation per 1000 ml of fuel
Foam Decay Time to first spot(s)	25.7 sec	>11 minutes
Foam volume/ml	8.7 ml	30 ml

10: Oleic acid obtained from the Aldrich Chemical Company.

the scope of the present invention (Comparative Example 6) as is evidenced by the significantly lower values for the foam volume and time to first spot tests obtained in Example 3.

This invention is susceptible to considerable variation in its practice. Accordingly, this invention is not limited to the specific exemplifications set forth hereinabove.

Claims

1. A fuel additive composition comprising (i) a lubricity additive, (ii) an overbased metal detergent, and (iii) an antifoam agent which is substantially insoluble in water at 25°C.
2. The fuel additive composition as claimed in Claim 1 wherein the lubricity additive is a carboxylic acid, a carboxylic acid amide or a carboxylic acid ester.
3. The fuel additive composition as claimed in Claim 1 or Claim 2 wherein the lubricity additive is selected from the group consisting of oleyl ethanolamide and oleyl diethanolamide.
4. The fuel additive composition as claimed in any of the preceding claims wherein the overbased metal detergent

is selected from the group consisting of calcium sulfonates, magnesium sulfonates, calcium sulfurized phenates, magnesium sulfurized phenates, calcium salicylates, and magnesium salicylates, wherein the detergent has a total base number (TBN) per ASTM D 2896-88 of at least 200.

- 5 **5.** The fuel additive composition as claimed in any of the preceding claims wherein the antifoam agent is a silicone antifoam agent which is substantially insoluble in water at 25°C.
- 6 **6.** The fuel additive composition as claimed in Claim 5 wherein the silicone antifoam agent is a polyether polysiloxane copolymer which is substantially insoluble in water at 25°C.
- 10 **7.** The fuel additive composition as claimed in any of the preceding claims which further comprises at least one member selected from the group consisting of dispersants, metal based emissions improving additives, demulsifying agents and corrosion inhibitors.
- 15 **8.** The fuel additive composition as claimed in Claim 7 wherein the dispersant is a hydrocarbon-soluble dispersant selected from the group consisting of long chain succinimides, long chain succinic esters, long chain succinic ester-amides, long chain polyamines, and long chain Mannich bases.
- 20 **9.** The fuel additive composition as claimed in Claim 7 wherein the metal based emissions improving additive is a cyclopentadienyl manganese tricarbonyl compound.
- 25 **10.** An additive concentrate comprising from 99 to 1% by weight of the additive as claimed in any of the preceding claims 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.
- 30 **11.** A fuel composition comprising (a) a major portion of a base fuel and (b) a minor amount of the fuel additive as claimed in any one of Claims 1 to 9, wherein the fuel additive is present in an amount sufficient to improve the foam behavior of the fuel.
- 35 **12.** A fuel composition obtained by combining (a) a major portion of a base fuel and (b) a minor amount of the fuel additive as claimed in any one of Claims 1 to 9, wherein the fuel additive is present in an amount sufficient to improve the foam behavior of the fuel.
- 40 **13.** A method of reducing foam in a fuel composition containing an overbased metal detergent and a silicone antifoam agent which is substantially insoluble in water at 25°C, wherein a lubricity additive is combined with said fuel composition.
- 45 **14.** The method as claimed in Claim 13 wherein the lubricity additive is a carboxylic acid, a carboxylic acid amide or a carboxylic acid ester.
- 50 **15.** The method as claimed in Claim 13 wherein the silicone antifoam agent is a polyether polysiloxane copolymer which is substantially insoluble in water at 25°C.
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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 1109

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)		
X	EP 0 681 023 A (ETHYL) 8 November 1995 * page 3, line 37 - line 39 * * page 6, line 1 - line 7 * * page 8, line 29 - page 9, line 3 * ----	1,2,4-12	C10L1/14		
Y	EP 0 476 196 A (ETHYL) 25 March 1992 * page 10, line 37 - line 41 * * page 11, line 17 - line 18 * ----	1,2,4-12			
Y	EP 0 654 525 A (DOW CORNING) 24 May 1995 * the whole document * ----	1,2,4-12			
A	WO 95 03377 A (EXXON) 2 February 1995 * claim 1 * ----	1-15			
A	EP 0 698 656 A (SHELL) 28 February 1996 * page 6, line 1 - line 38 * ----	1-15			
A	WO 95 33021 A (EXXON) 7 December 1995 * page 9, line 20 - line 28 * ----	1			
A	US 5 334 227 A (GRABOWSKI) 2 August 1994 * the whole document * -----	5	<table border="1"> <thead> <tr> <th>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</th> </tr> </thead> <tbody> <tr> <td>C10L</td> </tr> </tbody> </table>	TECHNICAL FIELDS SEARCHED (Int.Cl.6)	C10L
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Place of search THE HAGUE		Date of completion of the search 27 May 1998	Examiner De La Morinerie, B		
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