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(54) Environmentally-friendly fuel compositions

(57) Fuel additive packages and fuel compositions having environmentally compatible characteristics as defined by European Council Directive 67/548/EEC is disclosed. Such additive packages and compositions may include components selected from non-persistent materials, non-bioaccumulative materials, or non-toxic materials.

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Description

TECHNICAL FIELD

[0001] The present disclosure relates to the field of fuels and fuel compositions, specifically liquid fuel compositions having environmentally-friendly characteristics.

BACKGROUND

[0002] As concern for the environment grows worldwide, the safety of the various chemical substances used in fuel compositions and fuel additive concentrates is becoming more of a concern for manufacturers and distributors. It is paramount for the industry to examine the use of functional fuel additive components that are also compatible with environmental regulations. In particular, substances that are persistent in the environment, bioaccumulative, and toxic may be banned from use Hence, there exists a need for fuel additive compositions and fuel formulations containing such additive compositions that incorporate more environmentally acceptable materials.

SUMWARY

[0003] In an embodiment described herein, an environmentally compatible fuel additive composition may comprise four or more functional components, wherein each component is selected from the group consisting of a non-persistent material, a non-bioaccumulative material, and a non-toxic material, and wherein the additive composition is devoid of components that are persistent, bioaccumulative, and toxic.

[0004] In another embodiment, an environmentally compatible fuel composition, may comprise a) a major amount of a fuel; and b) a minor amount of an additive composition, comprising four or more functional components, wherein each component comprises at least one of: an acceptable level of biodegradation as determined by a biodegradation test, a bioconcentration factor below 2000, or is devoid of a toxic effect at an aqueous concentration below 0.01 mg/L on a toxicity test.

[0005] In another embodiment, a method of making an environmentally compatible fuel composition, comprising combining a major amount of a fuel and a minor amount of an additive composition, comprising four or more functional components, wherein each component is selected from: a material having an acceptable level of biodegradation, a material having a bioconcentration factor below 2000, and a material that is devoid of a toxic effect at an aqueous concentration below 0.01 mg/L on a toxicity test, wherein the fuel composition complies with European Council Directive 67/548/EEC.

[0006] In another embodiment, an environmentally compatible fuel composition may comprise: a) a major amount of a fuel; and b) a minor amount of an additive composition, comprising four or more functional components, wherein each component is selected from the group consisting of non-persistent materials, non-bioaccumulative materials and non-toxic materials, and wherein the additive composition is devoid of components that are persistent, bioaccumulative, and toxic.

[0007] An advantage of embodiments of the disclosure is that an impact on the environment by the use of materials disclosed herein is perceived to be lessened. A further advantage is that accidental or inadvertent spills of the compositions and fuels may not pose long term threats to humans and wildlife. Still further advantages of the compositions and methods described herein may be acceptable to national and state regulatory agencies.

[0008] As used herein, the terms "fuel oil composition," "fuel composition," "fully formulated fuel composition," and "fuel" are considered synonymous, fully interchangeable terminology referring to the finished fuel product comprising a major amount of a fuel or base oil (carrier fluid) plus a minor amount of a fuel additive composition. "Fuel" herein can in one embodiment be selected from the group consisting of one or more of gasoline, diesel fuel, middle distillate fuel, biodiesel fuel, an alcohol, such as but not limited to an ethanol, bioethanol, a biobutanol, an aviation fuel, jet fuel, marine fuel, bunker fuel, burner fuel, home heating oil (for example, home heating oil no. 6), a gas-to-liquid (GTL) base oil, a Group I base oil, a Group II base oil, a Group III base oil, a Group IV base oil, an ester, a vegetable oil, and mixtures thereof.

[0009] As used herein, the terms "additive package," "additive concentrate," and "additive composition" are considered synonymous, fully interchangeable terminology referring to the portion of the fuel composition excluding the major amount of fuel or base oil stock mixture (carrier fluid).

[0010] As used herein, a "functional" component means a component that is used in a fuel formulation to provide a measurable change in a characteristic or property of a fuel containing the component or in a property of the system delivering the fuel, or the system combusting the fuel, or the system exhausting the products from the combustion of the fuel.

[0011] As used herein, the terms "agent" and "additive" are considered synonymous, fully interchangeable terminology referring to any single component of a fuel composition excluding the major amount of fuel in the mixture.

[0012] Additional objects and advantages of the disclosure will be set forth in part in the description which follows, and/or can be learned by practice of the disclosure. The objects and advantages of the disclosure will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

[0013] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the disclosure, as claimed.

DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

[0014] Exemplary embodiments of the disclosure will now be provided to illustrate limited aspects of the preferred embodiments thereof, including various examples and illustrations of the formulation and use of the disclosed embodiments. It will be understood that these embodiments are presented solely for the purpose of illustrating the embodiments and shall not be considered as a limitation upon the scope thereof.

[0015] European Council Directive 76/548/EEC, incorporated herein by reference, provides regulatory guidance for the registration and evaluation of chemical substances that may be exposed to the environment during the normal course of use. Guidelines and testing procedures are enumerated therein, so that the potential environmental impact of any substance may be quantified.

[0016] A number of diagnostic tests have been developed to measure the effects of certain chemical substances upon various aspects of the environment. In particular, three main parameters are used to classify such substances: namely, persistence, bioaccumulation, and toxicity.

PERSISTENCE

[0017] The persistence of a substance in the environment may be inversely related to the biodegradability of the substance. Biodegradability is the ability of microbes occurring in an environment to break down a substance into simpler substances. The persistence, or biodegradability, criterion is defined in European Council Directive 76/548/EEC Annex XIII section 1.1, which is herein incorporated by reference, as a substance fulfilling one of the following criteria: having a half-life in marine water longer than 60 days, having a half-life in fresh or estuarine water longer than 40 days, having a half-life in marine sediment longer than 180 days, having a half-life in fresh or estuarine water sediment longer than 120 days, or having a half-life in soil longer than 120 days.

[0018] A material's persistence in the environment may be determined by a number of different test procedures, including the following tests: a dissolved organic carbon (DOC) die-away test, a modified OECD screening dissolved organic carbon die-away test, a carbon dioxide evolution test, a manometric respirometry test, a closed bottle test, a MITI test, a Zahn-Wellens test, an activated sludge simulation test, an activated sludge respiration inhibition test, and a modified SCAS test. The above test procedures are set forth in European Council Directive 76/548/EEC Annex V, sections C.4, C.9, C.10, C.11, and C.12, which are incorporated in full herein by reference, and are summarized below.

[0019] Six test methods are described that permit the screening of chemicals for ready biodegradability in an aerobic aqueous medium:

(a) Dissolved Organic Carbon (DOC) Die-Away (Method C.4-A)
(b) Modified OECD Screening- DOC Die-Away (Method C.4-B)
(c) Carbon dioxide (CO_2) Evolution (Method C.4-C)
(d) Manometric Respirometry (Method C.4-D)
(e) Closed Bottle (Method C.4-E)
(f) MITI (Ministry of International Trade and Industry - Japan) (Method C.4-F)

[0020] For example, a solution, or suspension, of the test substance in a mineral medium is introduced into an inoculum and incubated under aerobic conditions in the dark or in diffuse light. The amount of dissolved organic carbon (DOC) in the test solution due to microbial inoculum should be kept as low as possible compared to the amount of DOC due to the test substance. Allowance is made for the endogenous activity of the inoculum by running parallel blank tests with inoculum but without test substance, although the endogenous activity of cells in the presence of the substance will not exactly match that in the endogenous control. A reference substance is run in parallel to check the operation of the procedures.

[0021] In general, degradation is followed by the determination of parameters, such as DOC, CO_2 production, and oxygen uptake, and measurements are taken at sufficiently frequent intervals to allow the identification of the beginning and end of biodegradation. With automatic respirometers the measurement is continuous. DOC is sometimes measured in addition to another parameter but this is usually done only at the beginning and the end of the test. Specific chemical analysis may also be used to assess primary degradation of the test substance, and to determine the concentration of any intermediate substances formed (obligatory in the MITI test).

[0022] Normally, the tests last for 28 days. Tests however may be ended before 28 days, i.e., as soon as the biodegradation curve has reached a plateau for at least 3 determinations. Tests may also be prolonged beyond 28 days when the curve shows that biodegradation has started but that the plateau has not been reached by day 28.

[0023] The inoculum may be derived from a variety of sources: activated sludge, unchlorinated sewage effluents, surface waters and soils, or from a mixture of these.

Dissolved Organic Carbon Die-Away Test and Modified OECD Screening Dissolved Organic Carbon Die-Away Test

[0024] In the dissolved organic carbon die-away test and the modified OECD screening dissolved organic carbon die-away test, a measured volume of inoculated mineral medium containing a known concentration of the test substance (10-40 mg DOC/l) as the nominal sole source of organic carbon is aerated in the dark or diffused light at 22 ± 2 °C. Degradation is followed by DOC analysis at frequent intervals over a 28-day period. The degree of biodegradation is calculated by expressing the concentration of DOC removed (corrected for that in the blank inoculum control) as a percentage of the concentration initially present. The degree of primary biodegradation may also be calculated from supplemental chemical analysis made at the beginning and end of incubation.

Carbon Dioxide Evolution Test

[0025] In the carbon dioxide evolution test a measured volume of inoculated mineral medium containing a known concentration of the test chemical (10-20 mg DOC or total organic carbon (TOC) per liter) as the nominal sole source of organic carbon is aerated by the passage of carbon dioxide-free air at a controlled rate in the dark or in diffuse light. Degradation is followed over 28 days by determining the carbon dioxide produced, which is trapped in barium or sodium hydroxide and which is measured by titration of the residual hydroxide or as inorganic carbon. The amount of carbon dioxide produced from the test chemical (corrected for that derived from the blank inoculum) is expressed as a percentage of theoretical maximum carbon dioxide produced ($ThCO_2$). The degree of biodegradation may also be calculated from supplemental DOC analysis made at the beginning and end of incubation.

[0026] The percentage degradation may be calculated by:

$$\text{\% degradation} = (\text{mg } CO_2 \text{ produced} \times 100) / (ThCO_2 \times \text{mg test chemical added})$$

Manometric Respirometry Test

[0027] In the manometric respirometry test a measured volume of inoculated mineral medium, containing a known concentration of test chemical (100 mg/liter of the test substance, to give at least 50-100 mg theoretical oxygen demand/titer) as the nominal sole source of organic carbon, is stirred in a closed flask at a constant temperature (± 1° C or closer) for up to 28 days. The consumption of oxygen may be determined either by measuring the quantity of oxygen (produced electrolytically) required to maintain constant gas volume in the respirometer flask, or from the change in volume or pressure (or a combination of the two) in the apparatus. Evolved carbon dioxide is absorbed in a solution of potassium hydroxide or another suitable absorbent. The amount of oxygen taken up by the test chemical (corrected for uptake by a blank inoculum, run in parallel) is expressed as a percentage of THOD (theoretical oxygen demand) or COD (chemical oxygen demand). Optionally, primary biodegradation may also be calculated from supplemental specific analysis made at the beginning and end of incubation, and ultimate biodegradation by DOC analysis.

Closed Bottle Test

[0028] In the closed bottle test a solution of the test chemical in mineral medium, usually at 2-5 mg/liter, is inoculated with a relatively small number of micro-organisms from a mixed population and kept in completely full closed bottles in the dark at constant temperature. Degradation is followed by analysis of dissolved oxygen over a 28-day period. The amount of oxygen taken up by the test chemical, corrected for uptake by a blank inoculum run in parallel as a control, is expressed as a percentage of THOD or COD.

MITI Test

[0029] In the MITI test, the oxygen uptake by a stirred solution, or suspension, of the test chemical in a mineral medium, inoculated with specially grown, unadapted micro-organisms, is measured automatically over a period of 28 days in a darkened, enclosed respirometer at 25 ± 1 °C. Evolved carbon dioxide is absorbed by soda lime. Biodegradability is expressed as the percentage oxygen uptake (corrected for blank uptake) of the theoretical oxygen uptake (ThOD). The percentage of primary biodegradability is also calculated from supplemental specific chemical analysis made at the beginning and end of incubation and, optionally, by DOC analysis.

Zahn-Wellens Test

[0030] The purpose of the Zahn-Wellens Test is the evaluation of the potential ultimate biodegradability of water-soluble, non-volatile organic substances when exposed to relatively high concentrations of micro-organisms in a static test. The substances to be studied are used in concentrations corresponding to DOC-values in the range of 50 to 400 mg/liter or COD-values in the range of 100 to 1000 mg/liter (DOC = dissolved organic carbon; COD = chemical oxygen demand). These relatively high concentrations have the advantage of analytical reliability. Compounds with toxic properties may delay or inhibit the degradation process. In this method, the measure of the concentration of dissolved organic carbon or the chemical oxygen demand is used to assess the ultimate biodegradability of the test substance. A simultaneous use of a specific analytical method may allow the assessment of the primary biodegradation of the substance (disappearance of the parent chemical structure). The method is applicable only to those organic test substances which, at the concentration used in the test are soluble in water under the test conditions, have negligible vapor pressure under the test conditions, are not inhibitory to bacteria, are adsorbed within the test system only to a limited extent, and are not lost by foaming from the test solution.

[0031] Activated sludge, mineral nutrients and the test material as the sole carbon source in an aqueous solution are placed together in a one to four liter glass vessel equipped with an agitator and an aerator. The mixture is agitated and aerated at 20 to 25 °C under diffuse illumination or in a dark room for up to 28 days. The degradation process is monitored by determination of the DOC (or COD) values in the filtered solution at daily or other appropriate regular time intervals. The ratio of eliminated DOC (or COD) after each interval to the value three hours after the start is expressed as percentage biodegradation and serves as the measure of the extent of degradation at this time. The result is plotted versus time to give the biodegradation curve.

Activated Sludge Simulation Test

[0032] The activated sludge simulation test is used to determine the primary biodegradability of a substance in an activated sludge plant model, at a concentration of about 20 mg/liter. This allows the assessment of the primary biodegradability of the substance (disappearance of the parent chemical structure). Another purpose of the method is the determination of ultimate biodegradability by the measurement of the removal of the substance and any metabolites in an activated sludge plant model at a concentration corresponding to > 12 mg DOC/liter (or approximately 40 mg COD/liter); wherein 20 mg DOC/liter seems to be optimal.

[0033] For the determination of ultimate biodegradability, two activated sludge pilot units are run in parallel. The test substance is added to the influent (synthetic or domestic sewage) of one of the units, while the other blank unit receives the sewage alone. For the determination of primary biodegradation with specific analysis in the influent and effluent, only one unit may be used.

[0034] The sludge growth/stabilization period is the period during which the concentration of the activated sludge suspended solids and the performance of the units' progress to a steady state under the operating conditions used.

[0035] The running-in period is the period which lasts from the time the test substance is first added to the time when its removal reaches a plateau (relatively constant value). This period must not exceed six weeks.

[0036] The evaluation period is a three week period, i.e., three weeks from the time that the removal of the test substance reaches a relatively constant, and usually high, value. For those substances which show little or no degradation in the first six weeks, the evaluation period is taken as the following three weeks.

[0037] Influent without substance to be tested must pass through an aeration vessel either at the rate of one liter per hour or a rate of one-half liter per hour thereby providing a mean retention time of either three or six hours. The rate of aeration should be regulated so that the content of the vessel is kept constantly in suspension while the dissolved oxygen content is at least 2 mg/liter.

[0038] The sludge which has accumulated around the top of the aeration vessel must be returned to the mixed liquor at least once each day by brushing or some other appropriate means.

[0039] The effluent is collected in a second vessel for 20 to 24 hours, and a sample is taken after thorough mixing.

[0040] In order to monitor and control the efficiency of the process, the chemical oxygen demand (COD) or the dissolved organic carbon (DOC) of the filtrate of the accumulated effluent is measured at least twice weekly, as well as that of the filtered influent (using a membrane of pore size 0.45 μm, wherein the first 20 ml (approximately) of the filtrate are discarded). The reduction in COD or DOC should level off when a roughly regular daily degradation is obtained.

[0041] The operating conditions of the running-in period are maintained and sufficient stock solution (approximately

1%) of the test material is added to the influent of the test unit so that the desired concentration of test material (approximately 10 to 20 mg DOC/liter or 40 mg COD/liter) in the sewage is obtained. This may be done by mixing the stock solution to the sewage daily or by means of a separate pumping system. This concentration may be reached progressively. If there are no toxic effects of the test substance on the activated sludge, higher concentrations may also be tested.

[0042] The blank unit is fed only with influent without added substances. Adequate volumes of the effluents are taken for analysis and filtered through membrane filters (0.45 μm), the first 20 ml (approximately) of filtrate being discarded.

[0043] The filtered samples have to be analyzed on the same day, otherwise they must be preserved by any suitable method, for example, by using 0.05 ml of a 1% mercuric chloride ($HgCl_2$) solution for each 10 ml of filtrate or by storing them at 2 to 4 °C up to 24 hours, or below -18 °C for longer periods.

[0044] The running-in time, with addition of test substance, should not exceed six weeks and the evaluation period should not be shorter than three weeks, so that about 14 to 20 determinations are available for calculation of the final result.

Activated Sludge Respiration Inhibition Test

[0045] The activated sludge respiration inhibition test assesses the effect of a test substance on micro-organisms by measuring the respiration rate under defined conditions in the presence of different concentrations of the test substance. The purpose of this method is to provide a rapid screening method whereby substances which may adversely affect aerobic microbial treatment may be identified, and to indicate suitable non-inhibitory concentrations of test substances to be used in biodegradability tests. Two controls without the test substance are included in the test design, one at the start and the other at the end of the test series. Each batch of activated sludge should also be checked using a reference substance.

[0046] The activated sludge respiration inhibition method is most readily applied to substances which, due to their water solubility and low volatility, are likely to remain in water. For substances with limited solubility in the test media, it may not be possible to determine the EC_{50}. Results based on oxygen uptake may lead to erroneous conclusions if the test substance has the propensity to uncouple oxidative phosphorylation, It may be useful to have the following information to perform the test: water solubility, vapor pressure, structural formula, and the purity of the test substance.

[0047] It is recommended that 3,5-dichlorophenol, as a known inhibitor of respiration, be used as a reference substance and tested for EC_{50} on each batch of activated sludge as a means of checking that the sensitivity of the sludge is not abnormal.

[0048] At least five concentrations, spaced by a constant factor preferably not exceeding 3.2, are used. At time '0', 16 ml of the synthetic sewage feed are made up to 300 ml with water. 200 ml of microbial inoculum are added and the total mixture (500 ml) poured into a first vessel (first control Cl). The test vessels should be aerated continuously so as to ensure that the dissolved O_2 does not fall below 2.5 mg/liter and that, immediately before the measurement of the respiration rate, the O_2 concentration is about 6.5 mg/liter.

[0049] At time '15 minutes' (15 minutes is an arbitrary, but convenient, interval) the above is repeated, except that 100 ml of the test substance stock solution are added to the 16 ml of synthetic sewage before adding water to 300 ml and microbial inoculum to make a volume of 500 ml. This mixture is then poured into a second vessel and aerated as above. This process is repeated at 15-minute intervals with different volumes of the test substance stock solution to give a series of vessels containing different concentrations of the test substance.

[0050] Finally, a second control is prepared (C2). After three hours the pH is recorded, and a well-mixed sample of the contents of the first vessel is poured into the measuring apparatus and the respiration rate is measured over a period of up to 10 minutes. This determination is repeated on the contents of each vessel at 15-minute intervals, in such a way that the contact time in each vessel is three hours. The reference substance may be tested on each batch of microbial inoculum in the same way.

Modified SCAS Test

[0051] The modified SCAS test is used to evaluate the potential ultimate biodegradability of water-soluble, non-volatile organic substances when exposed to relatively high concentrations of micro-organisms over a long time period. The viability of the microorganisms is maintained over this period by daily addition of a settled sewage feed.

[0052] The conditions provided by the test are highly favorable to the selection and/or adaptation of microorganisms capable of degrading the test compound, however the procedure may also be used to produce acclimatized inocula for use in other tests.

[0053] According to the method, the measure of the concentration of dissolved organic carbon is used to assess the ultimate biodegradability of the test substances. It is preferable to determine DOC after acidification and purging rather than as the difference of C_{total} - $C_{inorganic}$.

[0054] The method is applicable only to those organic test substances which, at the concentration used in the test are soluble in water (at least 20 mg dissolved organic carbon/liter), have negligible vapor pressure, are not inhibitory to bacteria, do not significantly adsorb within the test system, and are not lost by foaming from the test solution. The organic carbon content of the test substance must be established prior to running the test.

[0055] Activated sludge from a sewage treatment plant is placed in a semi-continuous activated sludge (SCAS) unit. The test compound and settled domestic sewage are added, and the mixture is aerated for 23 hours. The aeration is then stopped, the sludge allowed to settle, and the supernatant liquor is removed. The sludge remaining in the aeration chamber is then mixed with a further aliquot of test compound and sewage and the cycle is repeated.

[0056] Biodegradation is established by determining the dissolved organic carbon content of the supernatant liquor. This value is compared with that found for the liquor obtained from a control tube dosed with settled sewage only.

[0057] Ideally, the dissolved organic carbon in the supernatant liquors is determined daily, although less frequent analyses may be used. Before analysis the liquors are filtered through washed 0.45 μm membrane filters or centrifuged. Membrane filters are suitable if it is assured that they neither release carbon nor absorb the substance in the filtration step. The temperature of the sample must not exceed 40 °C while it is in the centrifuge. The length of the test for compounds showing little or no biodegradation is indeterminate, but experience suggests that this should be at least 12 weeks in general, but not longer than 26 weeks.

BIOACCUMULATION

[0058] Bioaccumulation, or bioconcentration, is defined as the increase in concentration of a test substance in or on an organism or specified tissues thereof relative to the concentration of the test substance in the surrounding medium. As used herein, the terms "bioaccumulation" and "bioconcentration" are used interchangeably to refer to the same criteria. The bioconcentration factor ("BCF") is calculated as the concentration of test substance in an organism (or specified tissues thereof) divided by the concentration of the substance in the surrounding medium. Both the uptake and depuration of substances by organisms, and the respective rates thereof, are considered in calculating bioaccumulation.

[0059] One predictive factor for bioaccumulation may be a substance's octanol-water partition coefficient (P_{OW}). The Pow is a substance's solubility in n-octanol and water at equilibrium. The logarithm of P_{OW} may be an indication of a substance's potential for bioaccumulation in aquatic organisms.

[0060] The criterion for acceptable bioaccumulation is defined in European Council Directive 76/548/EEC Annex XIII section 1.2, which is herein incorporated by reference, as a substance having a bioconcentration factor less than 2000. The bioconcentration factor of a material may be determined by test procedures set forth in European Council Directive 76/548/EEC Annex V, section C. 13 flow-through fish test, which is incorporated in full herein by reference.

Flow-Through Fish Test

[0061] The flow-through fish test consists of two phases: the exposure (uptake) phase and the post-exposure (depuration) phase. During the uptake phase, separate groups of fish of one species are exposed to at least two concentrations of the test substance. They are then transferred to a medium free of the test substance for the depuration phase. A depuration phase is always necessary unless uptake of the substance during the uptake phase has been insignificant (e.g., the BCF is less than 10). The concentration of the test substance in/on the fish (or specified tissue thereof) is followed through both phases of the test. In addition to the two test concentrations, a control group of fish is held under identical conditions except for the absence of the test substance, to relate possible adverse effects observed in the bioconcentration test to a matching control group and to obtain background concentrations of test substance.

[0062] The uptake phase is run for 28 days unless it is demonstrated that equilibrium has been reached earlier. The depuration period is then begun by transferring the fish to the same medium but without the test substance in another clean vessel. Where possible the bioconcentration factor is calculated preferably both as the ratio (BCF_{SS}) of concentration of the fish (C_f) and in the water (C_w) at apparent steady-state and as a kinetic bioconcentration factor, BCF_K as the ratio of the rate constants of uptake (k_1) and depuration (k_2) assuming first-order kinetics.

[0063] If a steady-state is not achieved within 28 days, the uptake phase should be extended until steady-state is reached, or 60 days, whichever comes first; the depuration phase is then begun.

[0064] The BCF is expressed as a function of the total wet weight of the fish. However, for special purposes, specified tissues or organs (e.g. muscle, liver), may be used if the fish are sufficiently large or the fish may be divided into edible (fillet) and non-edible (viscera) fractions. Since, for many organic substances, there is a clear relationship between the potential for bioconcentration and lipophilicity, there is also a corresponding relationship between the lipid content of the test fish and the observed bioconcentration of such substances. Thus, to reduce this source of variability in test results for those substances with high lipophilicity (i.e. with log P_{OW}>3), bioconcentration should be expressed in relation to lipid content in addition to whole body weight.

[0065] The lipid content is determined on the same biological material as is used to determine the concentration of the test substance, when feasible.

TOXICITY

[0066] The toxicity criterion is defined in European Council Directive 76/548/EEC Annex XIII section 1.3, which is herein incorporated by reference, as a substance having a long-term no-observed effect concentration (NOEC) for marine or freshwater organisms less than 0.01mg/L. Substances that are classified as carcinogenic, mutagenic, or toxic for reproduction may also be considered as toxic.

[0067] The toxicity of a material may be determined by test procedures, such as the acute toxicity for fish test, the acute toxicity for *Daphnia* test, and the algal inhibition test, set forth in European Council Directive 76/548/EEC Annex V, sections C.1, C.2, and C.3, which are incorporated in full herein by reference. These acute tests may be used for first cut screening (if LC50<1ppm), however chronic toxicity tests (usually in Daphnia but also other organisms) may be used for definitive Toxicity.

Acute Toxicity For Fish Test

[0068] The purpose of the acute toxicity for fish test is to determine the acute lethal toxicity of a substance to fish in fresh water. It is desirable to have, as far as possible, information on the water solubility, vapor pressure, chemical stability, dissociation constants, and biodegradability of the substance to help in the selection of the most appropriate test method (static, semi-static, or flow-through) for ensuring satisfactorily constant concentrations of the test substance over the period of the test.

[0069] Additional information (for instance structural formula, degree of purity, nature and percentage of significant impurities, presence and amounts of additives, and n-octanol/water partition coefficient) should be taken into consideration in both the planning of the test and interpretation of the results.

[0070] Acute toxicity is the discernible adverse effect induced in an organism within a short time (days) of exposure to a substance. In the present test, acute toxicity is expressed as the median lethal concentration (LC_{50}), the concentration in water which kills 50% of a test batch of fish within a continuous period of exposure which must be stated.

[0071] Three types of procedure may be used. The static test is a toxicity test in which no flow of test solution occurs. The solutions remain unchanged throughout the duration of the test. The semi-static test is a test without flow of test solution, but with regular batchwise renewal of test solutions after prolonged periods (e.g. 24 hours). The flow-through test is a toxicity test in which the water is renewed constantly in the test chambers, the chemical under test being transported with the water used to renew the test medium.

[0072] At least 7 fish per concentration being tested are exposed to the substance for a duration of 96 hours in tanks of suitable capacity. At least five concentrations differing by a constant factor not exceeding 2.2, and as far as possible spanning the range of 0 to 100 % mortality, should be tested for each substance. The fish may not be fed during the test. The fish are inspected after the first 2 to 4 hours and afterward at least at 24-hour intervals. Fish are considered dead if touching of the caudal peduncle produces no reaction, and no breathing movements are visible. Dead fish are removed when observed and mortalities are recorded. Records are kept of visible abnormalities (e.g. loss of equilibrium, changes in swimming behavior, respiratory function, pigmentation, etc.). Measurements of pH, dissolved oxygen and temperature must be carried out daily.

Acute Toxicity For *Daphnia* Test

[0073] The acute toxicity for *Daphnia* test is similar to the acute toxicity for fish test, but the purpose is to determine the median effective concentration for immobilization (EC_{50}) of a substance to *Daphnia* in fresh water. As with the toxicity for fish test, it is desirable to have, as far as possible, information on the water solubility, vapor pressure, chemical stability, dissociation constants, and biodegradability of the test substance before starting the test. Additional information (for instance structural formula, degree of purity, nature and percentage of significant impurities, presence and amount of additives, and n-octanol/water partition coefficient) should be taken into consideration in both the planning of the test and interpretation of the results.

[0074] The *Daphnia* are exposed to the test substance added to water at a range of concentrations for 48 hours. Under otherwise identical test conditions, and an adequate range of test substance concentrations, different concentrations of a test substance exert different average degrees of effect on the swimming ability of *Daphnia.* Different concentrations result in different percentages of *Daphnia* being no longer capable of swimming at the end of the test. The concentrations causing zero or 100% immobilization are derived directly from the test observations whereas the 48-hour EC_{50} may be determined by calculation if possible. A static system is used for this method, hence test solutions are not renewed during the exposure period.

[0075] Stock solutions of the required strength are prepared by dissolving the substance in deionized water or water. The chosen test concentrations are prepared by dilution of the stock solution. If high concentrations are tested, the substance may be dissolved in the dilution water directly.

[0076] The substances are normally only tested up to the limit of solubility. For some substances (e. g. substances having low solubility in water, or high P_{OW}, or those forming stable dispersion rather than true solution in water), it is acceptable to run a test concentration above the solubility limit of the substance to ensure that the maximum soluble/stable concentration has been obtained. It is important, however, that this concentration will not otherwise disturb the test system (e. g. film of the substance on the water surface preventing the oxygenation of the water, etc.).

[0077] *Daphnia magna* is the preferred test species although *Daphnia pulex* is also permitted. The test animals shall be less than 24 hours old at the beginning of the test, laboratory bred, free from overt disease, and with a known history (e.g. breeding, any pretreatments, etc.).

[0078] The *Daphnia* are exposed to the substance for 48 hours. At least 20 animals at each test concentration, preferably divided into four batches of five animals each or two batches of 10, are required. At least 2 ml of test solutions should be provided for each animal. The test solution should be prepared immediately before introduction of the *Daphnia,* preferably without using any solvent other than water. The concentrations are made up in a geometric series, at a concentration ratio not exceeding 2.2. Concentrations sufficient to give 0 and 100% immobilization after 48 hours and a range of intermediate degrees of immobilizations permitting calculation of the 48 hour EC50 should be tested together with controls. The test temperature should be between 18 and 22 °C, but for each single test it should be constant within ± 1 °C. The test solutions must not be bubble-aerated, and the animals may not be fed during the test. The pH and the oxygen concentration of the controls and of all the test concentrations should be measured at the end of the test; the pH of the test solutions should not be modified. Volatile compounds should be tested in completely filled closed containers, large enough to prevent lack of oxygen. The *Daphnia* are inspected at least after 24 hours exposure and again after 48 hours.

[0079] For each period where observations were recorded (24 and 48 h), the percentage mortality is plotted against concentration on logarithmic-probability paper. In those cases where the slope of the concentration/percentage response curve is too steep to permit calculation of the EC_{50}, a graphical estimate of this value is sufficient. When two immediately consecutive concentrations at a ratio of 2.2 give only 0 and 100% immobilization these two values are sufficient to indicate the range within which the EC_{50} falls.

Algal Inhibition Test

[0080] The algal inhibition test may be used to determine the effects of a substance on the growth of a unicellular green algal species. Relatively brief (72 hours) tests may assess effects over several generations. This method may be adapted for use with several different unicellular algal species. The method is most easily applied to water-soluble substances which, under the conditions of the test, are likely to remain in the water.

[0081] Exponentially-growing cultures of selected green algae are exposed to various concentrations of the test substance over several generations under defined conditions. The test solutions are incubated for a period of 72 hours, during which the cell density in each solution is measured at least every 24 hours. The inhibition of growth in relation to a control culture is determined.

[0082] Test cultures containing the desired concentrations of test substance and the desired quantity of algal inoculum are prepared by adding aliquots of stock solutions of the test substance to suitable amounts of pre-prepared algal cultures.

[0083] The culture flasks are shaken and placed in the culturing apparatus. The algal cells are kept in suspension by shaking, stirring, or bubbling with air, in order to improve gas exchange and reduce pH variation in the test solutions. The cultures are maintained at a temperature in the range of 21 to 25 °C, controlled at ± 2 °C.

[0084] The cell density in each flask is determined at least at 24, 48 and 72 hours after the start of the test. Filtered algal medium containing the appropriate concentration of the test chemical is used to determine the background when using cell density measurements other than direct counting methods.

[0085] A suitable fuel or fuel additive composition, according to one embodiment of the present disclosure, may use functional components that may not exhibit persistence, bioaccumulation, or toxicity when tested according to the procedures set forth above. Accordingly, a functional component that is found to be persistent, bioaccumulative, and toxic may not be included in fuel formulations of the present disclosure.

[0086] Acceptable functional components may include one or more components functionally described as: an antifoam agent, an anti-icing additive, an antiknock additive, an antioxidant, an antistatic additive, an anti-valve-seat recession additive, an antiwear agent, a biocide, a carrier fluid, a cetane improver, a combustion improver, a compatibilizer, a conductivity improver, a corrosion inhibitor, a dehazer, a demulsifier, a detergent, a dispersant, a drag reducing agent, a dye, an emulsifier, a foam inhibitor, a friction modifier, a fuel stabilizer, an injector deposit control additive, a lubricity additive, a marker or customer-specific "tag", a metal deactivator, an octane improver, a pour point depressant, a reodorant, a seal swell additive, a surfactant, and a wax anti-settling additive (a "WASA"). Such components may be deemed acceptable for use in compositions of the present disclosure upon receiving a passing evaluation in testing for persistence, bioaccumulation, and/or toxicity using the test methods and/or criteria described above.

[0087] Suitable embodiments of the present disclosure may incorporate one or more of the following substances: a succinimide, an alkenyl succinimide, a polyisobutylene, a silicon antifoamant, a dibutyl hydrogen phosphite, base oils, an organic acid, an organic solvent, a 2-ethylhexyl nitrate, a polymer having a molecular weight of about 1000 or more, a monoalkyl thiadiazole, a dialkyl thiadiazole, an organo molybdenum compound, and the like.

[0088] Other suitable embodiments of the present disclosure may incorporate one or more of the following substances: a zinc dialkyl dithiophosphate, a phenate, and a sulfonate.

[0089] Other embodiments may incorporate one or more of the following substances:

Amines, polyethylenepoly-
Amines, N-(C14-18 and C16-18-unsatd. alkyl)trimethylenedi-1-Propanamine, 3-(Isodecyloxy)-C13 H29NO
Amines, coco alkyl
Dibenz(a,h)anthracene
Isooctane
Amines, coco alkyldimethyl
Amines, tallow alkyl, ethoxylated
Amines, n-tallow alkyltrimethylenedi
Amines, C14-18 and C16-18-unsaturated alkyl
Triphenyl phosphite
Amines, dicoco alkylmethyl
Glycine n-methyl-n-(1-oxo-9-octadecenyl)
Alcohols, C12-14, ethoxylate
Amines, C 16-22-tert-alkyl
Polysulfides, di-tert-butyl-
Alcohols, C 12-16 ethoxylated
Alkylphenol polyoxyalkyl alkylamine (in FDE-1)
1-Hexadecanamine
N,N-dimethyl-1-octadecanamine
N alkyl (coco) diethanolamine
1,3-Propanediamine, n-9-Octadecenyl-, (z)-
Phenol, nonyl-
9-Octadece-1-amine, (Z)-
Phenyl-alpha-naphthalene
2,6-DTBP
S-Alkenyl-O,O-dialkyldithiophosphates

[0090] Suitable embodiments may comprise one or more of polyetheramine and/or at least one agent selected from the group consisting of succinimide dispersants, succinamide dispersants, amides, Mannich base dispersants, p-phenylenediamine, dicyclohexylamine, phenolics, hindered phenolics, aryl amines, diphenyl amines, monocarboxylic acids, dicarboxylic acids, polycarboxylic acids, methyl cyclopentadienyl manganese tricarbonyl, cyclopentadienyl manganese tricarbonyl, azides, peroxides, alkyl nitrates, oxylated alkylphenolic resins, formaldehyde polymer with 4-(1,1-dimethylethyl)phenol, methyloxirane and oxirane, octane enhancer materials, monoesters, diesters, ethers, diethers, methyloxirane, oxiranes, peroxides, alkyl nitrates, C1-C8 aliphatic hydrocarbons, ketones, butylene oxides, propylene oxides, ethylene oxides, epoxides, butane, pentane, nitrous oxide, nitromethane, xylene, diethyl ether, polyethers, glycols, phenates, salicylates, sulfonates, nonylphenol ethoxylates, alkali detergents and alkaline earth metal-containing detergents, tall oil fatty acids, dodecenyl succinic acid, and oleic acid plus N,N dimethylcyclohexylamine, 2,6-di t-butyl phenol, methylcyclopentadienyl manganese tricarbonyl, oleic acid plus N,N dimethylcyclohexylamine, dodecenyl succinic acid, polyisobutylene amine dispersant, 1,2 propane diamine salicylaldehyde, cresol Mannich base dispersant, diethanol amide of isostearic acid, and 2-ethyl hexyl nitrate.

[0091] An exemplary fuel composition containing functional components, wherein each component is selected from non-persistent, non-bioaccumulative, and non-toxic materials is illustrated in the following table.

Table 1-Conventional Fuel Additives

Component	Example 1 (mass % based on finished fuel)	Example 2 (mass % based on finished fuel)
Dispersant	0 - 60	10 - 55
Demulsifier	0 - 15	0.1 - 5
Compatibilizer	0 - 10.0	0.01 - 5.0

(continued)

Component	Example 1 (mass % based on finished fuel)	Example 2 (mass % based on finished fuel)
	0 - 5.0	0 - 2.0
Combustion improver		
Antifoaming agent	0-5.0	0,001 - 0,15
Pour point depressant	0 - 5.0	0.01 - 1.5
Friction modifier	0 - 1.25	0.05 - 1.0
Seal swell agent	0 - 15	1.5 - 10
Carrier Fluid/Solvent	0 - 30.0	0.1 - 25.0
Fuel	**Balance**	**Balance**

[0092] The conventional additives indicated in Table I may be combined with one or more fuels and/or one or more base oils. Suitable fuels may comprise any known hydrocarbon fuel or mixtures thereof. Suitable fuels may include one or more of gasoline, diesel fuel, middle distillate fuel, biodiesel fuel, an alcohol, such as but not limited to an ethanol, bioethanol, a biobutanol, an aviation fuel, jet fuel, marine fuel, bunker fuel, burner fuel, home heating oil (for example, home heating oil no. 6), a gas-to-liquid (GTL) base oil, a Group I base oil, a Group II base oil, a Group III base oil, a Group IV base oil, an ester, a vegetable oil, and mixtures thereof.

Gasolines

[0093] The fuel used in the fuel composition embodiments of the present disclosure may comprise a petroleum hydrocarbon useful as a fuel, e.g., gasoline, for internal combustion engines. Such fuels typically comprise mixtures of hydrocarbons of various types, including straight and branched chain paraffins, olefins, aromatics, and naphthenic hydrocarbons, and other liquid hydrocarbonaceous materials suitable for spark ignition gasoline engines.

[0094] These compositions are provided in a number of grades, such as unleaded and leaded gasoline, and are typically derived from petroleum crude oil by conventional refining and blending processes such as straight run distillation, thermal cracking, hydrocracking, catalytic cracking, and various reforming processes. Gasoline may be defined as a mixture of liquid hydrocarbons or hydrocarbon-oxygenates having an initial boiling point in the range of about 20 to 60 °C and a final boiling point in the range of about 150 to 230 °C, as determined by the ASTM D86 distillation method. The gasoline may contain other combustibles such as alcohol, for example methanol or ethanol.

[0095] The combustible fuels used in formulating the fuel compositions of the present disclosure may include any combustible fuels suitable for use in the operation of direct injection gasoline engines such as leaded or unleaded motor gasolines, and so-called reformulated gasolines which typically contain both hydrocarbons of the gasoline boiling range and fuel-soluble oxygenated blending agents ("oxygenates"), such as alcohols, ethers, and other suitable oxygen-containing organic compounds. Preferably, the fuel is a mixture of hydrocarbons boiling in the gasoline boiling range. This fuel may consist of straight chain or branch chain paraffins, cycloparaffins, olefins, aromatic hydrocarbons, or any mixture of these. The gasoline can be derived from straight run naptha, polymer gasoline, natural gasoline, or from catalytically reformed stocks boiling in the range from about 80 to about 450 °F. The octane level of the gasoline is not critical and any conventional gasoline may be employed in the practice of this invention.

[0096] Oxygenates suitable for use in the present invention include methanol, ethanol, isopropanol, t-butanol, mixed C_1 to C_5 alcohols, methyl tertiary butyl ether, tertiary amyl methyl ether, ethyl tertiary butyl ether and mixed ethers. Oxygenates, when used, will normally be present in the base fuel in an amount below about 30% by volume, and preferably in an amount that provides an oxygen content in the overall fuel in the range of about 0.5 to about 5 percent by volume.

Diesel

[0097] Diesel fuel contains hydrocarbons having higher boiling points than those of gasoline. Diesel fuel generally has a distillation range between 320 °F to 715 °F (about 160 °C. and 380 °C.). Gasoline generally distills below this temperature range, e.g., between about 100 °F to 400 °F (about 40 °C. and 205 °C). Diesel fuels generally contain more sulfur and nitrogen than gasoline. Moreover, gasoline is designed to resist burning when compressed in the absence of a spark. Such burning is undesired because it causes knocking. Diesel fuel is the opposite. Diesel fuel must ignite spontaneously and quickly (within 1 to 2 milliseconds) without a spark. The time lag between the initiation of injection and the initiation of combustion is called ignition delay. In high-speed diesel engines, a fuel with a long ignition delay tends to produce rough operation and knocking. Two major factors affect ignition delay: a mechanical factor and a chemical factor.

[0098] The mechanical factor is influenced by such things as compression ratio, motion of the air charge during ignition, and ability of the fuel injector to atomize fuel. The differences between diesel engines and gasoline engines are reflected by how their mechanical factors are affected differently by changing the dimensions of their mechanical parts. For example, the larger the cylinder diameter of a diesel engine, the simpler the development of good combustion. In contrast, the smaller the cylinder of a gasoline engine, the less the danger of premature detonation of fuel. High intake-air temperature and density (provided by a supercharger) aid combustion in a diesel engine. In contrast, high intake-air temperature and density (provided by a supercharger) increases the tendency to knock, necessitating higher octane fuel, in a gasoline engine.

[0099] The chemical factor is influenced by such things as the fuel's auto ignition temperature, specific heat, density, and other physical properties. The ability of a diesel fuel to ignite quickly after injection into a cylinder is known as its cetane number. The ability of a gasoline to resist burning prior to introduction of a spark is known as its octane number. A higher cetane number is equivalent to a lower octane number. Diesel fuels generally have a clear cetane number, i.e., a cetane number when devoid of any cetane improver, in the range of 40 to 60.

Biodiesel

[0100] Biodiesel fuel may comprise alkyl esters made from the transesterification of vegetable oils or animal fats. Biodiesel is biodegradable and non-toxic, and typically produces less net carbon dioxide emissions than petroleum-based diesel. Biodiesel may be manufactured from algae, vegetable oils, animal fats, or recycled restaurant greases. Examples of biodiesel include rapeseed methyl ester, vegetable methyl ester, and fat methyl ester (produced from vegetable and animal products), Suitable crops that may be processed to yield biodiesel may include corn (maize), cashew nuts, oats, lupine, kenaf, calendula, cotton, hemp, soybeans, coffee, linseed (flax), hazelnuts, euphorbia, pumpkin seeds, coriander, mustard seeds, camelina, sesame, safflower, rice, tung tree oil, sunflowers, cocoa (cacao), peanuts, opium poppy, rapeseed, olives, castor beans or seeds, pecan nuts, jojoba, jatropha, macadamia nuts, Brazil nuts, avocado, coconuts, palm oil, Chinese tallow, Algae, and the like. Other suitable biodiesel feedstocks may comprise waste vegetable oil such as animal fats including tallow, lard, yellow grease, chicken fat, and the by-products of the production of Omega-3 fatty acids from fish oil. Another source is sewage.

[0101] Chemically, transesterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. Typically, methanol is used to produce methyl esters, although ethanol can be used to produce an ethyl ester biodiesel and higher alcohols such as isopropanol and butanol. A lipid transesterification production process may be used to convert the base oil to the desired esters. Any Free fatty acids (FFAs) in the base oil may be either converted to soap and removed from the process, or they may be esterified (yielding more biodiesel) using an acidic catalyst.

[0102] A diesel fuel may comprise petroleum diesel, biodiesel or biodiesel blended with petroleum diesel in any ratio of from 99:1 to 1:99 v/v.

Biobutanol

[0103] Biobutanol may be produced from biomass as well as fossil fuels. Butanol may be produced by fermentation of biomass. The feedstocks are similar to those for producing ethanol; namely, energy crops such as sugar beets, sugar cane, corn grain, wheat and cassava as well as agricultural byproducts such as straw and corn stalks.

Ethanol

[0104] Suitable fuels may comprise an ethanol. Ethanol comprises ethyl alcohol, having the chemical compound C_2H_5OH. This can arise in or be provided in many qualities or grades, such as commercial or fuel grade, as well as pure or reagent grade ethanol, and can be derived from any source such as but not limited to petroleum refinery streams, distillation cuts, and bio-derived (e.g. bioethanol from corn or other crops). In some embodiments, ethanol may be present in an amount of from about 10 to about 100 wt% based on the total fuel composition. In another embodiment, the ethanol may be present in an amount of from about 15 to about 85 wt% based on the total fuel composition. In an even further embodiment, the ethanol may be present in an amount of from about 74 to about 85 wt% based on the total fuel composition. In another embodiment herein is provided a fuel composition that can be, or can comprise, 1.0 to 100 volume percent of one or more alcohols, and 0 to 99% gasoline.

[0105] In some embodiments, the ethanol fuel may comprise an ethanol having about 0.9 PTB or less of a corrosion inhibitor, such as Innospec DCI-11 corrosion inhibitor. In some embodiments, the ethanol may comprise about 32 PTB of corrosion inhibitor, such as Innospec DCI-11 corrosion inhibitor.

[0106] Ethanol may be produced from fossil fuel feedstocks or by fermentation of sugars derived from grains or other biomass materials. Therefore, ethanol suitable for use in accordance with the fuel compositions described herein may be fuel grade ethanol derived from yeast or bacterial fermentation of starch-based sugars. Such starch-based sugars may be extracted from corn, sugarcane, tapioca, sugar beet, and the like. Alternatively, fuel grade ethanol may be produced via known dilute and/or concentrated acid and/or enzymatic hydrolysis of a particular biomass material for example, from waste industrial sources including, cellulosic portions of municipal solid waste, waste paper, paper sludge, saw dust, and the like, Biomass may also be collected from agricultural residues including, for example, rice husks and paper-mill sludge.

[0107] A suitable fuel grade ethanol may contain none or only contaminant levels of water. Alternatively, a suitable fuel grade ethanol may contain higher amounts of water, up to 5% w/w (hydrous ethanol).

Fuel Oil

[0108] Suitable fuel oils may comprise any of fuel oils in class numbers 1-6, including those otherwise mentioned herein, and mixtures thereof. Fuel oils may comprise distillates, residuals, or mixtures thereof. Fuel oil may comprise aviation fuel, jet fuel, marine fuel, burner fuel, bunker fuel, home heating oil, diesel fuel, turbine engine fuel, kerosene, range oil, and the like.

Base Oils

[0109] Suitable base oils may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. Such base oil groups are as follows:

Table 2 - Base Oil Groups

Base Oil Group [1]	Sulfur (wt.%)		Saturates (wt.%)	Viscosity Index
Group I	> 0.03	and/or	<90	80 to 120
Group II	< 0.03	and	> 90	80 to 120
Group III	< 0.03	and	> 90	> 120
Group IV	all polyalphaolefins (PAOs)			
Group V	all others not included in Groups I-IV			
[1]Groups I-III are mineral oil base stocks.				

[0110] In addition to the above conventional base oils, the base oils may also be selected from gas-to-liquid (GTL) base oils. GTL base oils may be made by a process, such as the process described in U.S. Patent No. 6,497,812, the disclosure of which is incorporated herein by reference. The GTL process includes two primary steps, (1) conversion of a material existing in the gaseous state into a synthesis gas consisting primarily of carbon monoxide and hydrogen, and the conversion of the synthesis gas into a synthetic crude in a reaction based on a Fischer-Tropsch reaction. Direct conversion of gaseous hydrocarbon sources using various catalysts and/or catalytic systems may also be used as the GTL process.

[0111] Base oils derived from a gaseous source, hereinafter referred to as "GTL base oils," typically have a viscosity index of greater than about 130, a sulfur content af less than about 0.3 percent by weight, contain greater than about 90 percent by weight saturated hydrocarbons (isoparaffins), typically from about 95 to about 100 wt.% branched aliphatic hydrocarbons, have a pour point of below -15 to -20°C., and have a NOACK volatility of less than about 15 weight percent, and in another embodiment a NOACK volatility of less than about 10 weight percent. Other characteristics of the GTL base oil may be within the range of conventional fuel base oils. The base oil component of the fuel composition, as described herein, may include from about 5 to about 100 percent by weight of the GTL base oil with the balance of the base oil component being a conventional base oil. Because of the characteristically high content of branched alkanes in the GTL base oils, finished fuel formulations made with such GTL base oils include a solubilizing agent that aids in solubilizing additives and degradation products in the finished fuel formulation. The GTL base oils may be used alone or may be mixed with any one or more of the other base oils listed in Table II above.

Carrier Fluids/Diluents

[0112] In some embodiments, the additives or additive package may be used with a liquid carrier or induction aid.

Suitable carrier fluids may include any base oil as defined herein. Further suitable carrier fluids can be of various types, such as for example liquid poly-alpha-olefin oligomers, mineral oils, liquid poly(oxyalkylene) compounds, liquid alcohols or polyols, polyalkenes, liquid esters, and similar liquid carriers. Mixtures of two or more such carriers can be employed.

[0113] Liquid carriers can include butane not limited to 1) a mineral oil or a blend of mineral oils that have a viscosity index of less than about 120, 2) one or more poly-alpha-olefin oligomers, 3) one or more poly(oxyalkylene) compounds having an average molecular weight in the range of about 500 to about 3000, 4) polyalkenes, 5) polyalkyl-substituted hydroxyaromatic compounds or 6) mixtures thereof. The mineral oil carriers that can be used include paraffinic, naphthenic, and asphaltic oils, and can be derived from various petroleum crude oils and processed in any suitable manner. For example, the mineral oils may be solvent extracted or hydrotreated oils. Reclaimed mineral oils can also be used. Hydrotreated oils may also be used. The mineral oil may have a viscosity at 40 °C of less than about 1600 SUS, and as another example, between about 300 and 1500 SUS at 40 °C. Paraffinic mineral oils may have viscosities at 40 °C in the range of about 475 SUS to about 700 SUS. The mineral oil may have a viscosity index of less than about 100, such as less than about 70, and further such as in the range of from about 30 to about 60.

[0114] Suitable poly-alpha-olefins (PAO) may comprise the hydrotreated and unhydrotreated poly-alpha-olefin oligomers, i.e., hydrogenated or unhydrogenated products, primarily trimers, tetramers, and pentamers of alpha-olefin monomers, which monomers contain from 6 to 12, generally 8 to 12, and in some instances about 10 carbon atoms. Their synthesis is outlined in Hydrocarbon Processing, February 1982, page 75 et seq., and in U.S. Pat. Nos. 3,763,244; 3,780,128; 4,172,855; 4,218,330; and 4,950,822. The usual process essentially comprises catalytic oligomerization of short chain linear alpha olefins (suitably obtained by catalytic treatment of ethylene). The poly-alpha-olefins used as carriers will usually have a viscosity (measured at 100 °C) in the range of 2 to 20 centistokes (cSt). As another example, the poly-alpha-olefin has a viscosity of at least 8 cSt, and as an even further example, about 10 cSt at 100 °C.

[0115] The poly (oxyalkylene) compounds which are among the carrier fluids for use in this invention are fuel-soluble compounds which can be represented by the following formula a R_1-$(R_2$-$O)_n$--R_3 wherein R_1 is typically a hydrogen, alkoxy, cycloalkoxy, hydroxy, amino, hydrocarbyl (e.g., alkyl, cycloalkyl, aryl, alkylaryl, aralkyl, etc.), amino-substituted hydrocarbyl, or hydroxy-substituted hydrocarbyl group, R_2 is an alkylene group having 2-10 carbon atoms (preferably 2-4 carbon atoms), R_3 is typically a hydrogen, alkoxy, cycloalkoxy, hydroxy, amino, hydrocarbyl (e.g., alkyl, cycloalkyl, aryl, alkylaryl, aralkyl, etc.), amino-substituted hydrocarbyl, or hydroxy-substituted hydrocarbyl group, and n is an integer from 1 to 500 and such as in the range of from 3 to 120 representing the number (usually an average number) of repeating alkyleneoxy groups. In compounds having multiple --R_2--O-- groups, R_2 can be the same or different alkylene group and where different, can be arranged randomly or in blocks. Suitable poly (oxyalkylene) compounds are monools comprised of repeating units formed by reacting an alcohol with one or more alkylene oxides, preferably one alkylene oxide.

[0116] The average molecular weight of the poly (oxyalkylene) compounds used as carrier fluids may be in the range of from about 500 to about 3000, such as from about 750 to about 2500, and further such as from above about 1000 to about 2000.

[0117] A useful sub-group of poly (oxyalkylene) compounds is comprised of the hydrocarbyl-terminated poly(oxyalkylene) monools such as are referred to in the passage at column 6, line 20 to column 7 line 14 of U.S. Pat. No. 4,877,416 and references cited in that passage, said passage and said references being fully incorporated herein by reference.

[0118] A suitable sub-group of poly (oxyalkylene) compounds is comprised of one or a mixture of alkyl poly (oxyalkylene) monools which in its undiluted state is a gasoline-soluble liquid having a viscosity of at least about 70 centistokes (cSt) at 40 °C and at least about 13 cSt at 100°C. Of these compounds, monools formed by propoxylation of one or a mixture of alkanols having at least about 8 carbon atoms, and as another example in the range of about 10 to about 18 carbon atoms, are suitable.

[0119] The poly (oxyalkylene) carriers used in the practice of this invention may have viscosities in their undiluted state of at least about 60 cSt at 40 °C (as another example at least about 70 cSt at 40 °C) and at least about 11 cSt at 100 °C (as another example at least about 13 cSt at 100 °C). In addition, the poly (oxyalkylene) compounds used in the practice of this invention may have viscosities in their undiluted state of no more than about 400 cSt at 40 °C and no more than about 50 cSt at 100 °C. As another example, their viscosities will not exceed about 300 cSt at 40 °C and will not exceed about 40 cSt at 100 °C.

[0120] Suitable poly (oxyalkylene) compounds also include poly (oxyalkylene) glycol compounds and mono ether derivatives thereof that satisfy the above viscosity requirements and that are comprised of repeating units formed by reacting an alcohol or polyalcohol with an alkylene oxide, such as propylene oxide and/or butylene oxide with or without use of ethylene oxide, and especially products in which at least 80 mole % of the oxyalkylene groups in the molecule are derived from 1,2-propylene oxide. Details concerning preparation of such poly(oxyalkylene) compounds are referred to, for example, in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, Volume 18, pages 633-645 (Copyright 1982 by John Wiley & Sons), and in references cited therein, the foregoing excerpt of the Kirk-Othmer encyclopedia and the references cited therein being incorporated herein in total by reference. U.S. Pat. Nos. 2,425,755; 2,425,845; 2,448,664; and 2,457,139 also describe such procedures, and are fully incorporated herein by reference.

[0121] The poly (oxyalkylene) compounds, when used, may contain a sufficient number of branched oxyalkylene units (e.g., methyldimethyleneoxy units and/or ethyldimethyleneoxy units) to render the poly (oxyalkylene) compound gasoline soluble.

[0122] Suitable poly (oxyalkylene) compounds for use in the present invention include those taught in U.S. Pat. Nos. 5,514,190; 5,634,951; 5,697,988; 5,725,612; 5,814,111 and 5,873,917, the disclosures of which are incorporated herein by reference.

[0123] Suitable polyalkenes may also include polypropene and polybutene. The polyalkenes may have a molecular weight distribution (Mw/Mn) of less than 4. In an embodiment, the polyalkenes may have a MWD of 1.4 or below. Suitable polybutenes have a number average molecular weight (Mn) of from about 500 to about 2000, such as 600 to about 1000, as determined by gel permeation chromatography (GPC). Suitable polyalkenes for use in the present invention are taught in U.S. Pat. No. 6,048,373, which descriptions are incorporated herein by reference.

[0124] The polyalkyl-substituted hydroxyaromatic compounds suitable for use in the present invention include those compounds known in the art as taught in U.S. Pat. Nos. 3,849,085; 4,231,759; 4,238,628; 5,300,701; 5,755,835 and 5,873,917, the disclosures of which are incorporated herein by reference.

Anti-Icing Agents

[0125] Various compounds known for anti-icing may be utilized in the present embodiments. For example, suitable anti-icing agents may comprise ether polymers, glycols, and alcohols.

Antioxidants

[0126] Various compounds known for use as oxidation inhibitors can be utilized in embodiments disclosed herein. These include phenolic antioxidants, amine antioxidants, sulfurized phenolic compounds, aromatic amine antioxidants, and organic phosphites, among others. The antioxidant may be composed predominantly or entirely of either (1) a hindered phenol antioxidant such as 2-tert-butylphenol, liquid mixtures of tertiary butylated phenols, 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4,4'-methylenebis-(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), mixed methylene-bridged polyalkyl phenols, 4,4'-thiobis(2-methyl-6-tert-butyl phenol), and mixed methylene bridged polyalkyl phenols, or (2) an aromatic amine antioxidant such as the cycloalkyl-di-lower alkyl amines, and phenylenediamines, or a combination of one or more such phenolic antioxidants with one or more such amine antioxidants, or N,N'-di-sec-butyl-p-phenylenediamine, 4-isopropylaminodiphenyl amine, phenyl-naphthyl amine, phenyl-naphthyl amine, and ring-alkylated diphenylamines. Suitable antioxidants may comprise tertiary butyl phenols, such as 2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, o-tertbutylphenol.

Cold Flow Improvers

[0127] Suitable cold flow improvers may comprise ethylene-unsaturated ester copolymers, comb polymers, nitrogen-containing polar compounds, hydrocarbon polymers, linear compounds, and mixtures of any of these. Cold flow improvers which may be used are known in the art and are commercially available from a number of sources. As used herein the term "cold flow improver" also includes pour point depressants, wax crystal modifiers, and wax anti-settling additives of the types usually added to middle distillate fuels to improve low temperature properties. Such materials are known in the art and are commercially available.

[0128] Examples of cold flow improvers include copolymers of ethylene with ethylenically unsaturated esters, or derivatives thereof. Thus, the copolymer may be of ethylene with an ester of a saturated alcohol and an unsaturated carboxylic acid or, for example, the ester of an unsaturated alcohol with a saturated carboxylic acid. The use of ethylene-vinyl ester copolymers is suitable, as further examples, ethylene-vinyl acetate, ethylene-vinyl propionate, ethylene-vinyl hexanoate, and ethylene-vinyl octanoate copolymers are also suitable.

[0129] The copolymers usually contains from 1 to 40 wt %, as another example from 5 to 35 wt %, as an even further example from 10 to 35 wt % vinyl ester. Mixtures of two or more copolymers may also be used (see U. S. Pat. No. 3,961,916).

[0130] The number average molecular weight of the copolymer, as measured by vapor phase osmometry, is typically 1,000 to 10,000 or as another example 1,000 to 5,000. If desired, the copolymer may contain units derived from additional comonomers, e.g. a terpolymer, tetrapolymer, or a higher polymer, for example where the additional comonomer is isobutylene or diisobutylene.

[0131] The copolymers may be made by direct polymerization of comonomers, by transesterification, or by hydrolysis and re-esterifcation, of an ethylene unsaturated ester copolymer to give a different ethylene unsaturated ester copolymer.

[0132] Comb polymers are polymers in which branches containing hydrocarbyl groups are pendant from a polymer backbone (see "Comb-Like Polymers. Structure and Properties", N. A. Plate et al. Poly. Sci. Macromolecular Revs., 8, pages 117 to 253 (1974)).

[0133] The hydrocarbyl groups may have from 10 to 30 carbon atoms and are bonded directly or indirectly to the polymer backbone. Examples of indirect bonding include bonding via interposed atoms or groups. This can include covalent and/or electrovalent bonding such as in a salt.

[0134] The comb polymer is typically a homopolymer or a copolymer having at least 20 and as another example at least 40, and as an even further example at least 50, mole % of units having side branches containing at least 6, and as another example at least 10, carbon atoms. It is possible for the comb polymer to contain units derived from other monomers.

[0135] Examples of comb polymers which may be used include homopolymers of, for example fumaric or itaconic acid, and copolymers of maleic anhydride, fumaric acid or itaconic acid with another ethylenically unsaturated monomer, such as an alpha-olefin, for example 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene or an unsaturated ester, for example, vinyl acetate. The copolymer may be esterified by reaction with an alcohol such as n-decan-1-ol, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, n-octadecan-1-ol, 1-methylpentadecan-1-ol, or 2-methyltridecan-1-ol. Mixtures of alcohols may be used although it is typical to use pure alcohols rather than the commercially available alcohol mixtures.

[0136] Comb polymers such as the fumarate and itaconate polymers and copolymers are described in EP-A-153176, EP-A-153177, EP-A-225688, WO 91/16407, WO 95/03377, and WO 95/33805.

[0137] Suitable fumarate comb polymers are copolymers of (C_{12-20} alkyl) fumarates with vinyl acetate, especially those in which the alkyl groups have 14 carbon atoms or in which the alkyl groups are a mixture of C_{14} /C_{16} alkyl groups. These may be made by known techniques.

[0138] Other suitable comb polymers which may be used include the polymers and copolymers of a-olefins and esterified copolymers of styrene and maleic anhydride and esterified copolymers of styrene and fumaric acid.

[0139] Useful comb polymers may have a number average molecular weight, as measured by vapor phase osmometry, of 1,000 to 100,000, or as another example 1,000 to 30,000.

[0140] Polar nitrogen compounds which may be used as cold flow improvers are known in the art and usually contain one or more of the same or different nitrogen-bound hydrocarbyl groups, possibly in the form of a a cation.

[0141] The hydrocarbyl groups generally contain up to 40 carbon atoms. Examples of hydrocarbyl groups include aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic-substituted aromatic, and aromatic-substituted aliphatic and alicyclic group Aliphatic groups typically contain 12 to 24 carbon atoms and are advantageously saturated.

[0142] The hydrocarbyl groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group, such as keto, halo, hydroxy, nitro, cyano, alkoxy, and acyl groups. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred. Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl and propoxypropyl.

[0143] The hydrocarbyl groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include nitrogen, sulphur, and oxygen. The hydrocarbyl group may be bound to one or more nitrogen atoms via an intermediate linking group such as --CO--, --CO_2 (--), --SO_3 (--) or hydrocarbylene. When the polar nitrogen compound carries more than one nitrogen-bound substituent, the linking groups for each substituent may be the same or different.

[0144] The polar nitrogen compounds may contain amino substituents such as long chain C_{12} -C_{40}, alkyl primary, secondary, tertiary or quaternary amino substituents. The amino substituent may be a dialkylamino substituent which may be in the form of an amine salt thereof (tertiary and quaternary amines can form only amine salts). The alkyl groups may be the same or different.

[0145] Examples of primary amino substituents include dodecylamino, tetradecylamino, cocoamino, and hydrogenated tallow amino. Examples of secondary amino substituents include dioctadecylamino and methylbehenylamino. Mixtures of amino substituents may be present such as those derived from naturally occurring amines. A preferred amino substituent is the secondary hydrogenated tallow amino substituent, the alkyl groups of which are derived from hydrogenated tallow fat. These are typically composed of approximately 4% C_{14}, 31% C_{16} and 59% C_{18} n-alkyl groups by weight.

[0146] The polar nitrogen compounds may contain imino substituents such as long chain C_{12} -C_{40} alkyl substituents. The substituents may be monomeric (cyclic or non-cyclic) or polymeric. When non-cyclic, the substituent may be obtained from a cyclic precursor such as an anhydride. The cyclic precursor may include homocyclic, heterocyclic, or fused polycyclic assemblies, or a system where two or more identical or different such cyclic assemblies are joined to one another. Where there are two or more such cyclic assemblies, the substituents may be on the same or different assemblies. Each cyclic assembly may be aromatic or may comprise a benzene ring. The cyclic ring system may comprise a single benzene ring having substituents in the ortho- or meta-positions. The benzene ring may be optionally further substituted. The ring atoms in the cyclic assembly or assemblies may for example include one or more N, S or O atom.

[0147] Examples of polycyclic assemblies include: (a) condensed benzene structures such as naphthalene, anthracene, phenanthrene, and pyrene; (b) condensed ring structures such as azulene, indene, hydroindene, fluorine, and diphenylene oxides; (c) joined rings such as diphenyl; (d) heterocyclic compounds such as quinoline, indole, 2,3-dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophen, carbazole, and thiodiphenylamine; (e) partially saturated or non-aromatic ring systems such as decalin (i.e. decahydronaphthalene), alpha.-pinene, cardinene, and bomylene; and (f) three-dimensional structures such as norbornene, bicycloheptane (i.e. norbomane), bicyclooctane, and bicyclooctene.

[0148] Further and specific examples of polar nitrogen compounds which may be used in the present embodiments can be found in the art for example in U.S. Pat. No. 4,211,534, U.S. Pat. No. 4,147,520, U.S. Pat. No. 4,631,071, U.S. Pat. No. 4,639,256, DE-A-3,916,366, EP-A-413,279, EP-A-0,261,957, EP-A-272,889, EP-A-31b,108, GB-A-2,121,807, FR-A-2,592,387, DE-A-941,561, EP-A-283,292 and EP-A-353,981.

[0149] Hydrocarbon polymer cold flow improvers are known from for example WO 91/11488, WO 95/03377, and WO 95/33805.

[0150] The hydrocarbon polymers may be made directly from monoethylenically unsaturated monomers or indirectly by hydrogenating polymers from polyunsaturated monomers, e.g. isoprene and butadiene.

[0151] Also suitable are ethylene a-olefin copolymers having a number average molecular weight of at least 30,000 as measured by gel permeation chromatography (GPC) relative to polystyrene standards. Viscosity mixing difficulties may arise when the molecular weight is above about 150,000.

[0152] The alpha-olefin may have at most 30 carbon atoms. Examples of such include propylene, 1-butene, isobutene, n-octene-1, isooctene-1, n-decene-1, and n-dodecene-1. The copolymer may also comprise small amounts, e.g. up to 10% by weight, of other copolymerisable monomers, for example olefins other than alpha-olefins, and non-conjugated dienes. The preferred copolymer is an ethylene-propylene copolymer.

[0153] Usually, the copolymer has a molar ethylene content of between 50 and 85%, preferably 60 to 75%, and most preferably 65 to 70%.

[0154] The ethylene a-olefin copolymers may be ethylene-propylene copolymers with a number average molecular weight in the range 60,000 to 120,000, such as from 80,000 to 100,000.

[0155] The hydrocarbon polymers may be prepared by any of the methods known in the art, for example, using a Ziegler type catalyst. The polymers may be substantially amorphous, since highly crystalline polymers are relatively insoluble in fuel oil at low temperatures.

[0156] Other suitable hydrocarbon polymers include low molecular weight ethylene-a-olefin copolymers, typically with a number average molecular weight (by GPC) of at most 7500, for example from 1,000 to 6,000, such as from 2,000 to 5,000, as measured by vapor phase osmometry. Appropriate alpha-olefins are as given above. Styrene may also be used.

[0157] Linear cold flow improver compounds typically comprise a compound in which at least one substantially linear alkyl group having 10 to 30 carbon atoms is linked via an optional linking group to a non-polymeric residue, such as an inorganic residue, to provide at least one linear chain of atoms that includes the carbon atoms of the alkyl groups and one or more non-terminal oxygen, sulphur, and/or nitrogen atoms. The linking group may be polymeric. Polyoxyalkylene compounds are frequently used.

[0158] By substantially linear" is meant that the alkyl group is straight chain although alkyl groups having a small degree of branching such as in the form of a single methyl group branch may be used.

[0159] The oxygen atom or atoms, if present, may be directly interposed between carbon atoms in the chain and may be provided in the linking group, if present, in the form of a mono-or poly-oxyalkylene group, the oxyalkylene group may have 2 to 4 carbon atoms. Examples include oxyethylene and oxypropylene.

[0160] The linear compound may be an ester, the alkyl groups of which may be derived from an acid and the remainder of the compound may be derived from a polyhydric alcohol or vice-versa. Alternatively, the linear compound may be an ether or a mixed ester/ether, It may contain different ester groups.

[0161] Examples of linear compounds which may be used include polyoxyalkylene esters, ethers, ester/ethers, and mixtures thereof, particularly those containing at least one, and in some cases at least two, C_{10-30} linear alkyl groups and a polyoxyalkylene glycol group of number average molecular weight (by GPC) up to 5,000, such as 200 to 5,000 (see EP-A-61895 and in U.S. Pat. No. 4,491,455).

[0162] Polyoxyalkylene diesters, diethers, ether/esters, and mixtures thereof are also suitable as the cold flow improver. Suitable examples include the stearic or behenic diesters of polyethylene glycol, polypropylene glycol, or polyethylene/polypropylene glycol mixtures.

[0163] Examples of other linear cold flow improver compounds are described in Japanese Patent Publications Nos. 2-51477 and 3-34790, EP-A-117,108, EP-A-326,356, WO 95/03377, and WO 95/33805. Cyclic esterified ethoxylates are described in EP-A-356,256.

[0164] As noted above, mixtures of these cold flow improvers may be use, for example mixtures of ethylene-unsaturated ester copolymers and comb polymers, for example a mixture of an ethylene-vinyl acetate copolymer and a fumarate comb polymer.

Combustion Improvers

[0165] Suitable combustion improvers may comprise one or more of a manganese compound, ferrocene, platinum, cerium, cerium oxide, and the like. For example, a non-limiting example of a useful manganese compound is an alkylcycloalkyldienyl manganese tricarbonyl, such as methylcyclopentadienyl manganese tricarbonyl. It generally is added in treat rates of about 0.0156 to about 0.125 gram of manganese per gallon of fuel.

[0166] Cyclopentadienyl manganese tricarbonyl compounds such as methylcyclopentadienyl manganese tricarbonyl are suitable combustion improvers because of their outstanding ability to reduce tailpipe emissions such as NO_x and smog forming precursors and to significantly improve the octane quality of gasolines, both of the conventional variety and of the "reformulated" types.

Corrosion Inhibitors

[0167] A variety of materials are available for use as corrosion inhibitors in the practice of embodiments disclosed herein. Thus, use can be made of dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Another useful type of corrosion inhibitor for use in the practice of this invention are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Further suitable materials are the aminosuccinic acids or derivatives thereof, such as a tetralkenyl succinic acid.

Demulsifiers

[0168] A wide variety of demulsifiers may be suitable for use with embodiments disclosed herein, including, for example, polyoxyalkylene glycols, oxyalkylated phenolic resins, and like materials.

Detergents

[0169] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or corrosion inhibitors, thereby reducing wear, deposits and corrosion and extending engine life for engines combusting fuel formulations. Detergents generally comprise a polar head with a long hydrophobic tail where the polar head comprises a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal, in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as measured by ASTM D2896) of from 0 to less than 150. Large amounts of a metal base may be included by reacting an excess of a metal compound such as an oxide or hydroxide with an acidic gas such as carbon dioxide. The resulting overbased detergent comprise micelles of neutralized detergent surrounding a core of inorganic metal base (e.g., hydrated carbonates). Such overbased detergents may have a TBN of 150 or greater, and typically ranging from 250 to 450 or more.

[0170] Suitable detergents for use in some embodiments may comprise one or more of Mannich base detergents, polyetheramines, and combinations thereof.

[0171] Suitable Mannich base detergents may comprise the reaction products of an alkyl-substituted hydroxy aromatic compound, aldehydes, and amines. The alkyl-substituted hydroxyaromatic compound, aldehydes and amines used in making the Mannich reaction products of the present invention may be any such compounds known and applied in the art, in accordance with the foregoing limitations.

[0172] Representative alkyl-substituted hydroxyaromatic compounds that may be used in forming the present Mannich base products are polypropylphenol (formed by alkylating phenol with polypropylene), polybutylphenols (formed by alkylating phenol with polybutenes and/or polyisobutylene), and polybutyl-co-polypropylphenols (formed by alkylating phenol with a copolymer of butylene and/or butylene and propylene). Other similar long-chain alkylphenols may also be used. Examples include phenols alkylated with copolymers of butylene and/or isobutylene and/or propylene, and one or more mono-olefinic comonomers copolymerizable therewith (e.g., ethylene, 1-pentene, 1-hexene, 1-octene, 1-decene, etc.) where the copolymer molecule contains at least 50% by weight, of butylene and/or isobutylene and/or propylene units. The comonomers polymerized with propylene or such butenes may be aliphatic and can also contain non-aliphatic groups, e.g., styrene, o-methylstyrene, p-methylstyrene, divinyl benzene and the like. Thus in any case the resulting polymers and copolymers used in forming the alkyl-substituted hydroxyaromatic compounds are substantially aliphatic hydrocarbon polymers.

[0173] In some embodiments, polybutylphenol (formed by alkylating phenol with polybutylene) may be used in forming the Mannich base detergent. Unless otherwise specified herein, the term "polybutylene" is used in a generic sense to include polymers made from "pure" or "substantially pure" 1-butene or isobutene, and polymers made from mixtures of two or all three of 1-butene, 2-butene, and isobutene. Commercial grades of such polymers may also contain insignificant amounts of other olefins. So-called high reactivity polybutylenes having relatively high proportions of polymer molecules having a terminal vinylidene group, formed by methods such as described, for example, in U.S. Pat. No. 4,152,499 and W. German Offenlegungsschrift 29 04 314, are also suitable for use in forming the long chain alkylated phenol reactant.

[0174] The alkylation of the hydroxyaromatic compound is typically performed in the presence of an alkylating catalyst at a temperature in the range of about 50 to about 200 °C. Acidic catalysts are generally used to promote Friedel-Crafts alkylation. Typical catalysts used in commercial production include sulphuric acid, BF_3, aluminum phenoxide, methanesulphonic acid, cationic exchange resin, acidic clays, and modified zeolites.

[0175] The long chain alkyl substituents on the benzene ring of the phenolic compound are derived from polyolefin having a number average molecular weight (MW of from about 500 to about 3000 (preferably from about 500 to about 2100) as determined by gel permeation chromatography (GPC). It is also preferred that the polyolefin used have a polydispersity (weight average molecular weight/number average molecular weight) in the range of about 1 to about 4 (preferably from about 1 to about 2) as determined by GPC.

[0176] The Mannich detergent may be made from a long chain alkylphenol. However, other phenolic compounds may be used including high molecular weight alkyl-substituted derivatives ofresorcinol, hydroquinone, catechol, hydroxydiphenyl, benzylphenol, phenethylphenol, naphthol, tolylnaphthol, among others. Preferred for the preparation of the Mannich condensation products are the polyalkylphenol and polyalkylcresol reactants, e.g., polypropylphenol, polybutylphenol, polypropyleresol, and polybutylcresol, wherein the alkyl group has a number average molecular weight of about 500 to about 2100, while the most preferred alkyl group is a polybutyl group derived from polybutylene having a number average molecular weight in the range of about 800 to about 1300.

[0177] The preferred configuration of the alkyl-substituted hydroxyaromatic compound is that of a para-substituted mono-alkylphenol or a para-substituted mono-alkyl ortho-cresol. However, any alkylphenol readily reactive in the Mannich condensation reaction may be employed. Thus, Mannich products made from alkylphenols having only one ring alkyl substituent, or two or more ring alkyl substituents are suitable. The long chain alkyl substituents may contain some residual unsaturation, but in general, are substantially saturated alkyl groups.

[0178] Representative amine reactants include, but are not limited to, linear, branched, or cyclic alkylene monoamines or polyamines having at least one suitably reactive primary or secondary amino group in the molecule. Other substituents such as hydroxyl, cyano, amido, etc., can be present in the amine. In some embodiments, the alkylene polyamine is a polyethylene polyamine. Suitable alkylene polyamine reactants include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethyleneheptamine, heptaethyleneoctamine, octaethylenenonamine, nonaethylenedecamine, decaethyleneundecamine and mixtures of such amines having nitrogen contents corresponding to alkylene polyamines of the formula $H_2N\text{-}(A\text{-}NH\text{--})_nH$, where A is divalent ethylene or propylene and n is an integer of from 1 to 10. The alkylene polyamines may be obtained by the reaction of ammonia and dihaloalkanes, such as dichloro alkanes. Thus, the alkylene polyamines obtained from the reaction of 2 to 11 moles of ammonia with 1 to 10 moles of dichloro alkanes having 2 to 6 carbon atoms and the chlorines on different carbon atoms are suitable alkylene polyamine reactants.

[0179] In another preferred embodiment of the present invention, the amine is an aliphatic linear, branched, or cyclic diamine having one primary or secondary amino group and one tertiary amino group in the molecule. Examples of suitable polyamines include N,N,N",N"-tetraalkyl-dialkylenetriamines (two terminal tertiary amino groups and one central secondary amino group), N,N,N',N"-tetraalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), N,N,N',N",N"'-pentaalkyltrialkylene-tetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal secondary amino group), N,N-dihydroxyalkyl-alpha, omega-alkylenediamines (one terminal tertiary amino group and one terminal primary amino group), N,N,N'-trihydroxy-alkyl-alpha, omega-alkylenediamines (one terminal tertiary amino group and one terminal secondary amino group), tris(dialkylaminoalkyl)aminoalkylmethanes (three terminal tertiary amino groups and one terminal primary amino group), and like compounds, wherein the alkyl groups are the same or different and typically contain no more than about 12 carbon atoms each, and which preferably contain from 1 to 4 carbon atoms each. These alkyl groups are typically methyl and/or ethyl groups. Typical polyamine reactants are N,N-dialkyl-alpha, omega-alkylenediamine, such as those having from 3 to about 6 carbon atoms in the alkylene group and from 1 to about 12 carbon atoms in each of the alkyl groups, which most preferably are the same but which can be different. Also suitable is N,N-dimethyl-1,3-propanediamine and N-methyl piperazine.

[0180] Examples of polyamines having one reactive primary or secondary amino group that can participate in the Mannich condensation reaction, and at least one sterically hindered amino group that cannot participate directly in the Mannich condensation reaction to any appreciable extent include N-(tert-butyl)-1,3-propanediamine, N-neopentyl-1,3-propanediamine, N-(tert-butyl)-1-methyl-1,2-ethanediamine, N-(tert-butyl)-1-methyl-1,3-propanediamine, and 3,5-di (tert-butyl)aminoethy-1-piperazine.

[0181] Representative aldehydes for use in the preparation of the Mannich base products include the aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, and stearaldehyde. Aromatic aldehydes which may be used include benzaldehyde and salicylaldehyde. Illustrative heterocyclic aldehydes for use herein are furfural and thiophene aldehyde, etc. Also useful are formaldehyde-producing reagents such as paraformaldehyde, or aqueous formaldehyde solutions such as formalin.

[0182] The condensation reaction among the alkylphenol, the specified amine(s) and the aldehyde may be conducted at a temperature in the range of about 40 to about 200°C. The reaction can be conducted in bulk (no diluent or solvent) or in a solvent or diluent. Water is evolved and can be removed by azeotropic distillation during the course of the reaction. Typically, the Mannich reaction products are formed by reacting the alkyl-substituted hydroxyaromatic compound, the amine and aldehyde in the molar ratio of 1.0:0.5-2.0:1.0-3.0, respectively.

[0183] Suitable Mannich base detergents may also include those detergents taught in U.S. Pat. Nos. 4,231,759; 5,514,190; 5,634,951; 5,697,988; 5,725,612; and 5,876,468, the disclosures of which are incorporated herein by reference.

[0184] Preparation of polyetheramine compounds useful as the detergent is described in the literature, for example, U.S. Pat. No., the disclosure of which is incorporated herein in its entirety.

[0185] Suitable polyetheramines may comprise "single molecule" additives, incorporating both amine and polyether functionalities within the same molecule. The polyether backbone can in one embodiment herein be based on propylene oxide, ethylene oxide, butylene oxide, or mixtures of these. The polyetheramines can be monoamines, diamines, or triamines.

[0186] Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, and salicylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which may both be present. Mixtures of calcium and/or magnesium with sodium are also useful. Particularly convenient metal detergents are neutral and overbased calcium or magnesium sulfonates having a TBN of from 20 to 450 TBN, neutral and overbased calcium or magnesium phenates and sulfurized phenates having a TBN of from 50 to 450, and neutral or overbased calcium or magnesium salicylates having a TBN of from 130 to 350. Mixtures of such salts may also be used. When used, the presence of at least one overbased detergent is desirable.

[0187] Sulfonates may be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples include those obtained by alkylating benzene, toluene, xylene, naphthalene, diphenyl or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation may be carried out in the presence of a catalyst with alkylating agents having from 3 to more than 70 carbon atoms. The alkaryl sulfonates usually contain from 9 to 80 or more carbon atoms, typically from 16 to 60 carbon atoms per alkyl substituted aromatic moiety.

[0188] The oil-soluble sulfonates or alkaryl sulfonic acids may be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulphides, hydrosulfides, nitrates, borates and ethers of the alkali metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from 100 to 220 wt % (desirably at least 125 wt %) of that stoichiometrically required.

[0189] Metal salts of alkyl phenols and sulfurized alkyl phenols are prepared by reaction with an appropriate metal compound such as an oxide, hydroxide or alkoxide, and overbased products may be obtained by methods well known in the art. Sulfurized alkyl phenols may be prepared by reacting an alkyl phenol with sulphur or a sulphur-containing compound such as hydrogen sulphide, sulphur monohalide or sulphur dihalide, to form products which are generally mixtures of compounds in which 2 or more phenols are bridged by sulphur-containing bridges. The starting alkyl phenol may contain one or more alkyl substituents. These may be branched or unbranched, and depending on the number of substituents may have from 1 to 30 carbon atoms (provided the resulting alkyl phenol is oil-soluble), with from 9 to 18 carbon atoms being particularly suitable. Mixtures of alkyl phenols with different alkyl substituents may be used.

[0190] Metal salts of carboxylic acids (including salicylic acids) may be prepared in a number of ways: for example, by adding a basic metal compound to a reaction mixture comprising the carboxylic acid (which may be part of a mixture with another organic acid such as a sulfonic acid) or its metal salt and promoter, and removing free water from the reaction mixture to form an metal salt, then adding more basic metal compound to the reaction mixture and removing free water from the reaction mixture. The carboxylate is then overbased by introducing the acidic material such as carbon dioxide to the reaction mixture while removing water. This can be repeated until a product of the desired TBN is obtained.

[0191] The overbasing process is well known in the art and typically comprises reacting acidic material with a reaction mixture comprising the organic acid or its metal salt, a metal compound. That acidic material may be a gas such as carbon dioxide or sulphur dioxide, or it may be boric acid. Processes for the preparation of overbased alkali metal sulfonates and phenates are described in U.S. Pat. No. 4,839,094. A process suitable for overbased sodium sulfonates is described in EP-A-235929. A process for making overbased salicylates is described in U.S. Pat. No. 5,451,331.

Deposit Inhibitor Compound/Dispersants

[0192] The dispersants useful in the fuel compositions described herein include at least one oil-soluble ashless dispersant having a basic nitrogen and/or at least one hydroxyl group in the molecule. Suitable dispersants include alkenyl succinimides, alkenyl succinic acid esters, alkenyl succinic ester-amides, and Mannich bases.

[0193] Suitable succinimides, for example, include alkenyl succinimides comprising the reaction products obtained by reacting an alkenyl succinic anhydride, acid, acid-ester or lower alkyl ester with an amine containing at least one primary amine group. Representative non-limiting examples are given in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,219,666; 3,272,746, 3,254,025,3,216,936, 4,234,435; and 5,575,823. The alkenyl succinic anhydride may be prepared readily by heating a mixture of olefin and maleic anhydride to about 180-220 °C.The olefin is, in an embodiment, a polymer or copolymer of a lower monoolefin such as ethylene, propylene, isobutene and the like. In another embodiment the source of alkenyl goup is from polyisobutene having a molecular weight up to 10,000 or higher. In another embodiment the alkenyl is a polyisobutene group having a molecular weight of about 200-5,000 or, in another example, about 700-2,100.

[0194] Amines which may be employed include any that have at least one primary amine group which can react to form an imide group. A few representative examples are: methylamine, 2-ethylhexylamine, n-dodecylamine, stearylamine, N,N-dimethyl-propanediamine, N-(3-aminopropyl)morpholine, N-dodecyl propanediamine, N-aminopropyl piperazine ethanolamine, N-ethanol ethylene diamine and the like. Other suitable amines include the alkylene polyamines such as propylene diamine, dipropylene triamine, di-(1,2-butylene)-triamine, tetra-(1,2-propylene)pentaamine.

[0195] In one embodiment the amines are the ethylene polyamines that have the formula $H_2N(CH_2CH_2NH)_nH$ wherein n is an integer from one to ten. These ethylene polyamines include ethylene diamine, diethylene triamine, triethylene tetraamine, tetraethylene pentaamine, pentaethylene hexaamine, and the like, including mixtures thereof in which case n is the average value of the mixture. These ethylene polyamines have a primary amine group at each end so can form mono-alkenylsuccinimides and bis-alkenylsuccinimides.

[0196] Thus ashless dispersants for use in the present invention also include the products of reaction of a polyethylenepolyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon substituted carboxylic acid or anhydride made by reaction of a polyolefin, such as polyisobutene, having a molecular weight of 500 to 5,000, especially 700 to 2000, with an unsaturated polycarboxylic acid or anhydride, e.g. maleic anhydride.

[0197] Also suitable for use as the succinimides are succinimide-amides prepared by reacting a succinimide-acid with a polyamine or partially alkoxylated polyamine, as taught in U.S. Pat. No. 6,548,458. The succinimide-acid compounds of the present invention are prepared by reacting an alpha-omega amino acid with an alkenyl or alkyl-substituted succinic anhydride in a suitable reaction media. Suitable reaction media include, but are not limited to, an organic solvent, such as toluene, or process oil. Water is a by-product of this reaction. The use of toluene allows for azeotropic removal of water.

[0198] The mole ratio of maleic anhydride to olefin can vary widely. It may vary, in one example, from 5:1 to 1:5, and in another example the range is 3:1 to 1:3 and in yet another embodiment the maleic anhydride is used in stoichiometric excess, e.g. 1.1 to 5 moles maleic anhydride per mole of olefin. The unreacted maleic anhydride can be vaporized from the resultant reaction mixture.

[0199] The alkyl or alkenyl-substituted succinic anhydrides may be prepared by the reaction of maleic anhydride with the desired polyolefin or chlorinated polyolefin, under reaction conditions well known in the art. For example, such succinic anhydrides may be prepared by the thermal reaction of a polyolefin and maleic anhydride, as described, for example in U.S. Pat. Nos. 3,361,673 and 3,676,089. Alternatively, the substituted succinic anhydrides can be prepared by the reaction of chlorinated polyolefins with maleic anhydride, as described, for example, in U.S. Pat. No. 3,172,892. A further discussion of hydrocarbyl-substituted succinic anhydrides can be found, for example, in U.S. Pat. Nos. 4,234,435; 5,620,486 and 5,393,309.

[0200] Polyalkenyl succinic anhydrides may be converted to polyalkyl succinic anhydrides by using conventional reducing conditions such as catalytic hydrogenation. For catalytic hydrogenation, a suitable catalyst is palladium on carbon. Likewise, polyalkenyl succinimides may be converted to polyalkyl succinimides using similar reducing conditions.

[0201] The polyalkyl or polyalkenyl substituent on the succinic anhydrides employed in the invention is generally derived from polyolefins which are polymers or copolymers of mono-olefins, particularly 1-mono-olefins, such as ethylene, propylene, butylene, and the like. The mono-olefin employed may have 2 to about 24 carbon atoms, or as another example, about 3 to 12 carbon atoms. Also, the mono-olefins can include propylene, butylene, particularly isobutylene, 1-octene, and 1-decene. Polyolefins prepared from such mono-olefins include polypropylene, polybutene, polyisobutene, and the polyalphaolefins produced from 1-octene and 1-decene.

[0202] In one embodiment the polyalkyl or polyalkenyl substituent is one derived from polyisobutene. Suitable polyisobutenes for use in preparing the succinimide-acids of the present invention include those polyisobutenes that comprise at least about 20% of the more reactive methylvinylidene isomer, such as at least 50% and further such as at least 70%. Suitable polyisobutenes include those prepared using BF_3 catalysts. The preparation of such polyisobutenes in which the methylvinylidene isomer comprises a high percentage of the total composition is described in U.S. Pat. Nos. 4,152,499 and 4,605,808. Examples of suitable polyisobutenes having a high alkylvinylidene content include a polyisobutene having a number average molecular weight of about 1300 and a methylvinylidene content of about 74%, and a polyisobutene having a number average molecular weight of about 950 and a methylvinylidene content of about 76%, and materials comprising the beta isomer thereof.

[0203] Suitable alpha-omega amino acids are disclosed in U.S. Pat. No. 6,548,458 which is incorporated herein by reference in its entirety. Suitable alpha-omega amino acids include glycine, beta-alanine, gamma-amino butyric acid, 6-amino caproic acid, 11-amino undecanoic acid.

[0204] The molar ratio of anhydride to alpha-omega amino acid ranges from 1:10 to 1:1, and as another example, the molar ratio of anhydride to alpha-omega amino acid is 1:1.

[0205] The succinimide-acid compounds are typically prepared by combining the substituted-succinic anhydride and amino acid with a reaction media in a suitable reaction vessel. When the reaction media used is process oil, the reaction mixture is heated to between 120 and 180 °C under nitrogen. The reaction generally requires 2 to 5 hours for complete removal of water and formation of the succinimide product. When toluene (or other organic solvent) is used as the reaction media, the reflux temperature of the water/toluene (solvent) azeotrope determines the reaction temperature.

[0206] Reaction of the pendant carboxylic acid moiety of the succinimide-acid compound with an amine results in the formation of an amide bond. The reaction is conducted at a temperature and for a time sufficient to form the succinimide-amide reaction product. Typically, the reaction is conducted in a suitable reaction media such as an organic solvent, for example, toluene, or process oil. The reaction is typically conducted at a temperature of from 110 to 180°C for 2 to 8 hours.

[0207] The ratio of succinimide-acid compound to polyamine ranges from n: 1 to 1:1 where n is the number of reactive nitrogen atoms (i.e., unhindered primary and secondary amines capable of reacting with the succinimide-acid) within the polyamine.

[0208] In one embodiment the amines are polyamines and partially alkoxylated polyamines. Examples of polyamines that may be used include, but are not limited to, aminoguanidine bicarbonate (AGBC), diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), pentaethylene hexamine (PEHA), and heavy polyamines. A heavy polyamine is a mixture of polyalkylenepolyamines comprising small amounts of lower polyamine oligomers such as TEPA and PEHA but primarily oligomers with 7 or more nitrogens, 2 or more primary amines per molecule, and more extensive branching than conventional polyamine mixtures. Examples of a partially alkoxylated polyamines include aminoethylethanolamine (AEEA), aminopropyldiethanolamine (APDEA), diethanolamine (DEA), and partially propoxylated hexamethylenediamine (for example HMDA-2PO or HMDA-3PO). When partially alkoxylated polyamines are used, the reaction products of the succinimide-acid and the partially alkoxylated polyamine may contain mixtures of succinimide-amides and succinimide-esters as well as any unreacted components.

[0209] In one embodiment, the fuels will contain minor amounts of the triazine compounds that control, eliminate, or reduce formation of engine deposits, especially injector deposits and/or control soot formation. Generally speaking the fuels of the invention will contain an amount of the triazine compound sufficient to provide from about 0.0078 to about 0.25 gram of manganese per gallon of fuel, and preferably from about 0.0156 to about 0.125 gram of manganese per gallon.

[0210] The Mannich base dispersants are usually a reaction product of an alkyl phenol, typically having a long chain alkyl substituent on the ring, with one or more aliphatic aldehydes containing from 1 to about 7 carbon atoms (especially formaldehyde and derivatives thereof), and polyamines (especially polyalkylene polyamines). Examples of Mannich condensation products, and methods for their production are described in U.S. Pat. Nos. 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,493,520; 3,539,633; 3,559,743; 3,586,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,872,019; 3,904,595; 3,957,746; 3,980,569; 3,985,802; 4,006,089; 4,011,380; 4,025,451; 4,058,468; 4,083,699; 4,090,854; 4,354,950; and 4,485,023.

[0211] The various types of ashless dispersants described above can be phosphorylated by procedures described in U.S. Pat. Nos. 3,184,411; 3,342,735; 3,403,102; 3,502,607; 3,511,780; 3,513,093; 3,513,093; 4,615,826; 4,648,980; 4,857,214 and 5,198,133.

[0212] The dispersants of the present disclosure may be boronated. Methods for boronating (borating) the various types of ashless dispersants described above are described in U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 2,284,409; 2,284,410; 3,338,832; 3,344,069; 3,533,945; 3,658,836; 3,703,536; 3,718,663; 4,455,243; and 4,652,387.

[0213] Suitable procedures for phosphorylating and/or boronating ashless dispersants such as those referred to above are set forth in U.S. Pat. Nos. 4,857,214 and 5,198,133.

Viscosity Modifiers

[0214] Viscosity modifiers for use in finished fuel compositions as described herein may comprise an olefin (co)polymer (s). A suitable viscosity modifier may include a mixture of olefin (co)polymers. A fully formulated fuel composition as described herein may contain 0.1 to 40 wt. % olefin (co)polymer.

[0215] The olefin (co)polymer which may be used is a homopolymer, copolymer, or terpolymer resulting from the polymerization of C_2-C_{10} olefins having a number average molecular weight of from about 1,000 to about 10,000, for example, about 1,000 to about 3,000, as determined by gel permeation chromatography (GPC). The C_2-C_{10} olefins include ethylene, propylene, 1-butene, isobutylene, 2-butene, isoprene, 1-octene, and 1-decene. Exemplary (co)polymers include polypropylene, polyisobutylene, ethylene/propylene copolymers, styrene/isoprene copolymers, and 1-butene/isobutylene copolymers, and mixtures of the polymers thereof.

Friction Modifiers and Lubricity Additives

[0216] For certain applications it may be desirable to use one or more friction modifiers also referred to as lubricity additives in preparing the finished fuel formulation. Suitable lubricity additives include such compounds as aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic amines, or mixtures thereof. The aliphatic group typically contains at least about eight carbon atoms so as to render the compound suitably fuel soluble. Also suitable are aliphatic substituted succinimides formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia.

[0217] The use of lubricity additives is optional and will depend of the inherent lubricity of the fuel. However, in applications where friction modifiers are used, finished fuel formulations may contain up to about 1.25 wt %, and usually from about 0.05 to about 1 wt % of one or more friction modifiers.

Inhibitors

[0218] Finished fuel compositions as described herein typically will contain some inhibitors. The inhibitor components serve different functions including corrosion inhibition and foam inhibition. The inhibitors may be introduced in a pre-formed additive package that may contain in addition one or more other components used in the finished fuel compositions. Alternatively these inhibitor components may be introduced individually or in various sub-combinations. While amounts of inhibitors used may be varied within reasonable limits, the finished fuel compositions of this disclosure will typically have a total inhibitor content in the range of about 0 to about 15 wt %, on an "active ingredient basis," i.e., excluding the weight of inert materials such as solvents or diluents normally associated therewith.

[0219] Foam inhibitors form one type of inhibitor suitable for use as an inhibitor component in the finished fuel compositions. Useful foam inhibitors include silicones, surfactants, and the like.

[0220] Corrosion inhibitors constitute another class of additives suitable for inclusion in the finished fuel compositions. Such compounds include thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercapto benzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbyhhio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles. In one embodiment the compounds are the 1,3,4-thiadiazoles, a number of which are available as articles of commerce, and also combinations of triazoles such as tolyltriazole with a 1,3,5-thiadiazole such as a 2,5-bis(alkyldithio)-1,3,4-thiadiazole. The 1,3,4-thiadiazoles are generally synthesized from hydrazine and carbon disulfide by known procedures. See, for example, U.S. Pat. Nos. 2,765,289; 2,749,311; 2,760,933; 2,850,453; 2,910,439; 3,663,561; 3,862,798; and 3,840,549. Further suitable corrosion inhibitors may include monocarboxylic acids and polycarboxylic acids. Examples of suitable monocarboxylic acids are octanoic acid, decanoic acid and dodecanoic acid. Suitable polycarboxylic acids include dimer and trimer acids such as are produced from such acids as tall oil fatly acids, oleic acid, linoleic acid, or the like.

[0221] Another useful type of corrosion inhibitor for use in the disclosed fuel compositions is comprised of the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable corrosion inhibitors include acid phosphates; ethoxylated phenols, and ethoxylated alcohols; imidazolines; aminosuccinic acids or derivatives thereof, and the like. Materials of these types are available as articles of commerce. Mixtures of such corrosion inhibitors can be used.

Antiwear Agents

[0222] Various types of sulfur-containing antiwear agents may be used in the finished fuel formulations described herein. Examples include dihydrocarbyl polysulfides; sulfurized olefins; sulfurized fatty acid esters of both natural and synthetic origins; trithiones; sulfurized thienyl derivatives; sulfurized terpenes; sulfurized oligomers of C2-C8 monoolefins; and sulfurized Diels-Alder adducts such as those disclosed in U.S. Pat. No. Re 27,331. Specific examples include sulfurized polyisobutene, sulfurized isobutylene, sulfurized diisobutylene, sulfurized triisobutylene, dicyclohexyl polysulfide, diphenyl polysulfide, dibenzyl polysulfide, dinonyl polysulfide, and mixtures of di-tert-butyl polysulfide such as mixtures of di-tert-butyl trisulfide, di-tert-butyl tetrasulfide and di-tert-butyl pentasulfide, among others. Combinations of such categories of sulfur-containing antiwear agents may also be used, such as a combination of sulfurized isobutylene and di-tert-butyl trisulfide, a combination of sulfurized isobutylene and dinonyl trisulfide, a combination of sulfurized tall oil and dibenzyl polysulfide.

Pour point depressants

[0223] The fuel additive package or fuel composition may also contain one or more pour point depressants. Pour point depressants may be used in compositions described herein to improve low temperature properties of the compositions. Examples of useful pour point depressants are polyaorylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkylfumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this disclosure and techniques for their preparation are described in U.S. Pat. Nos. 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715 which are herein incorporated by reference for their relevant disclosures.

[0224] In one embodiment, the pour point depressant is represented by the general structural formula: $Ar(R)-(Ar_1(R_1))_n-Ar_2$, wherein the Ar, Ar_1 and Ar_2 are aromatic groups of up to about 12 carbon atoms, (R) and (R_1) are independently an alkylene group containing 1 to 100 carbon atoms with the proviso that at least one of (R) or (R_1) is CH_2, and n is 0 to about 1000 with the proviso that if n is 0, then (R) is CH_2 and at least one aromatic moiety has at least one substituent, the substituents being selected from the group consisting of a substituent derived from an olefin containing about 8 to about 30 carbon atoms, and a substituent derived from a chlorinated hydrocarbon usually containing about 8 to about 50 carbon atoms and about 2.5 chlorine atoms for each 24 carbon atoms.

Seal swell agents

[0225] Seal swell agents may be included in the finished fuel compositions of the disclosed embodiments particularly when the fuel compositions are used as power transmission fluids. Suitable seal swell agents may be selected from oil-soluble diesters, oil-soluble sulfones, silicon containing organic compounds, and mixtures thereof. Generally speaking the most suitable diesters include the adipates, azelates, and sebacates of C8-C13 alkanols (or mixtures thereof), and the phthalates of C4-C13 alkanols (or mixtures thereof). Mixtures of two or more different types of diesters (e.g., dialkyl adipates and dialkyl azelates, etc.) may also be used. Examples of such materials include the n-octyl, 2-ethylhexyl, isodecyl, and tridecyl diesters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and tridecyl diesters of phthalic acid. Other esters which may give generally equivalent performance are polyol esters.

[0226] Suitable sulfone seal swell agents are described in U.S. Pat. Nos. 3,974,081 and 4,029,587. Typically these products are employed at levels in the range of about 0.25 to about 1 wt % in the finished transmission fluid.

[0227] In one embodiment, the seal swell agents are the oil-soluble dialkyl esters of (i) adipic acid, (ii) sebacic acid, or (iii) phthalic acid. The adipates and sebacates should be used in amounts in the range of from about 4 to about 15 wt % in the finished fuel. In the case of the phthalates, the levels in the fuel should fall in the range of from about 1.5 to about 10 wt %. Generally speaking, the higher the molecular weight of the adipate, sebacate or phthalate, the higher should be the treat rate within the foregoing ranges.

Thickening agents

[0228] A wide variety of thickening agents may be used for providing fuels containing the base oil component. Included among the thickening agents are alkali and alkaline earth metal soaps of fatty acids and fatty materials having from about 12 to about 30 carbon atoms per molecule. The metal cations of the metal soaps are typified by sodium, lithium, calcium, magnesium, and barium. Fatty materials are illustrated by stearic acid, hydroxystearic acid, stearin, cottonseed oil acids, oleic acid, palmitic acid, myristic acid and hydrogenated fish oils.

[0229] Other thickening agents include salt and salt-soap complexes such as calcium stearate-acetate (U.S. Pat. No. 2,197,263), barium stearate acetate (U.S. Pat. No. 2,564,561), calcium stearate-caprylate-acetate complexes (U.S. Pat. No. 2,999,065), calcium-caprylate-acetate (U.S. Pat. No. 2,999,066), and calcium salts and soaps of low-, intermediate-, and high-molecular weight acids and of nut oil acids. Another group of thickening agents comprises substituted ureas, phthalocyanines, indanthrene, pigments such as perylimides, pyromellitdiimides, ammeline, and hydrophobic clays.

[0230] Some of the additive components described above may be supplied in the form of solutions of active ingredient (s) in an inert diluent or solvent, such as a diluent oil. Unless expressly stated to the contrary, the amounts and concentrations of each additive component are expressed in terms of active additive, i.e., the amount of solvent or diluent that may be associated with such component as received is excluded.

[0231] It will be appreciated that the individual components employed may be separately blended into the fuel or carrier fluid or may be blended therein in various sub-combinations, if desired. Ordinarily, the particular sequence of such blending steps is not crucial. Moreover, such components may be blended in the form of separate solutions in a diluent. It may be preferable, however, to blend the additive components used in the form of a concentrate, 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.

[0232] Additive concentrates may thus be formulated to contain all of the additive components and if desired, some of the base fuel component, in amounts proportioned to yield finished fuel blends consistent with the concentrations described above. In most cases, the additive concentrate will contain one or more diluents such as light carrier oils, to facilitate handling and blending of the concentrate. Thus concentrates containing up to about 50 wt. % of one or more diluents or solvents may be used, provided the solvents are not present in amounts that interfere with the low and high temperature and flash point characteristics and the performance of the finished power transmission fluid composition. In this regard, the additive components used pursuant to this disclosure may be selected and proportioned such that an additive concentrate or package formulated from such components will have a flash point of about 170°C or above, using the ASTM D-92 test procedure.

[0233] Such additive concentrates are suitably devoid of materials or components that are bioaccumulative, toxic, and persistent as indicated by the tests described above. Examples of such materials, include but are not limited to, certain alkanes, alkoxy alkylamines, alkyl methacrylates, alkyl phenols, alkylphenols, polyoxyalkyl alkylamines, aryl amines, aryl phosphites, branched alkyl phenols, branched alkyl polysulfides, branched long-chain alkyl amines, long-chain alkenyl alkyl amine, long-chain alkenyl alkylene amines, long-chain alkenyl amines, long-chain alkoxylated amines, long-chain alkyl alkoxylated alcohols, long-chain alkyl alkylene amines, long-chain alkyl amines, long-chain alkyl methacrylates, long-chain alkyoxylated amines, long-chain hydroxyalkyl amines, polyaryls, and polyolefin polyamines.

[0234] Fuels and fuel additives of the embodiments herein may be formulated to provide enhanced fuel and engine performance properties and/or improved low temperature viscometric properties for various applications. A fuel composition according to the present disclosure may be used for combustion in gasoline or diesel engines as well as stationary burners, power plants, and home heating operations.

[0235] Fuels of the present disclosure may be used in various engine applications, including but not limited to, internal combustion engines, rotary engines, gas turbine engines, four-stroke engines, and two-stroke engines.

[0236] In one embodiment, a composition of the present disclosure may be manufactured in the United States of America or Canada.

[0237] In a further embodiment, a composition of the present disclosure may be transported to Europe by ship, air, rail, or truck.

[0238] At numerous places throughout this specification, reference has been made to a number of U.S. Patents. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0239] Other embodiments of the present disclosure will be apparent to those skilled in the art from consideration of the specification and practice of the embodiments disclosed herein. As used throughout the specification and claims, "a" and/or "an" may refer to one or more than one. Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, percent, ratio, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the specification and claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

[0240] The foregoing embodiments are susceptible to considerable variation in practice. Accordingly, the embodiments are not intended to be limited to the specific exemplifications set forth hereinabove. Rather, the foregoing embodiments are within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

[0241] The patentees do not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part hereof under the doctrine of equivalents.

The invention also relates to the following numbered embodiments:

1. An environmentally compatible fuel additive composition comprising four or more functional components, wherein each component is selected from the group consisting of a non-persistent material, a non-bioaccumulative material,

and a non-toxic material, and the additive composition is devoid of components that are persistent, bioaccumulative, and toxic.

2. The fuel additive composition of embodiment 1, wherein the functional components comprise materials selected from the group consisting of: an antifoam agent, an anti-icing additive, an antiknock additive, an antioxidant, an antistatic additive, an anti-valve-seat recession additive, an antiwear agent, a biocide, a carrier fluid, a cetane improver, a combustion improver, a compatibilizer, a conductivity improver, a corrosion inhibitor, a dehazer, a demulsifier, a detergent, a dispersant, a drag reducing agent, a dye, an emulsifier, a foam inhibitor, a friction modifier, a fuel stabilizer, an injector deposit control additive, a lubricity additive, a marker or customer-specific "tag", a metal deactivator, an octane improver, a pour point depressant, a reodorant, a seal swell additive, a surfactant, and a wax anti-settling additive (a "WASA").

3. The fuel additive composition of embodiment 1, wherein the non-persistent material is determined by a biodegradation test selected from the group consisting of a dissolved organic carbon die-away test, a modified OECD screening dissolved organic carbon die-away test, a carbon dioxide evolution test, a manometric respirometry test, a closed bottle test, a MITI test, a Zahn-Wellens test, an activated sludge simulation test, an activated sludge respiration inhibition test, and a modified SCAS test.

4. The fuel additive composition of embodiment 1, wherein the non-bioaccumulative material is determined by a bioconcentration factor test comprising a flow-through fish test.

5. The fuel additive composition of embodiment 1, wherein the non-bioaccumulative material has bioconcentration factor test result below 2000.

6. The fuel additive composition of embodiment 1, wherein the non-toxic material is determined by a toxicity test selected from the group consisting of an acute toxicity for fish test, an acute toxicity for *Daphnia* test, and an algal inhibition test.

7. The fuel additive composition of embodiment 1, wherein the non-toxic material is devoid of a toxic effect at an aqueous concentration below 0.01 mg/L on a toxicity test.

8. The fuel additive composition of embodiment 1, wherein a non-persistent material is a material having an acceptable score on a biodegradation test selected from at least one of the following:

a) a half-life in marine water is less than 60 days;
b) a half-life in fresh or estuarine water is less than 40 days;
c) a half-life in marine sediment is less than 180 days;
d) a half-life in fresh or estuarine water sediment less than 120 days; or
e) a half-life in soil less than 120 days.

9. The fuel additive composition of embodiment 1, wherein at least one of the components is selected from the group consisting of: a sulfurized neopentyl glycol phosphate, a substituted succinimide, a reaction product of a C_{16} alkyl dicarboxylic acid and ammonia, a fatty amine ethoxylate, an oleamide, and a dodecyl succinic acid.

10. The fuel additive composition of embodiment 1, wherein at least one of the components comprises a pour point depressant.

11. The fuel additive composition of embodiment 1, wherein at least one of the components comprises a combustion improver.

12. The fuel additive composition of embodiment 1, wherein at least one of the components comprises a foam inhibitor.

13. The fuel additive composition of embodiment 1, wherein at least one of the components comprises a cetane number improver.

14. The fuel additive composition of embodiment 1, wherein at least one of the components comprises an adipate.

15. The fuel additive composition of embodiment 1, wherein at least one of the components comprises a sulfurized

isobutylene.

16. The fuel additive composition of embodiment 1, wherein at least one of the components comprises an alkylthiadiazole.

17. The fuel additive composition of embodiment 1, wherein at least one of the components comprises an alkylpolymethacrylate comprising less than 0.3% weight of unreacted monomer.

18. The fuel additive composition of embodiment 1, wherein at least one of the components, comprises an olefin copolymer or a multifunctional olefin copolymer viscosity index improver comprising less than 0.3% weight of unreacted monomer.

19. The fuel additive composition of embodiment 1, wherein at least one of the components comprises a polyalphaolefin.

20. The fuel additive composition of embodiment 1, wherein the additive is useful in gasoline compositions.

21. The fuel additive composition of embodiment 1, wherein the additive is useful in diesel fuel compositions.

22. The fuel additive composition of embodiment 1, wherein said composition is transported to any site within Europe by a method selected from ship, air, rail, and truck.

23. The fuel additive composition of embodiment 1, wherein said composition is manufactured in the USA or Canada.

24. An environmentally compatible fuel composition, comprising:

a) a major amount of a fuel; and
b) a minor amount of an additive composition, comprising four or more functional components, wherein each component comprises at least one of: an acceptable level of biodegradation as determined by a biodegradation test, a bioconcentration factor below 2000, or is devoid of a toxic effect at an aqueous concentration below 0.01 mg/L an a toxicity test.

25. The fuel composition of embodiment 24, wherein the functional components comprise materials selected from the group consisting of: an antifoam agent, an anti-icing additive, an antiknock additive, an antioxidant, an antistatic additive, an anti-valve-seat recession additive, an antiwear agent, a biocide, a carrier fluid, a cetane improver, a combustion improver, a compatibilizer, a conductivity improver, a corrosion inhibitor, a dehazer, a demulsifier, a detergent, a dispersant, a drag reducing agent, a dye, an emulsifier, a foam inhibitor, a friction modifier, a fuel stabilizer, an injector deposit control additive, a lubricity additive, a marker or customer-specific "tag", a metal deactivator, an octane improver, a pour point depressant, a reodorant, a seal swell additive, a surfactant, and a wax anti-settling additive (a "WASA").

26. The fuel composition of embodiment 24, wherein the biodegradation test is selected from the group consisting of a dissolved organic carbon die-away test, a modified OECD screening dissolved organic carbon die-away test, a carbon dioxide evolution test, a manometric respirometry test, a closed bottle test, a MITI test, a Zahn-Wellens test, an activated sludge simulation test, an activated sludge respiration inhibition test, and a modified SCAS test.

27. The fuel composition of embodiment 24, wherein the bioconcentration factor test comprises a flow through fish test.

28. The fuel composition of embodiment 24, wherein the toxicity test is selected from the group consisting of an acute toxicity for fish test, an acute toxicity for *Daphnia* test, and an algal inhibition test.

29. The fuel composition of embodiment 24, wherein the acceptable score on a biodegradation test comprises at least one of the following:

a) a half-life in marine water is less than 60 days;
b) a half-life in fresh or estuarine water is less than 40 days;
c) a half-life in marine sediment is less than 180 days;

d) a half-life in fresh or estuarine water sediment less than 120 days; or
e) a half-life in soil less than 120 days.

30. The fuel composition of embodiment 24, wherein the fuel is selected from the group consisting of one or more of gasoline, diesel fuel, middle distillate fuel, biodiesel fuel, an alcohol, such as but not limited to an ethanol, bioethanol, a biobutanol, an aviation fuel, jet fuel, marine fuel, bunker fuel, burner fuel, home heating oil, a gas-to-liquid (GTL) base oil, a Group I base oil, a Group II base oil, a Group III base oil, a Group IV base oil, an ester, a vegetable oil, and mixtures thereof.

31. A method of making an environmentally compatible fuel composition, comprising combining a major amount of a fuel and a minor amount of an additive composition, comprising four or more functional components, wherein each component is selected from: a material having an acceptable level of biodegradation, a material having a bioconcentration factor below 2000, and a material that is devoid of a toxic effect at an aqueous concentration below 0.01 mg/L on a toxicity test, wherein the fuel composition complies with European Council Directive 67/548/EEC.

32. The method of embodiment 31, wherein the functional component further comprises a material selected from the group consisting of: an antifoam agent, an anti-icing additive, an antiknock additive, an antioxidant, an antistatic additive, an anti-valve-seat recession additive, an antiwear agent, a biocide, a carrier fluid, a cetane improver, a combustion improver, a compatibilizer, a conductivity improver, a corrosion inhibitor, a dehazer, a demulsifier, a detergent, a dispersant, a drag reducing agent, a dye, an emulsifier, a foam inhibitor, a friction modifier, a fuel stabilizer, an injector deposit control additive, a lubricity additive, a marker or customer-specific "tag", a metal deactivator, an octane improver, a pour point depressant, a reodorant, a seal swell additive, a surfactant, and a wax anti-settling additive (a "WASA").

33. The method of embodiment 31, wherein the biodegradation test is selected from the group consisting of a dissolved organic carbon die-away test, a modified OECD screening dissolved organic carbon die-away test, a carbon dioxide evolution test, a manometric respirometry test, a closed bottle test, a MITI test, a Zahn-Wellens test, an activated sludge simulation test, an activated sludge, respiration inhibition test, and a modified SCAS test.

34. The method of embodiment 31, wherein the bioconcentration factor test comprises a flow-through fish test.

35. The method of embodiment 31, wherein the toxicity test is selected from the group consisting of an acute toxicity for fish test, an acute toxicity for *Daphnia* test, and an algal inhibition test.

36. The method of embodiment 31, wherein the acceptable score an a biodegradation test comprises at least one of the following:

a) a half-life in marine water is less than 60 days;
b) a half-life in fresh or estuarine water is less than 40 days;
c) a half-life in marine sediment is less than 180 days;
d) a half-life in fresh or estuarine water sediment less than 120 days; or
e) a half-life in soil less than 120 days.

37. An environmentally compatible fuel composition comprising:

a) a major amount of a fuel; and
b) a minor amount of an additive composition, comprising four or more functional components, wherein each component is selected from the group consisting of non-persistent materials, non-bioaccumulative materials and non-toxic materials, and the additive composition is devoid of components that are persistent, bioaccumulative, and toxic.

38. The fuel composition of embodiment 37, wherein the functional components comprise materials selected from the group consisting of: an antifoam agent, an anti-icing additive, an antiknock additive, an antioxidant, an antistatic additive, an anti-valve-seat recession additive, an antiwear agent, a biocide, a carrier fluid, a cetane improver, a combustion improver, a compatibilizer, a conductivity improver, a corrosion inhibitor, a dehazer, a demulsifier, a detergent, a dispersant, a drag reducing agent, a dye, an emulsifier, a foam inhibitor, a friction modifier, a fuel stabilizer, an injector deposit control additive, a lubricity additive, a marker or customer-specific "tag", a metal deactivator, an octane improver, a pour point depressant, a reodorant, a seal swell additive, a surfactant, and a wax

anti-settling additive (a "WASA").

39. A method of fueling an engine comprising supplying to an engine a fuel composition of embodiment 37.

40. The method of embodiment 39, wherein said engine is a spark-ignition engine.

41. The method of embodiment 39, wherein said engine is a compression ignition engine.

42. The method of embodiment 39, wherein said engine is selected from the group consisting of an internal combustion engine, a rotary engine, a gas turbine engine, a four-stroke engine, a two-stroke engine, and an outboard motor engine.

Claims

1. **1.** An environmentally compatible fuel additive composition comprising four or more functional components, wherein each component is selected from the group consisting of a non-persistent material, a non-bioaccumulative material, and a non-toxic material, and the additive composition is devoid of components that are persistent, bioaccumulative, and toxic.

2. The fuel additive composition of claim 1, wherein the functional components comprise materials selected from the group consisting of: an antifoam agent, an anti-icing additive, an antiknock additive, an antioxidant, an antistatic additive, an anti-valve-seat recession additive, an antiwear agent, a biocide, a carrier fluid, a cetane improver, a combustion improver, a compatibilizer, a conductivity improver, a corrosion inhibitor, a dehazer, a demulsifier, a detergent, a dispersant, a drag reducing agent, a dye, an emulsifier, a foam inhibitor, a friction modifier, a fuel stabilizer, an injector deposit control additive, a lubricity additive, a marker or customer-specific "tag", a metal deactivator, an octane improver, a pour point depressant, a reodorant, a seal swell additive, a surfactant, and a wax anti-settling additive (a "WASA").

3. The fuel additive composition of claim 1 or 2, wherein the non-persistent material is determined by a biodegradation test selected from the group consisting of a dissolved organic carbon dieaway test, a modified OECD screening dissolved organic carbon die-away test, a carbon dioxide evolution test, a manometric respirometry test, a closed bottle test, a MITI test, a Zahn-Wellens test, an activated sludge simulation test, an activated sludge respiration inhibition test, and a modified SCAS test and/or
wherein the non-bioaccumulative material is determined by a bioconcentration factor test comprising a flow-through fish test and/or
wherein the non-toxic material is determined by a toxicity test selected from the group consisting of an acute toxicity for fish test, an acute toxicity for *Daphnia* test, and an algal inhibition test.

4. The fuel additive composition of any one of claims 1 to 3, wherein the non-bioaccumulative material has bioconcentration factor test result below 2000; and/or wherein the non-toxic material is devoid of a toxic effect at an aqueous concentration below 0.01 mg/L, on a toxicity test; and/or wherein the non-persistent material is a material having an acceptable score on a biodegradation test selected from at least one of the following:

a) a half-life in marine water is less than 60 days;
b) a half-life in fresh or estuarine water is less than 40 days;
c) a half-life in marine sediment is less than 180 days;
d) a half-life in fresh or estuarine water sediment less than 120 days; or
e) a half-life in soil less than 120 days.

5. The fuel additive composition of any one of claims 1 to 4, wherein at least one of the components is selected from the group consisting of: a sulfurized neopentyl glycol phosphate, a substituted succinimide, a reaction product of a C_{16} alkyl dicarboxylic acid and ammonia, a fatty amine ethoxylate, an oleamide, and a dodecyl succinic acid.

6. The fuel additive composition of any one of claims 1 to 5, wherein at least one of the components comprises at least one of the group consisting of:

a pour point depressant, a combustion improver, a foam inhibitor, a cetane number improver, an adipate, a sulfurized isobutylene, an alkylthiadiazole, an alkylpolymethacrylate comprising less than 0.3% weight of unreacted monomer, an olefin copolymer or a multifunctional olefin copolymer viscosity index improver comprising less than 0.3% weight of unreacted monomer, and a polyalphaolefin.

7. Use of the fuel additive composition of any one of claims 1 to 6 in gasoline compositions or diesel fuel compositions.

8. An environmentally compatible fuel composition, comprising:

a) a major amount of a fuel; and
b) a minor amount of an additive composition according to any one of claims 1 to 6.

9. The fuel composition of claim 8, wherein the fuel is selected from the group consisting of one or more of gasoline, diesel fuel, middle distillate fuel, biodiesel fuel, an alcohol, such as but not limited to an ethanol, bioethanol, a biobutanol, an aviation fuel, jet fuel, marine fuel, bunker fuel, burner fuel, home heating oil, a gas-to-liquid (GTL) base oil, a Group I base oil, a Group II base oil, a Group III base oil, a Group IV base oil, an ester, a vegetable oil, and mixtures thereof.

10. A method of making an environmentally compatible fuel composition according to claim 8 or 9, comprising combining a major amount of the fuel and a minor amount of an additive composition according to any one of claims 1 to 6.

11. A method of fueling an engine comprising supplying to an engine a fuel composition of claim 8 or 9.

12. The method of claim 11, wherein said engine is a spark-ignition engine or a compression ignition engine.

13. The method of claim 11 or 12, wherein said engine is selected from the group consisting of an internal combustion engine, a rotary engine, a gas turbine engine, a four-stroke engine, a two-stroke engine, and an outboard motor engine.

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PARTIAL EUROPEAN SEARCH REPORT

which under Rule 63 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

Application Number
EP 08 16 1416

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 97/01620 A (EXXON CHEMICAL PATENTS INC [US]) 16 January 1997 (1997-01-16) * page 2, line 20 - line 25; claims 1-4,7; example 1 * * page 3, line 19 - line 33 * * page 17, line 15 - line 24 * * page 17, line 32 - page 18, line 12 * -----	1-13	INV. C10L1/14
A	WO 92/02601 A (MOBIL OIL CORP [US]) 20 February 1992 (1992-02-20) * page 12, line 19 - line 22; claims 1-4,6,8,11-15,17,19,22-24; tables I,II * -----	1-13	
A	US 5 551 957 A (CUNNINGHAM LAWRENCE J [US] ET AL) 3 September 1996 (1996-09-03) * column 7, line 1 - line 27; claims 1-9; examples 1,16,17 * * column 14, line 25 - line 58 * -----	1-13	
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INCOMPLETE SEARCH

The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.

Claims searched completely :

Claims searched incompletely :

Claims not searched :

Reason for the limitation of the search:

see sheet C

Place of search	Date of completion of the search	Examiner
The Hague	20 November 2008	de La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

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PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 08 16 1416

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 5 962 378 A (TIFFANY GEORGE M [US] ET AL) 5 October 1999 (1999-10-05) * column 1, line 10 - line 14; claims 1-6; examples A-1; tables 1,2 * * column 1, line 66 - column 2, line 3 * * column 9, line 37 - line 43 * * column 11, line 21 - line 32 * * column 11, line 38 - line 60 * * column 12, line 40 - line 44 * * column 12, line 55 - line 62 * * column 13, line 52 - line 57 * * column 14, line 12 - line 21 * -----	1-13	
A	AT 400 242 B (OEMV AG [AT]) 27 November 1995 (1995-11-27) * page 3, line 57 - page 4, line 1; claim 1 * * page 4, line 30 - line 38 * -----	1-13	TECHNICAL FIELDS SEARCHED (IPC)
A	EP 0 468 109 A (ETHYL PETROLEUM ADDITIVES LTD [GB]) 29 January 1992 (1992-01-29) * column 6, line 58 - column 7, line 7; claims 1-4,6; examples 1-3 * * column 7, line 20 - line 55 * * column 12, line 2 - line 17 * * column 12, line 29 * * column 12, line 34 - line 39 * * column 12, line 53 - column 13, line 5 * -----	1-6	
A	WO 94/05745 A (HENKEL CORP [US]) 17 March 1994 (1994-03-17) * page 1, line 2 - line 6; claims 13,14; table II * * page 3, line 6 - line 15 * * page 4, line 15 - line 24 * * page 10, line 10 - line 23 * * page 13, line 32 - page 14, line 4 * ----- -/--	1-13	

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EPO FORM 1503 03.82 (P04C10)

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PARTIAL EUROPEAN SEARCH REPORT

Application Number
EP 08 16 1416

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	WO 2004/099350 A (LUBRIZOL CORP [US]; HOBSON DAVID [GB]; PSAILA ALEX [GB]; DI BIASE STEP) 18 November 2004 (2004-11-18) * page 1, line 13 - line 22; claims 1-4,6-10; examples 8,9 * * page 12, line 11 - line 15 * -----	1-13	
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			TECHNICAL FIELDS SEARCHED (IPC)

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EPO FORM 1503 03.82 (P04C10)

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INCOMPLETE SEARCH SHEET C

Application Number
EP 08 16 1416

Claim(s) searched completely:
None

Claim(s) searched incompletely:
1-13

Claim(s) not searched:
-

Reason for the limitation of the search:

The terms "non-persistent", "non-bioaccumulative" and "non-toxic" used in claim 1 are vague and unclear and leave the reader in doubt as to the meaning of the technical features to which they refer, thereby rendering the definition of the subject-matter of said claim unclear (Article 84 EPC).

The present claim 1 relates to an extremely large number of possible additive compositions, combinations of compounds. Support and disclosure in the sense of Article 84 and 83 EPC is to be found however for no composition, even if a huge number of possibly non-persistent and/or non-bioaccumulative and/or non-toxic compounds, are mentioned in the description (Paragraphs 87-91, 112-230, 233). The non-compliance with the substantive provisions is to such an extent, that a meaningful search of the whole claimed subject-matter of the claim could not be carried out (Rule 63 EPC and Guidelines B-VIII, 3). The extent of the search was consequently limited.

Also, the components of the composition as claimed in claim 1 are non-persistent and/or non-bioaccumulative and/or non-toxic compounds. These compounds are not clearly defined in the claim because this would require an equally unquantifiable and thus unreasonable amount of experimentation, imposing a severe and undue burden on all those wishing to ascertain the scope of the claim, which is not in compliance with the clarity requirement of Article 84 EPC. The non-compliance with the substantive provisions is to such an extent, that a meaningful search of the whole claimed subject-matter of the claim could not be carried out (Rule 63 EPC and Guidelines B-VIII, 3).

Only liquid fuels are mentioned in the description.

Thus the search of claims 1-13 was restricted to a fuel additive composition used in a liquid fuel and comprising a combination of four different compounds, chosen among the specific components disclosed in dependent claims 5 and 6, at least one being a specific compound mentioned in claim 5 and at least one being a specific compound mentioned in claim 6, the composition comprising no compound belonging to the group of specific compounds mentioned in paragraph 233 of the description, unless the compound is also mentioned in an other paragraph of the description as being a possible compound, as it is the case, for example, for aryl amines mentioned in paragraph 90 and paragraph 233.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 16 1416

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