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(54) **Environmentally-Friendly Lubricant Compositions**

(57) A lubricant additive composition having environ-  
mentally compatible characteristics as defined by Euro-  
pean Council Directive 67/548/EEC is disclosed. Such a  
composition may include components selected from non-

persistent materials, non-bioaccumulative materials, or  
non-toxic materials.

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**Description****CROSS REFERENCES TO RELATED APPLICATIONS**

5 [0001] This patent application claims priority from and is related to U.S. Provisional Patent Application Serial No. 60/916,106 filed May 4, 2007, entitled: "ENVIRONMENTALLY-FRIENDLY LUBRICANT COMPOSITIONS." This U.S. Provisional Patent Application is incorporated by reference in its entirety herein.

**TECHNICAL FIELD**

10 [0002] The present disclosure relates to the field of lubricants and lubricant compositions, specifically lubricant compositions having environmentally-friendly characteristics.

**BACKGROUND**

15 [0003] As concern for the environment grows worldwide, the safety of the various chemical substances used in lubricant compositions and additive concentrates is becoming more of a concern for manufacturers and distributors of lubricant compositions. It is paramount for the industry to examine the use of tribologically functional 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 additive compositions and lubricant formulations containing such compositions that incorporate more environmentally acceptable materials.

**SUMMARY**

25 [0004] One embodiment of the present disclosure provides an environmentally compatible lubricant additive composition. The additive composition may contain four or more tribologically 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.

30 [0005] Another embodiment of the present disclosure provides an environmentally compatible lubricant composition. The composition may contain a major amount of a base oil and a minor amount of an additive composition. The additive composition may include four or more tribologically 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.

35 [0006] Another embodiment provides a method of lubricating a machine part comprising lubricating said machine part with a lubricant composition as disclosed herein.

[0007] Another embodiment provides an environmentally compatible lubricating composition, comprising a) a major amount of a base oil; and b) a minor amount of an additive composition, comprising four or more tribologically functional components, wherein each component comprises at least one of: an acceptable level 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.

40 [0008] Another embodiment provides a method of making an environmentally compatible lubricant composition, comprising combining a major amount of a base oil and a minor amount of an additive composition, comprising four or more tribologically 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 lubricant composition complies with European Council Directive 67/548/EEC.

45 [0009] A further embodiment of the present disclosure may provide a method of making an environmentally compatible lubricant composition. The method may include combining a major amount of a base oil and a minor amount of an additive composition, having four or more tribologically 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.

50 [0010] 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 lubricants 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.

55 [0011] As used herein, the terms "oil composition," "lubrication composition," "lubricating oil composition," "lubricating oil," "lubricant composition," "fully formulated lubricant composition," and "lubricant" are considered synonymous, fully interchangeable terminology referring to the finished lubrication product comprising a major amount of a base oil plus

a minor amount of an additive composition.

**[0012]** As used herein, the terms "additive package," "additive concentrate," and "additive composition" are considered synonymous, fully interchangeable terminology referring to the portion of the lubricating composition excluding the major amount of base oil stock mixture.

**[0013]** As used herein, the terms "tribologically" and "tribological" are considered terms that relate to the science and mechanism of friction, lubrication, and wear of interacting surfaces and fluids for lubricating such surfaces. Accordingly, a "tribologically functional" component means a component that is used in a lubricating formulation to provide a measurable change in a characteristic or property of a fluid containing the component including those properties not necessarily associated directly with the surface such as oxidation inhibitors, dispersants, detergents, and the like.

**[0014]** As used herein, the terms "agent" and "additive" are considered synonymous, fully interchangeable terminology referring to any single component of a lubricating composition excluding the major amount of base oil stock mixture.

**[0015]** 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.

**[0016]** 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

**[0017]** 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.

**[0018]** 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.

**[0019]** 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

**[0020]** 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.

**[0021]** 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.

**[0022]** 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<sub>2</sub>) 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)

**[0023]** 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.

**[0024]** In general, degradation is followed by the determination of parameters, such as DOC, CO<sub>2</sub> 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).

**[0025]** 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.

**[0026]** 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**

**[0027]** 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**

**[0028]** 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<sub>2</sub>). The degree of biodegradation may also be calculated from supplemental DOC analysis made at the beginning and end of incubation.

**[0029]** The percentage degradation may be calculated by:

$$\% \text{ degradation} = (\text{mg CO}_2 \text{ produced} \times 100) / (\text{ThCO}_2 \times \text{mg test chemical added})$$

### **Manometric Respirometry Test**

**[0030]** 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/liter) 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**

**[0031]** 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**

**[0032]** 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  $25 \pm 1$  °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**

**[0033]** 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.

**[0034]** 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**

**[0035]** 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.

**[0036]** 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.

**[0037]** 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.

**[0038]** 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.

**[0039]** 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.

[0040] 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.

[0041] 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.

[0042] The effluent is collected in a second vessel for 20 to 24 hours, and a sample is taken after thorough mixing.

[0043] 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  $\mu$ m, 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.

[0044] 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.

[0045] 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  $\mu$ m), the first 20 ml (approximately) of filtrate being discarded.

[0046] 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 ( $\text{HgCl}_2$ ) 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.

[0047] 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**

[0048] 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.

[0049] 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  $\text{EC}_{50}$ . 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.

[0050] It is recommended that 3,5-dichlorophenol, as a known inhibitor of respiration, be used as a reference substance and tested for  $\text{EC}_{50}$  on each batch of activated sludge as a means of checking that the sensitivity of the sludge is not abnormal

[0051] 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 C1). The test vessels should be aerated continuously so as to ensure that the dissolved  $\text{O}_2$  does not fall below 2.5 mg/liter and that, immediately before the measurement of the respiration rate, the  $\text{O}_2$  concentration is about 6.5 mg/liter.

[0052] 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.

[0053] 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**

**[0054]** 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.

**[0055]** 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.

**[0056]** 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  $C_{\text{total}} - C_{\text{inorganic}}$ .

**[0057]** 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.

**[0058]** 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.

**[0059]** 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.

**[0060]** 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  $\mu\text{m}$  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**

**[0061]** 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.

**[0062]** One predictive factor for bioaccumulation may be a substance's octanol-water partition coefficient ( $P_{\text{ow}}$ ). The  $P_{\text{ow}}$  is a substance's solubility in n-octanol and water at equilibrium. The logarithm of  $P_{\text{ow}}$  may be an indication of a substance's potential for bioaccumulation in aquatic organisms.

**[0063]** 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 higher 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**

**[0064]** 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.

**[0065]** 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 ( $\text{BCF}_{\text{ss}}$ ) 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.

[0066] 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.

[0067] 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.

[0068] The lipid content is determined on the same biological material as is used to determine the concentration of the test substance, when feasible.

## TOXICITY

[0069] 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 0.01 mg/L. Substances that are classified as carcinogenic, mutagenic, or toxic for reproduction may also be considered as toxic.

[0070] 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  $LC_{50} < 1$  ppm), however chronic toxicity tests (usually in *Daphnia* but also other organisms) may be used for definitive Toxicity.

### Acute Toxicity For Fish Test

[0071] 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.

[0072] 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.

[0073] 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.

[0074] 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.

[0075] 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

[0076] 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.

**[0077]** 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<sub>50</sub> 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.

**[0078]** 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.

**[0079]** 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<sub>OW</sub>, 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.).

**[0080]** *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.).

**[0081]** 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 EC<sub>50</sub> 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.

**[0082]** 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<sub>50</sub>, 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<sub>50</sub> falls.

#### **Algal Inhibition Test**

**[0083]** 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.

**[0084]** 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.

**[0085]** 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.

**[0086]** 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.

**[0087]** 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.

**[0088]** A suitable lubricant or lubricant additive composition, according to the present disclosure, may use tribologically functional components that may not exhibit persistence, bioaccumulation, or toxicity when tested according to the procedures set forth above. Accordingly, a tribologically functional component that is found to be persistent, bioaccumulative, and toxic may not be included in lubricating formulations of the present disclosure.

**[0089]** Acceptable tribologically functional components may include one or more components functionally described as: antioxidants, dispersants, detergents, viscosity index improvers, friction modifiers, pour point depressants, antiwear agents, extreme pressure agents, rust inhibitors, corrosion inhibitors, foam inhibitors, seal swell additives, and diluents. Such components may be deemed acceptable for use in compositions of the present disclosure upon receiving a passing evaluation in testing for persistence, bioaccumulation, or toxicity using the test methods and/or criteria described above.

**[0090]** Suitable embodiments of the present disclosure may incorporate one or more of the following substances: a sulfurized neopentyl glycol phosphate, a succinimide, a fatty amine ethoxylate, an oleamide, a dodecyl succinic acid, an adipate, a sulfurized isobutylene, an alkylthiadiazole, a polyalphaolefin, an alkylpolymethacrylate comprising less than 0.3% weight of unreacted monomer, and/or an olefin copolymer or multifunctional olefin copolymer comprising less than 0.3% weight of unreacted monomer.

**[0091]** An exemplary fluid composition containing tribologically 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 Additives**

Component	Example 1 (Wt. % based on finished fluid)	Example 2 (Wt. % based on finished fluid)
Dispersant	0-5.0	0.5-4.5
Detergent	0-15	0.1 -10
Antioxidant	0-5.0	0.01-3.0
Corrosion inhibitor	0-5.0	0-2.0
Antiwear agent and/or Extreme pressure agent	0-7.0	0.1-5.0
Antifoaming agent	0-5.0	0.001-0.15
Pour point depressant	0-5.0	0.01-1.5
Viscosity modifier	0-12.00	0.01-10.0
Friction modifier	0-1.25	0.05-1.0
Seal swell agent	0-15	1.5-10
Process oil	0-10.0	0.1-5.0
Base oil	Balance	Balance

**[0092]** The conventional additives indicated in Table I may be combined with one or more base oils 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 <sup>1</sup>	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			

Groups I-III are mineral oil base stocks.

**[0093]** 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.

**[0094]** 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 of 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 lubricant base oils. The base oil component of the lubricant 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 lubricant formulations made with such GTL base oils include a solubilizing agent that aids in solubilizing additives and degradation products in the finished lubricant 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.

### **Viscosity Modifiers**

**[0095]** Viscosity modifiers for use in finished lubricant 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 lubricant composition as described herein may contain 0.1 to 40 wt. % olefin (co)polymer.

**[0096]** The olefin (co)polymer which may be used is a homopolymer, copolymer, or terpolymer resulting from the polymerization of C<sub>2</sub>-C<sub>10</sub> 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<sub>2</sub>-C<sub>10</sub> 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.

### **Dispersants**

**[0097]** The dispersants useful in the lubricant 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.

**[0098]** The alkenyl succinimides in which the succinic group contains a hydrocarbyl substituent containing at least 30 carbon atoms are described for example in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435. Such alkenyl succinimides may be derived from polyisobutenyl succinic anhydride (PIBSA) having a number average molecular weight ranging from about 200 to about 2100 as determined by gel permeation chromatography. Alkenyl succinic acid esters and diesters of polyhydric alcohols containing 2-20 carbon atoms and 2-6 hydroxyl groups can be used in forming the phosphorus-containing ashless dispersants. Representative examples are described in U.S. Pat. Nos. 3,331,776; 3,381,022; and 3,522,179. The alkenyl succinic portion of these esters corresponds to the alkenyl succinic portion of the succinimides described above.

**[0099]** Suitable alkenyl succinic ester-amides for forming phosphorylated ashless dispersant are described for example in U.S. Pat. Nos. 3,184,474; 3,576,743; 3,632,511; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,991,098; 4,071,548; and 4,173,540.

**[0100]** 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; 3,558,743; 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.

**[0101]** 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.

**[0102]** 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.

**[0103]** Suitable procedures for phosphorylating and boronating ashless dispersants such as those referred to above are set forth in U.S. Pat. Nos. 4,857,214 and 5,198,133.

**[0104]** The amount of ashless dispersant on an "active ingredient basis" (i.e., excluding the weight of impurities, diluents and solvents typically associated therewith) is generally within the range of about 0.5 to about 7.5 weight percent (wt %), typically within the range of about 0.5 to 5.0 wt %, notably within the range of about 0.5 to about 3.0 wt %, and usually within the range of about 2.0 to about 3.0 wt %, based on the finished oil.

### **Friction Modifiers**

**[0105]** For certain applications it may be desirable to use one or more friction modifiers in preparing the finished lubricating oil formulation. Suitable friction modifiers include such compounds as aliphatic fatty acid amides, aliphatic carboxylic acids, aliphatic carboxylic esters, aliphatic carboxylic ester-amides, aliphatic phosphonates, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, organic molybdenum compounds, or mixtures thereof. The aliphatic group typically contains at least about eight carbon atoms so as to render the compound suitably oil soluble. Also suitable are aliphatic substituted succinimides formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia.

**[0106]** The use of friction modifiers is optional. However, in applications where friction modifiers are used, finished lubricant 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**

**[0107]** Finished lubricant compositions as described herein typically will contain some inhibitors. The inhibitor components serve different functions including rust inhibition, 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 lubricant 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 lubricant 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.

**[0108]** Foam inhibitors form one type of inhibitor suitable for use as an inhibitor component in the finished lubricant compositions. Useful foam inhibitors include silicones, surfactants, and the like.

**[0109]** Copper corrosion inhibitors constitute another class of additives suitable for inclusion in the finished lubricant compositions. Such compounds include thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltria-zole, decyltriazone, dodecyltriazone, 2-mercapto benzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-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.

**[0110]** Rust or corrosion inhibitors comprise another type of inhibitor additive for use in finished lubricant compositions. Such materials 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 fatty acids, oleic acid, linoleic acid, or the like.

**[0111]** Another useful type of rust inhibitor for use in the disclosed lubricant 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 rust or 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 rust or corrosion inhibitors can be used.

**Antioxidants**

**[0112]** Antioxidants may also be present in the finished lubricant formulations of the disclosure. Suitable antioxidants include phenolic antioxidants, aromatic amine antioxidants, and sulfurized phenolic antioxidants, among others. Examples of phenolic antioxidants include 2,6-di-tert-butylphenol, liquid mixtures of tertiary butylated phenols, 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), mixed methylene-bridged polyalkyl phenols, and 4,4'-thiobis(2-methyl-6-tert-butylphenol). N,N'-di-sec-butyl-p-phenylenediamine, 4-isopropylaminodiphenyl amine, phenyl-naphthyl amine, phenyl-naphthyl amine, and ring-alkylated diphenylamines serve as examples of aromatic amine antioxidants. In one embodiment, the antioxidants are the sterically hindered tertiary butylated phenols, the ring alkylated diphenylamines, and combinations thereof.

**Detergents**

**[0113]** Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life for lubricant formulation used in crankcase applications. 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 comprises 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.

**[0114]** 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.

**[0115]** 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.

**[0116]** 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.

**[0117]** 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.

**[0118]** 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.

**[0119]** 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.

[0120] The overbased metal detergents may also be borated. The boron may be introduced by using boric acid as the acidic material used in the overbasing step. However a desirable alternative is to borate the overbased product after formation by reacting a boron compound with the overbased metal salt. Boron compounds include boron oxide, boron oxide hydrate, boron trioxide, boron trifluoride, boron tribromide, boron trichloride, boron acid such as boronic acid, boric acid, tetraboric acid and metaboric acid, boron hydrides, boron amides and various esters of boron acids. Generally, the overbased metal salt may be reacted with a boron compound at from 50° C to 250° C, in the presence of a solvent such as mineral oil or xylene. The borated, overbased alkali metal salt comprises at least 0.5%, and typically from 1% to 5%, by weight boron.

[0121] The amount of detergent in a finished lubricant composition according to the disclosed embodiments may range from about 0.1 to about 15 percent by weight based on the total weight of the finished lubricant composition.

### **Antiwear and Extreme Pressure Agents**

[0122] Various types of sulfur-containing antiwear and/or extreme pressure agents may be used in the finished lubricant 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 and/or extreme pressure 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.

[0123] Use may also be made of a wide variety of phosphorus-containing oil-soluble antiwear and/or extreme pressure additives such as the oil-soluble organic phosphates, organic phosphites, organic phosphonates, organic phosphonites, etc., and their sulfur analogs. Also useful as the phosphorus-containing antiwear and/or extreme pressure additives that may be used in the disclosed lubricant compositions include those compounds that contain both phosphorus and nitrogen. Phosphorus-containing oil-soluble antiwear and/or extreme pressure additives useful in the disclosed embodiments include those compounds taught in U.S. Pat. Nos. 5,464,549; 5,500,140; and 5,573,696, the disclosures of which are hereby incorporated by reference.

[0124] The phosphorus-containing antiwear agents may include an organic ester of phosphoric acid, phosphorous acid, or an amine salt thereof. For example, phosphorus-containing antiwear agent may include one or more of a dihydrocarbyl phosphite, a trihydrocarbyl phosphite, a dihydrocarbyl phosphate, a trihydrocarbyl phosphate, any sulfur analogs thereof, and any amine salts thereof.

[0125] The phosphorus-containing antiwear agent may be present in an amount sufficient to provide about 10 to about 500 parts per million by weight of phosphorus in the finished lubricant composition. As a further example, the phosphorus-containing antiwear agent may be present in an amount sufficient to provide about 150 to about 300 parts per million by weight of phosphorus in the finished lubricant composition.

[0126] One such type of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additives which may be used are the phosphorus- and nitrogen-containing compositions of the type described in G.B. 1,009,913; U.S. Pat. No. 3,197,405 and/or U.S. Pat. No. 3,197,496. In general, these compositions are formed by forming an acidic intermediate by the reaction of a hydroxy-substituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide or phosphorus halide, and neutralizing a substantial portion of said acidic intermediate with an amine or hydroxy-substituted amine. Other types of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additive that may be used in the lubricant compositions described herein include the amine salts of hydroxy-substituted phosphetanes or the amine salts of hydroxy-substituted thiophosphetanes and the amine salts of partial esters of phosphoric and thiophosphoric acids.

### **Pour point depressants**

[0127] The lubricant additive package or lubricant compositions disclosed herein 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 polyacrylamides; condensation products of halo-paraffin 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.

[0128] In one embodiment, the pour point depressant is represented by the general structural formula: Ar(R)-(Ar<sup>1</sup>(R<sup>1</sup>))-Ar<sup>2</sup>, wherein the Ar, Ar<sup>1</sup> and Ar<sup>2</sup> are aromatic groups of up to about 12 carbon atoms, (R) and (R<sup>1</sup>) are independently an alkylene group containing 1 to 100 carbon atoms with the proviso that at least one of (R) or (R<sup>1</sup>) is CH<sub>2</sub>, and n is 0 to about 1000 with the proviso that if n is 0, then (R) is CH<sub>2</sub> 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

[0129] Seal swell agents may be included in the finished lubricant compositions of the disclosed embodiments particularly when the lubricant 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 C<sub>8</sub>-C<sub>13</sub> alkanols (or mixtures thereof), and the phthalates of C<sub>4</sub>-C<sub>13</sub> 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.

[0130] 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.

[0131] 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 fluid. In the case of the phthalates, the levels in the transmission fluid 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

[0132] A wide variety of thickening agents may be used for providing lubricants and greases 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.

[0133] 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, pyro-mellitdiimides, ammeline, and hydrophobic clays.

[0134] 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.

[0135] It will be appreciated that the individual components employed may be separately blended into the base 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.

[0136] Additive concentrates may thus be formulated to contain all of the additive components and if desired, some of the base oil component, in amounts proportioned to yield finished fluid blends consistent with the concentrations described above. In most cases, the additive concentrate will contain one or more diluents such as light mineral 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.

**[0137]** 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 alkoxyated amines, long-chain alkyl alkoxyated alcohols, long-chain alkyl alkylene amines, long-chain alkyl amines, long-chain alkyl methacrylates, long-chain alkoxyated amines, long-chain hydroxyalkyl amines, polyaryls, and polyolefin polyamines.

**[0138]** Lubricating fluids of the embodiments herein may be formulated to provide lubrication and/or enhanced friction performance properties and/or improved low temperature viscometric properties for various applications. A lubricant composition according to the present disclosure may be used for lubricating a machine part.

**[0139]** Such fluids may be suitable for automatic or manual transmissions, including step automatic transmissions, continuously variable transmissions (chain, belt, or disk type), semi-automatic transmissions, automated manual transmissions, toroidal transmissions, and dual clutch transmissions. Example automatic transmissions include four-, five-, six-, and seven-speed transmissions. Further, the lubricating fluids of the present disclosure also are suitable for use in transmissions with an electronically controlled converter clutch, a slipping torque converter, a continuously slipping torque converter clutch, a lock-up torque converter, a starting clutch, and/or one or more shifting clutches.

**[0140]** A further aspect of the present disclosure may be directed specifically toward providing a fluid for a transmission. Exemplary transmissions may include those described in "Transmission and Driveline Design", SAE Paper Number SP-108, Society of Automotive Engineers, Warrendale PA 1995; "Design of Practices: Passenger Car Automotive Transmissions", The Third Edition, SAE Publication # AE-18, Society of Automotive Engineers, Warrendale PA 1994; and "Automotive Transmission Advancements", SAE Paper Number SP-854, Society of Automotive Engineers, Warrendale PA 1991.

**[0141]** Lubricating fluids according to the present disclosure may also be used in gear applications, such as industrial gear applications, automotive gear applications, axles, and stationary gearboxes. Gear-types may include, but are not limited to, spur, spiral, worm, rack and pinion, involute, bevel, helical, planetary, and hypoid gears.

**[0142]** The presently disclosed lubricating fluids may be used in axles, transfer cases, differentials, such as straight differentials, turning differentials, limited slip differentials, clutch-type differentials, and locking differentials, and the like.

**[0143]** Lubricating fluids 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. Engine components that may be lubricated with presently disclosed additives may include pistons, bearings, crankshafts, and/or camshafts.

**[0144]** Further, lubricating fluids of the present disclosure may also be useful in metalworking applications.

**[0145]** A further aspect of the present disclosure may provide lubricant composition comprising a lubricant additive as described herein, wherein the lubricant composition is suitable for lubricating moving components or parts of a truck, an automobile, and/or a piece of mechanized farm equipment, such as a tractor or reaper.

**[0146]** In another aspect, lubricant additive compositions of the present disclosure may further be useful in grease compositions, or in lubricants for cutting, quenching, or rolling applications.

**[0147]** In one embodiment, a composition of the present disclosure may be manufactured in the United States of America or Canada.

**[0148]** In a further embodiment, a composition of the present disclosure may be transported to Europe by ship, air, rail, or truck.

**[0149]** 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.

**[0150]** 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.

**[0151]** 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.

**[0152]** 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:**

**[0153]**

1. An environmentally compatible lubricant additive composition comprising four or more tribologically 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 lubricant additive composition of embodiment 1, wherein the tribologically functional components comprise materials selected from the group consisting of: antioxidants, dispersants, detergents, viscosity index improvers, friction modifiers, pour point depressants, antiwear agents, extreme pressure agents, rust inhibitors, corrosion inhibitors, foam inhibitors, seal swell additives, and diluents.

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

6. The lubricant 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 lubricant 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 lubricant 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 lubricant additive composition of embodiment 1, wherein at least one of the components is selected from the group consisting of: a sulfurized neopentyl glycol phosphates, a substituted succinimide, a reaction product of a C<sub>16</sub> alkyl dicarboxylic acid and ammonia, a fatty amine ethoxylate, an oleamide, and a dodecyl succinic acid.

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

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

viscosity index improver.

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

13. The lubricant additive composition of embodiment 1, wherein at least one of the components comprises a seal swell agent.

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

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

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

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

20. The lubricant additive composition of embodiment 1, wherein the additive is useful in grease compositions.

21. The lubricant additive composition of embodiment 1, wherein the additive is useful in cutting, quenching, or rolling applications.

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

24. An environmentally compatible lubricating composition, comprising:

- a) a major amount of a base oil; and
- b) a minor amount of an additive composition, comprising four or more tribologically functional components, wherein each component comprises at least one of: an acceptable level 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.

25. The lubricating composition of embodiment 24, wherein the tribologically functional components comprise materials selected from the group consisting of: antioxidants, dispersants, detergents, viscosity index improvers, friction modifiers, pour point depressants, antiwear agents, extreme pressure agents, rust inhibitors, corrosion inhibitors, foam inhibitors, seal swell additives, and diluents.

26. The lubricating 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 lubricating composition of embodiment 24, wherein the bioconcentration factor test comprises a flow-through

fish test.

28. The lubricating 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 lubricating 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 lubricating composition of embodiment 24, wherein the base oil is selected from 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 a mixture thereof.

31. The lubricating composition of embodiment 24, wherein at least one of the components comprises a pour point depressant.

32. The lubricating composition of embodiment 24, wherein at least one of the components comprises a viscosity index improver.

33. The lubricating composition of embodiment 24, wherein at least one of the components comprises a foam inhibitor.

34. The lubricating composition of embodiment 24, wherein at least one of the components comprises a seal swell additive.

35. The lubricating composition of embodiment 24, wherein at least one of the components comprises an adipate.

36. The lubricating composition of embodiment 24, wherein at least one of the components comprises a sulfurized isobutylene.

37. The lubricating composition of embodiment 24, wherein at least one of the components comprises an alkylthiadiazole.

38. The lubricating composition of embodiment 24, wherein at least one of the components comprises an alkylpolymethacrylate comprising less than 0.3% weight of unreacted monomer.

39. The lubricating composition of embodiment 24, 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.

40. The additive composition of embodiment 24, wherein at least one of the components comprises a polyalphaolefin.

41. The lubricating composition of embodiment 24, 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<sub>16</sub> alkyl dicarboxylic acid and ammonia, a fatty amine ethoxylate, an oleamide, and a dodecyl succinic acid.

42. A method of making an environmentally compatible lubricant composition, comprising combining a major amount of a base oil and a minor amount of an additive composition, comprising four or more tribologically 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 lubricant composition complies with European Council Directive 67/548/EEC.

43. The method of embodiment 42, wherein the tribologically functional component further comprises a material

selected from the group consisting of: antioxidants, dispersants, detergents, viscosity index improvers, friction modifiers, pour point depressants, antiwear agents, extreme pressure agents, rust inhibitors, corrosion inhibitors, foam inhibitors, seal swell additives, and diluents.

5 44. The method of embodiment 42, 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.

10 45. The method of embodiment 42, wherein the bioconcentration factor test comprises a flow-through fish test.

46. The method of embodiment 42, 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.

15 47. The method of embodiment 42, 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;
- 20 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.

25 48. An environmentally compatible lubricating composition comprising:

- a) a major amount of a base oil; and
- b) a minor amount of an additive composition, comprising four or more tribologically 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.

30 49. The lubricating composition of embodiment 48, wherein the tribologically functional components comprise materials selected from the group consisting of: antioxidants, dispersants, detergents, viscosity index improvers, friction modifiers, pour point depressants, antiwear agents, extreme pressure agents, rust inhibitors, corrosion inhibitors, foam inhibitors, seal swell additives, and diluents.

35 50. A method of lubricating a machine part comprising lubricating said machine part with a lubricant composition comprising an additive composition of embodiment 48.

40 51. The method of embodiment 50, wherein said machine part comprises a gear, an axle, a differential, an engine, a crankshaft, a transmission, or a clutch.

45 52. The method of embodiment 51, wherein said transmission is selected from the group consisting of an automatic transmission, a manual transmission, an automated manual transmission, a semi-automatic transmission, a dual clutch transmission, a continuously variable transmission, and a toroidal transmission.

50 53. The method of embodiment 51, wherein said transmission comprises a continuously slipping torque converter clutch, a slipping torque converter, a lock-up torque converter, a starting clutch, one or more shifting clutches, or an electronically controlled converter clutch.

54. The method of embodiment 51, wherein said gear is selected from the group consisting of an automotive gear, a stationary gearbox, and an axle.

55 55. The method of embodiment 51, wherein said gear is selected from the group consisting of a hypoid gear, a spur gear, a helical gear, a bevel gear, a worm gear, a rack and pinion gear, a planetary gear set, and an involute gear.

56. The method of embodiment 51, wherein said differential is selected from the group consisting of a straight differential, a turning differential, a limited slip differential, a clutch-type limited slip differential, and a locking differ-

ential.

57. The method of embodiment 51, 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, and a two-stroke engine.

58. The method of embodiment 51, wherein said engine comprises a piston, a bearing, a crankshaft, and/or a camshaft.

59. An environmentally compatible lubricant additive composition comprising four or more tribologically 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/or toxic.

60. The lubricant additive composition of embodiment 59, wherein the tribologically functional components comprise materials selected from the group consisting of: antioxidants, dispersants, detergents, viscosity index improvers, friction modifiers, pour point depressants, antiwear agents, extreme pressure agents, rust inhibitors, corrosion inhibitors, foam inhibitors, seal swell additives, and diluents.

61. The lubricant additive composition of embodiment 59 or 60, 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 and/or wherein the non-bioaccumulative material has bioconcentration factor test result below 2000, determined by a bioconcentration factor test comprising a flow-through fish test 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 selected from the group consisting of an acute toxicity for fish test, an acute toxicity for *Daphnia* test, and an algal inhibition test.

62. The lubricant additive composition of any one of embodiments 59 to 61, 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.

63. The lubricant additive composition of any one of embodiments 59 to 62, 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<sub>16</sub> alkyl dicarboxylic acid and ammonia, a fatty amine ethoxylate, an oleamide, and a dodecyl succinic acid.

64. The lubricant additive composition of embodiment 59, wherein at least one of the components comprises one or more of the following:

- a) a pour point depressant;
- b) a viscosity index improver;
- c) a foam inhibitor;
- d) a seal swell agent;
- e) an adipate;
- f) a sulfurized isobutylene;
- g) an alkylthiadiazole;
- h) an alkylpolymethacrylate comprising less than 0.3% weight of unreacted monomer;
- i) an olefin copolymer or a multifunctional olefin copolymer viscosity index improver comprising less than 0.3% weight of unreacted monomer;
- j) a polyalphaolefin.

65. Use of the lubricant additive composition of any one of embodiments 59 to 64, in grease compositions and/or in cutting, quenching, or rolling applications.

66. An environmentally compatible lubricating composition, comprising:

- a) a major amount of a base oil; and
- b) a minor amount of an additive composition according to any one of embodiments 59 to 65, preferably wherein each component of the four or more tribologically functional compounds comprises at least one of: an acceptable level 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.

67. The lubricating composition of embodiment 66, wherein the base oil is selected from 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 a mixture thereof.

68. A method of making an environmentally compatible lubricant composition according to embodiment 66 or 67, comprising combining a major amount of a base oil and a minor amount of an additive composition, comprising four or more tribologically functional components according to any one of claims 1 to 6, 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 lubricant composition complies with European Council Directive 67/548/EEC.

69. Use of a lubricating composition according to embodiment 67 or 68 for lubricating a machine part.

70. The use of embodiment 69, wherein said machine part comprises a gear, an axle, a differential, an engine, a crankshaft, a transmission, and/or a clutch, wherein said transmission is preferably selected from the group consisting of an automatic transmission, a manual transmission, an automated manual transmission, a semi-automatic transmission, a dual clutch transmission, a continuously variable transmission, and a toroidal transmission; wherein said transmission preferably comprises a continuously slipping torque converter clutch, a slipping torque converter, a lock-up torque converter, a starting clutch, one or more shifting clutches, or an electronically controlled converter clutch; wherein said gear is preferably selected from the group consisting of an automotive gear, a stationary gearbox, and an axle or from the group consisting of a hypoid gear, a spur gear, a helical gear, a bevel gear, a worm gear, a rack and pinion gear, a planetary gear set, and an involute gear; wherein said differential is preferably selected from the group consisting of a straight differential, a turning differential, a limited slip differential, a clutch-type limited slip differential, and a locking differential; and wherein said engine is preferably selected from the group consisting of an internal combustion engine, a rotary engine, a gas turbine engine, a four-stroke engine, and a two-stroke engine; said engine optionally comprising a piston, a bearing, a crankshaft, and/or a camshaft.

## Claims

1. An environmentally compatible lubricant additive composition comprising four or more tribologically functional components, wherein each component of the four or more tribologically functional components 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.
2. The lubricant additive composition of claim 1, wherein the tribologically functional components comprise materials selected from the group consisting of: antioxidants, dispersants, detergents, viscosity index improvers, friction modifiers, pour point depressants, antiwear agents, extreme pressure agents, rust inhibitors, corrosion inhibitors, foam inhibitors, seal swell additives, and diluents.
3. The lubricant additive composition of claim 1 or 2, 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 and/or

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.

- 5 4. The lubricant additive composition of any one of claims 1 to 3, wherein an acceptable level of a non-persistent biodegradation is determined by at least one of the following:

- 10 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.

- 15 5. The lubricant 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<sub>16</sub> alkyl dicarboxylic acid and ammonia, a fatty amine ethoxylate, an oleamide, and a dodecyl succinic acid.

- 20 6. The lubricant additive composition of claim 1, wherein at least one of the components comprises one or more of the following:

- 25 a) a pour point depressant;  
b) a viscosity index improver;  
c) a foam inhibitor;  
d) a seal swell agent;  
e) an adipate;  
f) a sulfurized isobutylene;  
g) an alkylthiadiazole;  
h) an alkylpolymethacrylate comprising less than 0.3% weight of unreacted monomer;  
30 i) an olefin copolymer or a multifunctional olefin copolymer viscosity index improver comprising less than 0.3% weight of unreacted monomer;  
j) a polyalphaolefin.

- 35 7. The lubricant additive composition of any one of claims 1 to 6, wherein the tribologically functional compounds are used in the lubricating formulation to provide a change in characteristic or property of the fluid containing the component, preferably wherein the characteristics or properties are not associated directly with the surface, preferably selected from oxidation inhibitors, dispersants and/or detergents.

- 40 8. Use of the lubricant additive composition of any one of claims 1 to 7, in grease compositions and/or in cutting, quenching, or rolling applications.

9. An environmentally compatible lubricant composition, comprising:

- 45 a) a major amount of a base oil; and  
b) a minor amount of an additive composition according to any one of claims 1 to 7.

- 50 10. The composition according to claim 9, wherein each component of the four or more tribologically functional compounds comprises at least one of: an acceptable level 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.

11. The lubricating composition of claim 10, wherein the base oil is selected from 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 a mixture thereof.

- 55 12. A method of making an environmentally compatible lubricant composition according to any one of claims 9 to 11, comprising combining a major amount of a base oil and a minor amount of an additive composition, comprising four or more tribologically functional components according to any one of claims 1 to 7, 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 lubricant composition complies with European Council Directive 67/548/EEC.

13. Use of a lubricating composition according to any one of claims 9 to 11 for lubricating a machine part.

14. The use of claim 13, wherein said machine part comprises a gear, an axle, a differential, an engine, a crankshaft, a transmission, and/or a clutch,  
wherein said transmission is preferably selected from the group consisting of an automatic transmission, a manual transmission, an automated manual transmission, a semi-automatic transmission, a dual clutch transmission, a continuously variable transmission, and a toroidal transmission;  
wherein said transmission preferably comprises a continuously slipping torque converter clutch, a slipping torque converter, a lock-up torque converter, a starting clutch, one or more shifting clutches, or an electronically controlled converter clutch;  
wherein said gear is preferably selected from the group consisting of an automotive gear, a stationary gearbox, and an axle or  
from the group consisting of a hypoid gear, a spur gear, a helical gear, a bevel gear, a worm gear, a rack and pinion gear, a planetary gear set, and an involute gear;  
wherein said differential is preferably selected from the group consisting of a straight differential, a turning differential, a limited slip differential, a clutch-type limited slip differential, and a locking differential; and  
wherein said engine is preferably selected from the group consisting of an internal combustion engine, a rotary engine, a gas turbine engine, a four-stroke engine, and a two-stroke engine;  
said engine optionally comprising a piston, a bearing, a crankshaft, and/or a camshaft.





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EP 11 15 8294

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