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(54) REDUCING HIGH-AQUEOUS CONTENT SLUDGE IN DIESEL ENGINES

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(57) ABSTRACT

Formation of high-aqueous content sludge may be reduced in a sump lubricated diesel engine lubricated with a lubricating oil formulation that contains at least 0.07 or 0.08 weight percent nitrogen derived from one or more nitrogen-containing ashless dispersants, by including in the lubricant a polyalkylene oxide.

REDUCING HIGH-AQUEOUS CONTENT SLUDGE IN DIESEL ENGINES

BACKGROUND OF THE INVENTION

[0001] The disclosed technology relates to lubricant formulations and methods for reducing or eliminating accumulation of high-aqueous content sludge, or reducing its formation or viscosity, in internal combustion engines.

[0002] Modern engine oil formulations, in particular for diesel (compression ignited) engines contain a variety of additives to impart desired lubricating performance. Recently, there has been increasing emphasis on providing lubricants with high content of nitrogen-containing dispersant. This development has not been without problems, however. In certain engines, especially those with restricted crankcase ventilation, an unusual form of sludge has been observed accumulating in cooler portions of the engine, such as on a rocker cover. This sludge may also be observed on other parts of the engine. We characterize this material as high-aqueous content sludge, as it is a sludge-like material that appears to be a combination of lubricant oil with relatively high amounts of water, e.g., up to 70-80 weight percent water. It is speculated that this sludge may arise due the accumulation of water from combustion in the lubricant oil, particularly when combustion products are not efficiently purged from the crankcase due to restricted ventilation. The accumulation of this sludge can lead to restrictive flow of lubricant and corrosion of metal surfaces. It is therefore desirable to reduce or eliminate the formation or accumulation of this sludge.

[0003] A variety of lubricants have been used for lubricating internal combustion engines. For instance, U.S. Pat. No. 6,642,189, Kurihara et al., Nov. 4, 2003, discloses engine oil compositions that may be used in motorcycle engines, automobile engines, diesel engines for land use, and marine diesel engines. The lubricant contains a lubricating base oil and a polymethacrylatebased viscosity index improver. It may also contain a molybdenum dithiocarbamate as well as one or more other engine oil additives. Among these are detergents, dispersants, oxidation inhibitors, friction modifiers, corrosion inhibitors, demulsifying agents such as polyalkylene glycol-based non-ionic surfactants, metal deactivators, and antifoamers.

[0004] U.S. Pat. No. 5,198,135, Galic et al., Mar. 30, 1993, discloses a crankcase lubricating oil composition containing as an antiemulsion agent an effective amount of a butylene oxide containing polymer. Other components that may be present include a hydrocarbon-soluble ashless dispersant, an alkali or alkaline earth metal detergent, a zinc dialkyldithiophosphate, an antioxidant, a viscosity modifier, a rust inhibitor, and a pour point depressant.

[0005] U.S. Pat. No. 3,509,052, Murphy, Apr. 28, 1970, discloses improved lubricating composition which contain a demulsifier. The compositions reduce or eliminate the formation of sludge on the internal metal surfaces of internal combustion engines. Polyoxyalkylene polyols are preferred demulsifiers. The sludges have been found in the rocker arm covers and oil-fill caps of, particularly, smaller car engines.

SUMMARY OF THE INVENTION

[0006] The disclosed technology provides, in one embodiment, a method for reducing accumulation of high-aqueous content sludge in a sump-lubricated diesel engine lubricated with a lubricating oil formulation that contains at least 0.07 or at least 0.08 weight percent nitrogen derived from one or more nitrogencontaining ashless dispersants, said method comprising: including in said lubricant at least 0.05 percent by weight of a polyalkylene oxide.

[0007] In another embodiment, the technology provides a method for reducing accumulation of high-aqueous content sludge in a sump-lubricated diesel engine lubricated with a lubricating oil formulation that contains at least one nitrogen-containing dispersant and optionally at least one dispersant viscosity modifier or polymeric material, wherein {the weight percent nitrogen derived from one or more nitrogen-containing ashless dispersants and nitrogencontaining dispersant viscosity modifiers} plus {0.1 times the weight percent of any aromatic carbon provided by the following aromatic containing materials: polymeric materials, dispersants, and dispersant viscosity modifiers} is at least 0.07 (or alternatively at least 0.08), said method comprising: including in said lubricant at least about 0.05 percent by weight of a polyalkylene oxide.

[0008] The disclosed technology also provides a lubricant composition suitable for reducing accumulation of high-aqueous content sludge in a sumplubricated diesel engine, comprising: an oil of lubricating viscosity; one or more nitrogen-containing ashless dispersants in an amount to provide at least 0.07 or 0.08 weight percent nitrogen to the lubricant composition; and at least 0.05 percent by weight of a polyalkylene oxide.

[0009] In another embodiment the formulation contains one or more nitrogen-containing ashless dispersants or dispersant viscosity modifiers such that the formulation contains at least one nitrogen-containing dispersant and optionally at least one dispersant viscosity modifier or polymeric material, wherein {the weight percent nitrogen derived from one or more nitrogen-containing ashless dispersants and nitrogen-containing dispersant viscosity modifiers} plus {0.1 times the weight percent of any aromatic carbon provided by the following aromatic containing materials: polymeric materials, dispersants, and dispersant viscosity modifiers} is at least 0.07.

DETAILED DESCRIPTION OF THE INVENTION

[0010] Various preferred features and embodiments will be described below by way of non-limiting illustration.

[0011] The technology described herein is suitable for use in a sumplubricated diesel engine, that is, a compression ignited engine. Diesel engines are commonly used in passenger cars, trucks, off-road vehicles, and marine vessels. The technology is particularly useful in those engines that are susceptible to contamination with high aqueous content sludge, as described above. While such sludge accumulation has been observed in a variety of diesel engines, it is believed to be particularly significant in engines having restricted crankcase ventilation, sometimes referred to as "closed crankcase" or "pseudo-closed crankcase" systems. In such systems, products of combustion such as water vapor may accumulate and, by combination with the lubricant or portions of the lubricant, by mechanisms that are not fully understood, may lead to formation of high water-based sludge in relatively cooler portions of the engine. A rocker cover, for example, may have an ambient operating temperature of only about 25° C. under certain conditions, and thus this is a location where collection of this sludge may be a problem.

[0012] One component of the sludge is the lubricating oil or at least a portion or components or elements of the overall lubricating oil composition. Lubricants for internal combustion engines typically include a number of components that have been selected to perform various important functions. One such component, and normally the majority component (by which is meant a component that is present in a major amount, that is, greater than 50 percent by weight), is an oil of lubricating viscosity.

[0013] The base oil used in the inventive lubricating oil composition may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows:

Base Oil Category	Sulfur (%)		Saturates (%)	Visc. 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, II, III or IV			

Groups I, II and III are mineral oil base stocks. "Gas-to-liquid" base stocks are also generally considered Group III. The oil of lubricating viscosity, then, can include natural or synthetic lubricating oils and mixtures thereof. Mixture of mineral oil and synthetic oils, particularly polyalphaolefin oils and polyester oils, are often used in lubricants. However, the problem of high aqueous sludge formation is sometimes more severe in some of the more highly refined base oils, in particularly, Group II or Group III or Group IV oils or mixtures thereof, or mixtures of oils that contain a significant amount of Group II or Group III or Group IV content (e.g., 50 percent by weight or more, or 80 or 90 percent or more, of the total amount of base oil). In another embodiment the oils may be Group II or Group III oils or such mixtures thereof.

[0014] Natural oils include animal oils and vegetable oils (e.g. castor oil, lard oil and other vegetable acid esters) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Hydrotreated or hydrocracked oils are included within the scope of useful oils of lubricating viscosity.

[0015] Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymerized olefins and mixtures thereof, alkylbenzenes, polyphenyl, (e.g., biphenyls, terphenyls, and alkylated polyphenyls), alkylated diphenyl ethers and alkylated diphenyl sulfides and their derivatives, analogs and homologues thereof. Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids and those made from C5 to C12 monocarboxylic acids and polyols or polyol ethers.

[0016] Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils, and silicate oils.

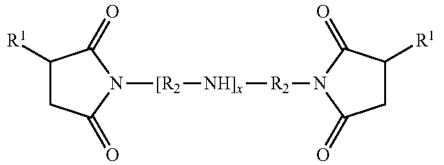
[0017] Hydrotreated naphthenic oils are also known and can be used. Synthetic oils may be used, such as those produced by Fischer-Tropsch reactions and typically may be hydroisomerised Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0018] Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0019] The amount of the oil will typically be greater than 50 percent by weight of the lubricant composition when the composition is a fully formulated lubricant. It may be equal to the balance of the total lubricant after the dispersant, polyalkylene oxide, and any other components are accounted for. Thus, it may be, in certain embodiments 70 to 96 percent or 80 to 95 percent or 85 to 90 percent . In certain embodiments, the lubricant composition may be in the form of a concentrate, suitable for subsequent dilution with additional oil and optionally addition of further components to prepare the fully formulated lubricant. In such cases the amount of the oil will be proportionally less, e.g., 20 to 80 percent.

[0020] The lubricants will also contain a dispersant, in particular, a nitrogen-containing dispersant. Dispersants are almost universally used in lubricants for diesel engines, and the problem of formation of high aqueous sludge is particularly prominent in lubricants containing a relatively large amount of nitrogen-containing dispersant.

[0021] Dispersants are well known in the field of lubricants and include primarily what is known as ashless dispersants and polymeric dispersants. Ashless dispersants are so-called because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However they may, of course, interact with ambient metals once they are added to a lubricant which includes metal-containing species. Such dispersants are typically referred to as "ashless" even if they have been post-treated with various agents, such as a borating agent to provide a borated dispersant. Such dispersants are ashless in the sense that they do not contain metal or contribute metal content to a lubricant, even though the presence of boron may make a small contribution to sulfated ash as measured by ASTM D 874. Such materials would typically be encompassed within the ashless dispersants of the present technology. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides (succinimide dispersants). having a variety of chemical structures including typically



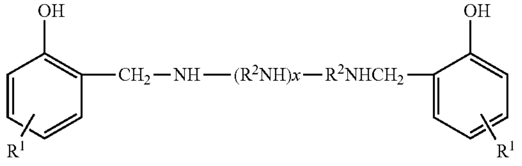
where each R^1 is independently an alkyl group, frequently a polyisobutylene group with a molecular weight (M_n) of 500-

5000 based on the polyisobutylene precursor, and R^2 are alkylene groups, commonly ethylene (C_2H_4) groups, and x is 0 to 6 or above, or 1 to 5. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylpentamine, and pentaethylhexamine. Also useful are mixtures of amines, both linear and branched in various manners, which are known commercially as amine bottoms or ethylene amine still bottoms. They may contain mixtures of N4, N5, N6, and N7 amines.

[0022] A wide variety of linkages between the acid and amine moieties is possible beside the simple imide structure shown above, including a variety of amides and ammonium salts. Also, a variety of modes of linkage of the R^1 groups onto the imide structure are possible, including various cyclic linkages. The ratio of the carbonyl groups of the acylating agent to the nitrogen atoms of the amine may be 1:0.5 to 1:3, and in other instances 1:1 to 1:2.75 or 1:1.5 to 1:2.5. Succinimide dispersants are more fully described in U.S. Pat. Nos. 4,234,435 and 3,172,892 and in EP 0355895.

[0023] In certain embodiments the dispersant may also contain ester functionality, such materials having been prepared by reacting a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol, in addition to an amine. Such materials are described in more detail in U.S. Pat. No. 3,381,022.

[0024] Another class of nitrogen-containing ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted phenol, an alkylene polyamine, and an aldehyde such as formaldehyde. Such materials may have the general structure



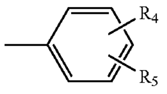
(including a variety of isomers and the like) where R^1, R^2, and x may be as described above. These are described in more detail in U.S. Pat. No. 3,634,515. Dispersants of the various types described herein can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. Pat. No. 4,654,403.

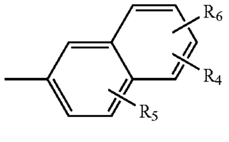
[0025] In certain embodiments of the present technology, Mannich dispersants may be present in relatively low amounts or may be absent altogether. If Mannich dispersants are the lubricating composition is substantially free from Mannich dispersants. This means that, for such embodiments, any Mannich dispersants may be present as less than 10% or less than 5% or less than 1% by weight of the total dispersant component, e.g., 0 or 0.001 to 5% or 0.01 to 3% or 0.1 to 1% of the total dispersant component. Low-Mannich formulations may be specified for any of a variety of reasons. In one aspect, Mannich dispersants may not be particularly desirable because they may not serve to effectively aid in soot formation, which other dispersants may do. In another aspect, Mannich dispersants would contribute both nitrogen and aromatic carbons to the overall dispersant component. It may therefore be desirable, in this instance, to avoid "double counting" any Mannich dispersant, to count the nitrogen that it contributes while not counting the aromatic carbon that it contributes, when calculating the minimum amount of N+ aromatic C as set forth elsewhere in this Specification.

[0026] Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer. The dispersant viscosity index modifiers, also referred to as dispersant viscosity modifiers or DVMs, can be functionalized versions of polymers which are generally used as viscosity index modifiers (as described below). Among the common classes of such polymers are olefin copolymers and acrylate or methacrylate copolymers. For example, when a small amount of a nitrogen-containing monomer is copolymerized with alkyl methacrylates, dispersancy properties may be incorporated into the product. Thus, such a product may have the multiple function of viscosity modification (as described below), pour point depressancy and dispersancy. Such products have been referred to in the art as dispersant-type viscosity modifiers or simply dispersant-viscosity modifiers. Vinyl pyridine, N-vinyl pyrrolidone and N,N'-dimethylaminoethyl methacrylate are examples of nitrogen-containing monomers. Polyacrylates obtained from the polymerization or copolymerization of one or more alkyl acrylates also are useful as viscosity modifiers. Derivatives of polyacrylate esters are well-known as dispersant viscosity index modifier additives. Dispersant acrylate or polymethacrylate viscosity modifiers such as Acryloid™ 985 or Viscoplex™ 6-054, from RohMax, are particularly useful.

[0027] Functionalized olefin copolymers can also be, for instance, interpolymers of ethylene and propylene which are grafted with an active monomer such as maleic anhydride and then derivatized with an alcohol or an amine, as described in U.S. Pat. No. 4,089,794. Other such copolymers are copolymers of ethylene and propylene which are reacted or grafted with nitrogen compounds, as described in U.S. Pat. No. 4,068,056.

[0028] The amines useful in preparing either dispersants (generally) or dispersant viscosity modifiers may, in certain embodiments, be aromatic amines containing at least one, and preferably exactly one, N—H group capable of condensing with a carboxylic acid functionality, to form nitrogen-containing carboxylic derivatives. Aromatic amines include those which can be represented by the general structure NHR—Ar, where R is hydrogen or a hydrocarbyl group and Ar is an aromatic group, including nitrogen-containing aromatic groups and Ar groups including any of the following structures





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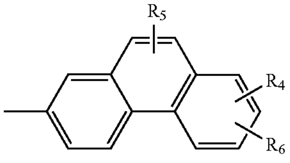
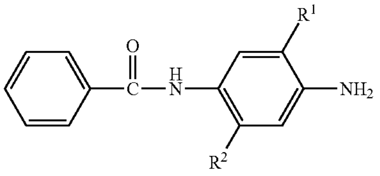


as well as multiple non-condensed aromatic rings. In these and related structures, R_4, R_5, and R_6 can be independently, among other groups disclosed herein, —H, —C_{1-18} alkyl groups, —NR—Ar, —NH—Ar, —N═N—Ar, —NH—CO—Ar, —OOC—Ar, —OOC—C_{1-18} alkyl, —COO—C_{1-18} alkyl, —OH, —O—(CH_2CH_2—O)$_n$$C_{1-18}$ alkyl groups, —NO_2, and —O—(CH_2CH_2O)$_n$Ar (where n is 0 to 10).

[0029] Examples of aromatic amines include aniline, N-alkylanilines such as N-methyl aniline, and N-butylaniline, di-(para-methylphenyl)amine, naphthylamine, 4-aminodiphenylamine, N,N-dimethylphenylenediamine, 4-(4-nitrophenylazo)aniline (disperse orange 3), sulfamethazine, 4-phenoxyaniline, 3-nitroaniline, 4-aminoacetanilide 4-amino-2-hydroxy-benzoic acid phenyl ester (phenyl amino salicylate), N-(4-amino-5-methoxy-2-methyl-phenyl)-benzamide (fast violet B), N-(4-amino-2,5-dimethoxy-phenyl)-benzamide (fast blue RR), N-(4-amino-2,5-diethoxy-phenyl)-benzamide (fast blue BB), N-(4-aminophenyl)-benzamide and 4-phenylazoaniline. Other examples include paraethoxyaniline, para-dodecylaniline, cyclohexyl-substituted naphthylamine, and thienyl-substituted aniline. Examples of other suitable aromatic amines include amino-substituted aromatic compounds and amines in which the amine nitrogen is a part of an aromatic ring, such as 3-aminoquinoline, 5-aminoquinoline, and 8-aminoquinoline. Also included are aromatic amines such as 2-aminobenzimidazole, which contains one secondary amino group attached directly to the aromatic ring and a primary amino group attached to the imidazole ring. Other amines include N-(4-anilinophenyl)-3-aminobutanamide (i.e., ϕ-NH-ϕ-NH—$COCH_2CH(CH_3)NH_2$). Additional aromatic amines and related compounds are disclosed in U.S. Pat. Nos. 4,863,623, 6,107,257, and 6,107,258; some of these include aminocarbazoles, aminoindoles, aminopyrroles, amino-indazolinones, mercaptotriazoles, aminophenothiazines, aminopyridines, aminopyrazines, aminopyrimidines, aminothiadiazoles, aminothiothiadiazoles, and aminobenzotriaozles. Other suitable amines include 3-amino-N-(4-anilinophenyl)-N-isopropyl butanamide, and N-(4-anilinophenyl)-3-{(3-aminopropyl)(cocoalkyl)amino} butanamide. Other aromatic amines which can be used include various aromatic amine dye intermediates containing multiple aromatic rings linked by, for example, amide structures. Examples include materials of the general structure



and isomeric variations thereof, where R^1 and R^2 are independently hydrogen, alkyl groups, or alkoxy groups such as methyl, methoxy, or ethoxy. In one instance, R^1 and R^2 are both —OCH_3 and the material is known as Fast Blue RR [CAS#6268-05-9]. In another instance, R^1 is —OCH_3 and R^2 is —CH_3, and the material is known as Fast Violet B [99-21-8]. When both R^1 and R^2 are ethoxy, the material is Fast Blue BB [120-00-3]. U.S. Pat. No. 5,744,429 discloses other aromatic amine compounds, particularly aminoalkylphenothiazines. N-aromatic substituted acid amide compounds, such as those disclosed in U.S. Patent application 2003/0030033 A1, may also be used for the purposes of this invention. Aromatic amines include those in which the amine nitrogen is a substituent on an aromatic carboxylic compound, that is, the nitrogen is not sp^2 hybridized within an aromatic ring.

[0030] Certain aromatic amines are commonly used as antioxidants. Of particular importance in that regard are alkylated diphenylamines such as nonyldiphenylamine and dinonyldiphenylamine. To the extent that these materials will condense with the carboxylic functionality of the polymer chain, they are also suitable for use within the present invention. Among such aromatic amines are 4-phenylazoaniline, 4-aminodiphenylamine, 2-aminobenzimidazole, 3-nitroaniline, 4-(4-nitrophenylazo)aniline (disperse orange 3), N-(4-amino-5-methoxy-2-methyl-phenyl)-benzamide (fast violet B), N-(4-amino-2,5-dimethoxy-phenyl)-benzamide (fast blue RR), N-(4-amino-2,5-diethoxyphenyl)-benzamide (fast blue BB), N-(4-amino-phenyl)-benzamide, and N,N-dimethylphenylenediamine.

[0031] The above-described aromatic amines can be used alone or in combination with each other. They can also be used in combination with additional, aromatic or non-aromatic, e.g., aliphatic, amines, which, in one embodiment, comprise 1 to 8 carbon atoms. Aliphatic monoamines include methylamine, ethylamine, propylamine and various higher amines. Diamines or polyamines can be used to functionalize a polymeric dispersant viscosity modifier, provided that, in certain embodiments, they have only a single reactive amino group, that is, a primary or secondary group. Suitable examples of such diamines include dimethylaminopropylamine, diethylaminopropylamine, dibutylaminopropylamine, dimethylaminoethylamine, diethylaminoethylamine, dibutylaminoethylamine, 1-(2-aminoethyl)piperidine, 1-(2-aminoethyl)pyrrolidone, aminoethylmorpholine, and aminopropylmorpholine.

[0032] The amount of dispersant present in the lubricant is that amount desirable to serve as its normal function of dispersing contaminants and maintaining cleanliness of the engine. The problem of formation of high aqueous content sludge tends to be more apparent however, at relatively higher dispersant levels, and it is at such levels that the benefits of the present invention are most evident. Thus, the present technology is typically associated with lubricating oil formulations that, in one embodiment, contain at least 0.07 or 0.08 weight percent of nitrogen derived from one or more nitrogen-containing ashless dispersants. In other embodiments, the amount of such nitrogen is at least 0.1% or at least 0.3%, and up to 0.5 or to 0.3 percent by weight. The amount of actual dispersant required to supply such amounts of nitrogen will, of course, vary with the nitrogen content of the dispersant. Certain common succinimide dispersants may contain 1.5 to 5 percent nitrogen (oil-free basis) or 2.5 to 4.5 percent or 3 to 4 percent. The total amount of dispersant may thus be, in certain circumstances, at least 2.5 or 3.0 or 3.5 weight percent of the lubricant, or at least 4.4 percent and up to 8 percent or to 7 percent or to 6 percent by weight (oil-free). The amount in a concentrate will be correspondingly greater, e.g., 7 to 30 percent. These amounts may be provided by one or more dispersants of similar or different types.

[0033] The problem may also be present in the presence of lubricants that contribute a large amount of aromatic content associated with polymeric additives or certain dispersants. Thus, certain polymers including those comprising vinyl aromatic monomer units such as styrene are sometimes included in lubricants to aid in soot dispersion, and such materials may also contribute to the tendency to form high aqueous content sludge. Examples include vinyl aromatic/olefin copolymers, vinyl aromatic/diene copolymers, vinyl aromatic/maleic ester copolymers, and vinyl aromatic/methacrylate ester copolymers. Such materials may be block or random copolymer, and they may be (hydrogenated or non-hydrogenated. Such polymers are typically distinguished from dispersant viscosity modifiers. They may be viscosity modifiers, but they are not dispersant viscosity modifiers because they do not contain the polar functionality (of greater polarity than that provided by an alkyl ester group) as provided by an amide or imide group with a polyamine or with an aromatic amine with further polar functionality. To take into account the presence of these aromatic-containing polymers, the total amount of nitrogen may be adjusted, as described below, if such materials are present.

[0034] Thus, in one embodiment the lubricating oil formulation contains at least 0.07 weight percent of the total of {weight percent nitrogen derived from one or more nitrogen-containing ashless dispersants and nitrogen-containing dispersant viscosity modifiers} plus {0.1 times the weight percent aromatic carbon provided by the following aromatic containing materials: polymeric materials, dispersants, and dispersant viscosity modifiers}, Other values for this total include at least 0.1% or at least 0.3%, and optionally up to 2.0 or 1.0 or 0.5 or to 0.3 percent by weight.

[0035] In another embodiment, the aromatic containing materials upon which the percent aromatic carbon is calculated are polymeric materials, dispersant viscosity modifiers, and dispersants other than Mannich dispersants. In yet another embodiment, the aromatic containing materials upon which the percent aromatic carbon is calculated are dispersants and all dispersant viscosity modifiers. In yet another embodiment, the aromatic containing materials upon which the percent aromatic carbon is calculated are dispersant viscosity modifiers and dispersants other than Mannich dispersants.

[0036] In any of the foregoing calculations, the amount of nitrogen derived from one or more nitrogen-containing ashless dispersants (which may include dispersant viscosity modifiers) plus 0.1 times the percent aromatic carbon provided by the aromatic materials as recited in any of the embodiments above may also be at least 0.08 weight percent or at least 0.1% or at least 0.3%, and optionally up to 2.0 or 1.0 or 0.5 or to 0.3 percent by weight.

[0037] The amount of nitrogen and aromatic carbon may be calculated by methods known to those skilled in the art. For example, a finished lubricant may be analyzed by first treating it with a separation process such as membrane dialysis, to separate relatively high molecular weight components such as dispersants, dispersant viscosity modifiers, and polymers. The amount of nitrogen in the separated component may be analyzed by conventional techniques. The amount of aromatic carbon in the separated component may be determined by conventional techniques such as ^{13}C NMR, and if desired the amount of aromatic carbon in any Mannich dispersants that may be present may be distinguished by determining the amount of aromatic carbons bonded to an —OH group and multiplying by six.

[0038] The problem of formation of high-aqueous content sludge in such engines and such lubricants may be solved or ameliorated by including within the lubricant one or more polyalkylene oxides. Polyalkylene oxides are known chemicals, sometimes referred to as a type of nonionic surfactant, having a general structure which may be represented, in its repeating unit, by $-(RO)_n-$ where R is an alkylene unit. When the material is terminated by OH groups it may be referred to as a polyalkylene glycol, $OH-(RO)-_nH$. Polyalkylene glycols may be prepared by alkali-catalyzed oligomerization of alkylene oxides.

[0039] Other terminating groups are possible, in which one (or optionally both) of the terminal OH groups are replaced by another functional group. For example, the reaction of monoalkyl ethers of alkylene glycol with alkylene oxide may provide the monoalkyl ether of the alkylene glycol, e.g., the monomethyl ether or the monoether of an alkyl group of up to 30 carbon atoms. Other such materials that may be useful include polyoxyalkylenated alkylphenol, polyoxyalkylenated straight-chain alcohols derived from such materials as coconut oil, tallow, or synthetic materials, polyoxyalkylenated silicones, and polyoxyalkylenated mercaptans. The polyoxyalkylene groups may be as described below.

[0040] The polyalkylene oxides (or, alternatively the polyoxyalkylene groups) useful in the present technology include those having a ratio of carbon to oxygen atoms of 2:1 or 2.25:1 or to 2.8:1, up to 6:1 or to 4:1 or to 3.5:1. Those would include polyethylene oxide, polypropylene oxide, and various polybutylene oxides and mixtures thereof, that is, copolymers of different alkylene oxides such as mixed poly (ethylene-propylene) oxides. A material having a C:O ratio of 2.25:1 could be prepared, for example, from a mixture of ethylene oxide and propylene oxide. In one embodiment, polybutylene oxide may be designated as polytetramethylene oxide or polytetrahydrofuran, which may be seen as the product of polymerization in a 1,4 manner, that is, poly(1,4-butanediol). Polypropylene oxide normally refers to the 1,2 addition product, although polytrimethylene oxide would be another possible material. Thus, suitable R units include CH_2CH_2, $CH_2CH_2CH_2$, $CH(CH_3)CH_2$, $CH_2CH(CH_3)$, $CH_2CH_2CH_2CH_2$, $CH(CH_3)CH_2CH_2$, $CH_2CH_2CH(CH_3)$, and mixtures and isomers thereof. If the polyalkylene oxide is prepared so as to have an alkoxy group at one terminus (rather than a hydroxy group), the C:O ratios for the molecule as a whole will differ somewhat from the C:O ratio for the molecule absent the alkoxy terminal group. The above-identified numerical ratios may be those for the molecule as a whole, containing any terminal alkoxy group, or they may be those for the polyalkylene oxide portion of the molecule, absent any terminal alkoxy group. These various values may be determined by appropriate NMR spectroscopy.

[0041] The polyalkylene oxides of the present technology may have a number average molecular weight of 500 to 10,000 or to even 50,000, or 800 to 5000, or 1000 to 4000, or 1500 to 4000, or 2000 to 3000. In certain embodiments, these materials may be of a similar molecular weight (and correspondingly similar viscosity) as similar materials that may be used as synthetic base oils. Their viscosity may encompass, for instance, ranges of 15-3500 or 50-2000 or 100-1500 or 150-1000 mm^2/s (cSt) at 25° C.; or 10-2000 or 20-1000 or 50-500 mm^2/s at 40° C.; or 2-400 or 2-150 mm^2/s at 100° C.

[0042] Polyalkylene oxides are commercially available under the trade names PPG4000™, PPG2000™, PPG1000™, Tolad 7™, Terathane 2000™, and Terathane 1000™.

[0043] The amount of the polyalkylene oxide in the lubricant formulation may typically be as low as 0.05 percent by weight in certain embodiments, or alternatively at least 0.08 or 0.1 percent by weight, for instance, 0.3 to 3 percent or 0.5 or 0.7 or 0.8 to 2 or to 1.5 percent by weight. The minimum amount will, of course, depend on the effectiveness of the particular polyalkylene oxide. For example, certain polyalkylene glycols with uncapped —OH end groups may be useful in amount of 0.05 percent and above. For polyalkylene glycols terminated with other functional groups, including all or any one of those classes of materials enumerated above, in certain embodiments the minimum amounts may also be 0.05 or 0.1 or 0.3 or 0.5 or 0.8 percent by weight. The amounts in a concentrate will be correspondingly greater, e.g., 0.3 to 15 percent or 0.5 or 1.0 to 10 percent.

[0044] While in some embodiments the polyalkylene oxide may be categorized as a nonionic surfactant, other surfactants may also be present. Surfactants in general may be classified as anionic, cationic, zwitterionic, or non-ionic. Anionic surfactants include substances containing a long lipophilic tail bonded to a water-soluble (hydrophilic) group at the other end, wherein the hydrophilic group contains an anionic moiety such as a carboxylic acid, sulfonic acid, or phenolic group, neutralized by a cation such as an alkali metal or ammonium. The lipophilic tail is preferably an alkyl group, typically having 8 to 21 carbon atoms.

[0045] Cationic surfactants are similar to anionic surfactants except that the surface-active portion of the molecule has a positive charge. Examples of cationic surfactants include long-chain amines and their salts, such as primary amines derived from animal and vegetable fatty acids and tall oil and synthetic C12-C18 primary, secondary, or tertiary amines; diamines and their salts, quaternary ammonium salts including tetraalkylammonium salts and imidazolinium salts derived from e.g. tallow or hydrogenated tallow, or N-Benzyl-N-alkyldimethylammonium halides; polyoxyethylenated long-chain amines; quaternized polyoxyethylenated long-chain amines; and amine oxides such as N-alkyldimethylamine oxides (which are actually zwitterionic) such as cetyl dimethylamine oxide or stearyl dimethylamine oxide.

[0046] Zwitterionic surfactants include amino acids such as N-alkylaminopropionic acids, N-alkyliminodipropionic acids, imidazoline carboxylates, N-alkylbetaines, sulfobetaines, and sultaines.

[0047] Nonionic surfactants, other than those described above as a required component of the present technology, include materials in which the polar functionality is not provided by an anionic or cation group, but by a neutral polar group such as typically an alcohol, amine, ether, ester, ketone, or amide function. Nonionic surfactants include long-chain carboxylic acid esters, alkanolamine condensates with fatty acids, and N-alkylpyrrolidones. Many of these and other ionic and non-ionic surfactants are discussed in Rosen, "Surfactants and Interfacial Phenomena," John Wiley & Sons, pp. 7-31, 1989.

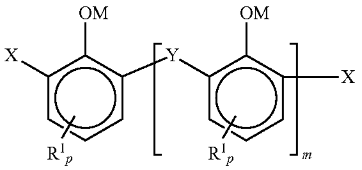
[0048] Other additives may be present, as in conventional in engine lubricants. Such additives may include metal-containing detergents. Metalcontaining detergents are typically overbased materials, or overbased detergents. Overbased materials, otherwise referred to as overbased or superbased salts, are generally homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials are prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid, such as carbon dioxide) with a mixture comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (e.g., mineral oil, naphtha, toluene, xylene) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a phenol or alcohol and optionally ammonia. The acidic organic material will normally have a sufficient number of carbon atoms, for instance, as a hydrocarbyl substituent, to provide a reasonable degree of solubility in oil. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

[0049] Overbased detergents are often characterized by Total Base Number (TBN). TBN is the amount of strong acid needed to neutralize all of the overbased material's basicity, expressed as potassium hydroxide equivalents (mg KOH per gram of sample). Detergents which are useful in the present invention may have a TBN (oil-free basis) of 100 to 800, and in one embodiment 150 to 750, and in another, 400 to 700.

[0050] The metal compounds useful in making the basic metal salts are generally any Group 1 or Group 2 metal compounds (CAS version of the Periodic Table of the Elements). The Group 1 metals of the metal compound include Group 1a alkali metals such as sodium, potassium, and lithium, as well as Group 1b metals such as copper. The Group 2 metals of the metal base include the Group 2a alkaline earth metals such as magnesium, calcium, and barium, as well as the Group 2b metals such as zinc or cadmium.

[0051] Overbased materials are well known to those skilled in the art. Patents describing techniques for making basic salts of sulfonic acids, carboxylic acids, (hydrocarbyl-substituted) phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Pat. Nos. 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109.

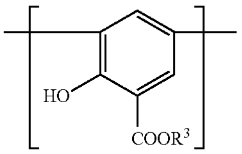
[0052] In one embodiment the lubricants of the present invention can contain an overbased sulfonate detergent. Another overbased material which can be present is an overbased phenate detergent. In yet another embodiment, the overbased material is an overbased saligenin detergent. Saligenin detergents are commonly overbased magnesium salts which are based on saligenin derivatives. A general example of such a saligenin derivative can be represented by the formula



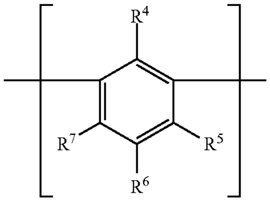
wherein X comprises —CHO or —CH_2OH, Y comprises —CH_2— or —CH_2OCH_2—; M is hydrogen, ammonium, or a valence of a metal ion such as Mg (that is to say generally, in the case of a multivalent metal ion, one of the valences is satisfied by the illustrated structure and other valences are satisfied by other species such as anions, or by another instance of the same structure), R^1 is a hydrocarbyl group containing 1 to 60 carbon atoms, m is 0 to typically 10, and each p is independently 0, 1, 2, or 3, provided that at least one aromatic ring contains an R^1 substituent and that the total number of carbon atoms in all R^1 groups is at least 7. When m is 1 or greater, one of the X groups can be hydrogen. Saligenin detergents are disclosed in greater detail in U.S. Pat. No. 6,310,009, with special reference to their methods of synthesis (Column 8 and Example 1) and amounts of the various species of X and Y (Column 6).

[0053] Salixarate detergents are overbased materials that can be represented by a substantially linear compound comprising at least one unit of formula (I) or formula (II):

(I)

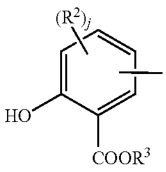


(II)

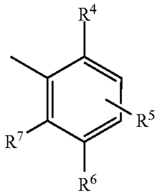


each end of the compound having a terminal group of formula (III) or (IV):

(III)

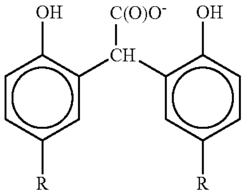


(IV)



such groups being linked by divalent bridging groups A, which may be the same or different for each linkage; wherein in formulas (I)-(IV) R^3 is hydrogen or a hydrocarbyl group; R^2 is hydroxyl or a hydrocarbyl group and j is 0, 1, or 2; R^6 is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group; either R^4 is hydroxyl and R^5 and R^7 are independently either hydrogen, a hydrocarbyl group, or hetero-substituted hydrocarbyl group, or else R^5 and R^7 are both hydroxyl and R^4 is hydrogen, a hydrocarbyl group, or a hetero-substituted hydrocarbyl group. At least one of R^4, R^5, R^6 and R^7 is hydrocarbyl containing at least 8 carbon atoms. The molecules on average contain at least one of unit (I) or (III) and at least one of unit (II) or (IV) and the ratio of the total number of units (I) and (III) to the total number of units of (II) and (IV) in the composition is 0.1:1 to 2:1. The divalent bridging group "A," which may be the same or different in each occurrence, includes —CH_2— and —CH_2OCH_2—. Salixarate derivatives and methods of their preparation are described in greater detail in U.S. Pat. No. 6,200,936 and PCT Publication WO 01/56968. It is believed that the salixarate derivatives have a predominantly linear, rather than macrocyclic, structure, although both structures are intended to be encompassed by the term "salixarate."

[0054] Glyoxylate detergents are similar overbased materials which are based on an anionic group which, in one embodiment, may have the structure



wherein each R is independently an alkyl group containing at least 4 or 8 carbon atoms; the total number of carbon atoms in all such R groups is at least 12 or 16 or 24. Overbased glyoxylic detergents and their methods of preparation are disclosed in greater detail in U.S. Pat. No. 6,310,011.

[0055] The overbased detergent can also be an overbased salicylate, that is, a salt of an alkylsalicylic acid. The salicylic acids may be hydrocarbyl-substituted salicylic acids wherein each substituent contains an average of at least 8 carbon atoms per substituent and 1 to 3 substituents per molecule. Overbased salicylate detergents and their methods of preparation are disclosed in U.S. Pat. Nos. 4,719,023 and 3,372,116.

[0056] Other overbased detergents can include overbased detergents having a Mannich base structure, as disclosed in U.S. Pat. No. 6,569,818.

[0057] The amount of the overbased detergent, in the formulations of the present invention, is typically at least 0.6 weight percent on an oil-free basis. In other embodiments, it can be present in amounts of 0.7 to 5 weight percent or 1 to 3 weight percent. Either a single detergent or multiple detergents can be present.

[0058] The lubricant may also contain a metal salt of a phosphorus acid. Metal salts of the formula

$$[(R^8O)(R^9O)P(=S)-S]_n\text{-M}$$

where R^8 and R^9 are independently hydrocarbyl groups containing 3 to 30 carbon atoms, are readily obtainable by heating phosphorus pentasulfide (P_2S_5) and an alcohol or phenol to form an O,O-dihydrocarbyl phosphorodithioic acid. The alcohol which reacts to provide the R^8 and R^9 groups may be a mixture of alcohols, for instance, a mixture of isopropanol and 4-methyl-2-pentanol, and in some embodiments a mixture of a secondary alcohol and a primary alcohol, such as isopropanol and 2-ethylhexanol. The resulting acid may be reacted with a basic metal compound to form the salt. The metal M, having a valence n, generally is aluminum, lead, tin, manganese, cobalt, nickel, zinc, or copper, and in many cases, zinc, to form zinc dialkyldithiophosphates. Such materials are well known and readily available to those skilled in the art of lubricant formulation.

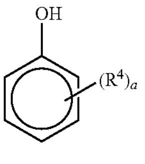
[0059] The lubricant may also contain a viscosity modifier, in addition to the dispersant viscosity modifier that has been discussed above. Viscosity modifiers, also known as viscosity index improvers, generally are polymeric materials characterized as being hydrocarbon-based polymers generally having number average molecular weights between 25,000 and 500,000, e.g., between 50,000 and 200,000.

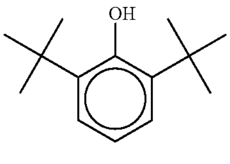
[0060] Hydrocarbon polymers can be used as viscosity index improvers. Examples include homopolymers and copolymers of two or more monomers of C2 to C30, e.g., C2 to C8 olefins, including both alphaolefins and internal olefins, which may be straight or branched, aliphatic, aromatic, alkyl-aromatic, or cycloaliphatic. Examples include ethylene-propylene copolymers, generally referred to as OCP's, prepared by copolymerizing ethylene and propylene by known processes.

[0061] Hydrogenated styrene-conjugated diene copolymers are another class of viscosity modifiers. These polymers include polymers which are hydrogenated or partially hydrogenated homopolymers, and also include random, tapered, star, and block interpolymers. The term "styrene" includes various substituted styrenes. The conjugated diene may contain four to six carbon atoms and may include, e.g., piperylene, 2,3-dimethyl-1,3-butadiene, chloroprene, isoprene, and 1,3-butadiene. Mixtures of such conjugated dienes are useful. The styrene content of these copolymers may be 20% to 70% by weight or 40% to 60%, and the aliphatic conjugated diene content may be 30% to 80% or 40% to 60%. These copolymers can be prepared by methods well known in the art and are typically hydrogenated to remove a substantial portion of their olefinic double bonds.

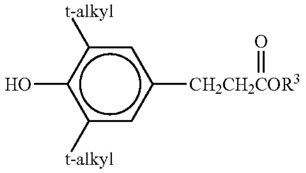
[0062] Esters obtained by copolymerizing styrene and maleic anhydride in the presence of a free radical initiator and thereafter esterifying the copolymer with a mixture of C4-18 alcohols also are useful as viscosity modifying additives in motor oils. Likewise, polymethacrylates (PMA) are used as viscosity modifiers. These materials are typically prepared from mixtures of methacrylate monomers having different alkyl groups, which may be either straight chain or branched chain groups containing 1 to 18 carbon atoms.

[0063] The lubricant formulation may also contain an antioxidant, that is, an ashless or metal-free antioxidant, in contrast to the above-described zinc dialkyldithiophosphate, which also has antioxidant properties. Antioxidants encompass phenolic antioxidants, which may be of the general formulas



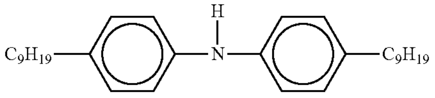


including the first, more general formula wherein R^4 is an alkyl group containing 1 to 24, or 4 to 18, carbon atoms and a is an integer of 1 to 5 or 1 to 3, or 2. Also included are the more specific formulas in which the phenol may be a butyl substituted phenol containing 2 or 3 t-butyl groups. The para position of the aromatic group may also be occupied by a hydrocarbyl group or a group bridging two aromatic rings. In certain embodiments the para position is occupied by an ester-containing group, such as, for example, an antioxidant of the formula



wherein R^3 is a hydrocarbyl group such as an alkyl group containing, e.g., 1 to 18 or 2 to 12 or 2 to 8 or 2 to 6 carbon atoms; and t-alkyl can be t-butyl. Such antioxidants are described in greater detail in U.S. Pat. No. 6,559,105.

[0064] Antioxidants also include aromatic amines based on an aromatic ring with an HNR^5 substituent, wherein R^5 can itself be an aromatic group such as a phenyl group, a naphthyl group, or a substituted phenyl group. Each of the aromatic groups may have one or more substituents which may independently be a hydrocarbyl or alkyl group containing 1 to 24 or 4 to 20 or 6 to 12 carbon atoms. In one embodiment, an aromatic amine antioxidant can comprise an alkylated diphenylamine such as nonylated diphenylamine of the formula



or a mixture of di-nonylated mono-nonylated diphenylamine.

[0065] Antioxidants also include sulfurized olefins such as mono- or disulfides or mixtures thereof. These materials generally have sulfide linkages having 1 to 10 sulfur atoms, for instance, 1 to 4, or 1 or 2. Materials which can be sulfurized to form the sulfurized organic compositions of the present invention include oils, fatty acids and esters, olefins and polyolefins made thereof, terpenes, or Diels-Alder adducts. Details of methods of preparing some such sulfurized materials can be found in U.S. Pat. Nos. 3,471,404 and 4,191,659.

[0066] Molybdenum compounds can also serve as antioxidants, and these materials can also serve in various other functions, such as antiwear agents. The use of molybdenum and sulfur containing compositions such as molybdenum dithiocarbamates in lubricating oil compositions as antiwear agents and antioxidants is known. U.S. Pat. No. 4,285,822, for instance, discloses lubricating oil compositions containing a molybdenum and sulfur containing composition prepared by (1) combining a polar solvent, an acidic molybdenum compound and an oil-soluble basic nitrogen compound to form a molybdenum-containing complex and (2) contacting the complex with carbon disulfide to form the molybdenum and sulfur containing composition.

[0067] Typical amounts of antioxidants will, of course, depend on the specific antioxidant and its individual effectiveness, but illustrative total amounts can be 0.01 to 5 percent by weight or 0.15 to 4.5 or 0.2 to 4 percent.

[0068] Yet other components may be present, including, corrosion inhibitors, extreme pressure and anti-wear agents. These materials include chlorinated aliphatic hydrocarbons; boron-containing compounds including borate esters; and molybdenum compounds.

[0069] Among the components that may also be present are various derivatives of hydroxycarboxylic acids, which may variously impart as one or more of friction modification, anti-wear, anti-corrosion, demulsification, and antioxidant activity. Examples suitable hydroxycarboxylic acids from which a derivative may be prepared include citric acid, tartaric acid, malic acid (or hydroxysuccinic acid), mandelic acid, lactic acid, glycolic acid, hydroxy-propionic acid, hydroxyglutaric acid, and mixtures thereof. In another embodiment the derivative may be prepared from tartaric acid, citric acid, hydroxy-succinic acid, dihydroxy monoacids, mono-hydroxy diacids, or mixtures thereof. In one embodiment the derivative includes a compound derived more particularly from tartaric acid.

[0070] In certain embodiments the derivative of hydroxycarboxylic acid may be an imide, di-ester, di-amide, or ester-amide derivative of tartaric acid, citric acid, or mixtures thereof. In one embodiment the derivative of hydroxycarboxylic acid may be an imide, di-ester, di-amide, or ester-amide derivative of tartaric acid. The derivatives may also be ester-imides or imide-amides (applicable for tri-acids and higher, such as citric acid) or di-imides (applicable for tetra-acids and higher).

[0071] Particular examples of such materials include tartrate diester of a C_6 to C_{15} alcohol, butyl citrate, and isotridecyloxy-propyl tartrimides. These and other such materials and their methods of preparation are more fully disclosed in PCT Publication WO 2006/044411 and in U.S. provisional application Ser. No. 61/037,837, filed Mar. 19, 2008.

[0072] Others compounds that may be present in the present formulations include pour point depressants, as described in page 8 of "Lubricant Additives" by C. V. Smalheer and R. Kennedy Smith (Lesius-Hiles Company Publishers, Cleveland, Ohio, 1967); also anti-foam agents such as silicones or organic polymers, described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162. Some of the additives described herein are also described in greater detail in U.S. Pat. No. 4,582,618 (column 14, line 52 through column 17, line 16, inclusive).

[0073] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

[0074] hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

[0075] substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

[0076] hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. Heteroatoms include sulfur, oxygen, and nitrogen. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0077] It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic or anionic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

Examples

[0078] The reduction of accumulation of high-aqueous content sludge is modeled by the reduction of its viscosity, water content, and problems derived therefrom. This may be accomplished by a bench test which involves combining 40 g deionized water and 10 g test lubricant oil in a 400 mL beaker. The water is added to the oil, which is stirred with a magnetic stir bar (setting at 3.5 units out of 10), over the course of about 4 minutes using a peristaltic pump. After the addition is complete, stirring is discontinued, the blend is allowed to sit for 10 minutes, and the blend is then poured into a 110 mL (4 oz) glass jar. When a high-aqueous content sludge forms, it is detected by observing a layer of such material in the jar, above a water layer, with sometimes a separate oil layer on the top. A sample of the high-aqueous sludge is removed and its viscosity at 25° C. is measured as well as its water content. Reduced water content and reduced viscosity appear to be roughly correlated, indicating that in desirable situations (a) little or less water is entrapped within the oil and (b) any sludge which may be formed, being less viscous, more readily drains from surfaces back into the oil sump or to hotter surfaces where it is dissipated or degraded.

[0079] The lubricant formulation to be tested as the baseline is described in the table below.

Component	amount, %
Base oil, API Group III	69.5
Succinimide dispersant(s) (including about 48% diluent oil)	10.7
Viscosity modifier(s) (including. about 94% diluent oil)	9.0
Dispersant viscosity modifier(s) (including. about 87% diluent oil)	4.0
Overbased Ca sulfonate detergent(s) (incl. about 47% diluent oil)	1.39
Overbased Ca salixarate detergent(s) (incl. about 51% diluent oil)	0.55
Overbased Ca phenate detergent(s) (incl. about 36% diluent oil)	1.04
Zinc dialkyldithiophosphate(s) (including about 10% diluent oil)	1.10
Mixed antioxidants: amine, sulfurized olefin, and phenolic	1.79
Pour point depressant(s) (including about 54% diluent oil)	0.2
Other minor components plus additional diluent oil	0.75

The baseline lubricant has a TBN (calculated) of 35 and sulfated ash (ASTM D 874) of 0.98.

[0080] The above base fluid, alone and with the additives identified in the following table, is tested using the above described methodology. Results are shown in the table below.

			Sludge	
Ex	Additive	Amount %	% H_2O	Viscosity (mPa-s)
1*	None		73^a	2277
2	Polypropylene glycol, M_n 4000	0.1	32	437
3	Polypropylene glycol, M_n 4000	1	7	245
4	Polypropylene glycol, M_n 2000	1	53	616
5	Polypropylene glycol, M_n 2000	2	2	261
6	Polypropylene glycol, M_n 1000	1	58	1565
7	Polypropylene glycol, M_n 1000	2	12	299
8	Commercial material believed to be mixed polyethylene oxide/propylene oxide, M_w 4000, 35% propylene oxide units at ends of polymer chains	1	40	869
9	Commercial material (Tolad 7 ™) believed to be ethylene oxide/ propylene oxide copolymer, M_w 5000-10,000 (50-60% active ingredient)	1	8	286
10	Ethylene oxide/propylene oxide copolymer, M_w 5000 (90-100% active ingred.)	1	56	1401
11	Same as 10, different source	2	16	321
12	Ethylene oxide/propylene oxide copolymer, M_w 2000 (90-100% active ingred.)	1	43	358
13	Same as 12	2	1	250
14	Polytetramethyleneether glycol, M_n 2000	1	55	860
15	Polytetramethyleneether glycol, M_n 2000	2	23	364
16	Polytetramethyleneether glycol, M_n 1000	0.1	25	422
17	Polytetramethyleneether glycol, M_n 1000	1	31	372
18	Polytetramethyleneether glycol, M_n 1000	2	11	318

*comparative

[a] average of 3 measurements: 78, 71, 69

For comparison, two commercial demulsifiers of unknown composition, Tolad 370™ and Tolad 9330™, are generally less effective at 1% nominal concentration, providing water content of 62% and 72%, respectively, and viscosity of 1155 and 1857 mPa-s, respectively. For reference, two other commercial materials, believed to contain ethoxylated alkyl phenol at very low concentrations (perhaps 5-10%), provide only slight benefit at 1% nominal concentration: water content 57 and 60 percent, respectively and viscosity 2210 and 1941 mPa-s, respectively.

[0081] Each of the documents referred to above is incorporated herein by reference. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.

1. A method for reducing accumulation of high-aqueous content sludge in a sump-lubricated diesel engine lubricated with a lubricating oil formulation that contains at least one nitrogen-containing dispersant and optionally at least one dispersant viscosity modifier or polymeric material, wherein {the weight percent nitrogen derived from one or more nitrogen-containing ashless dispersants and nitrogen-containing dispersant viscosity modifiers} plus {0.1 times the weight percent of any aromatic carbon provided by the following aromatic containing materials: polymeric materials, dispersants, and dispersant viscosity modifiers} is at least 0.07, said method comprising:

including in said lubricant at least about 0.05 percent by weight of a polyalkylene oxide.

2. The method of claim **1** wherein the aromatic containing materials upon which the percent aromatic carbon is calculated are polymeric materials, dispersant viscosity modifiers, and dispersants other than Mannich dispersants.

3.-**4**. (canceled)

5. The method of claim **1** wherein the total of {weight percent nitrogen derived from one or more nitrogen-containing ashless dispersants} plus {0.1 times the weight percent aromatic carbon provided by the recited aromatic materials} is at least 0.08 weight percent.

6. (canceled)

7. The method of claim **1** wherein the nitrogen derived from one or more nitrogen-containing ashless dispersants is at least 0.07 weight percent.

8. The method of claim **1** wherein the amount of the nitrogen derived from one or more nitrogen-containing ashless dispersants is at least 0.08 weight percent

9. The method of claim **1** wherein the diesel engine has restricted crankcase ventilation.

10. The method of claim **1** wherein the engine contains a rocker cover which is susceptible to formation of high-aqueous content sludge thereon.

11. The method of claim **1** wherein the lubricating oil formulation contains at least about 3.0 percent by weight of one or more nitrogen-containing ashless dispersants.

12. The method of claim **1** wherein the nitrogen-containing ashless dispersant comprises a succinimide dispersant.

13. The method of claim **1** wherein the lubricant formulation comprises a dispersant viscosity modifier.

14. The method of claim **1** wherein the amount of the polyalkylene oxide is about 0.1 to about 3 percent by weight.

15. (canceled)

16. The method of claim **1** wherein the polyalkylene oxide is a polyethylene oxide, a polypropylene oxide, a polytetramethylene oxide, or a mixed poly(ethylene-propylene) oxide, having a number average molecular weight of about 500 to about 10,000.

17. The method of claim **1** wherein the polyalkylene oxide is a diol.

18. The method of claim **1** wherein the lubricant comprises an oil of lubricating viscosity and further comprises at least one additional component selected from the group consisting of an overbased metal detergent, a zinc dialkyldithiophosphate, and an antioxidant.

19. (canceled)

20. A lubricant composition suitable for reducing accumulation of high-aqueous content sludge in a sump-lubricated diesel engine, comprising:

an oil of lubricating viscosity;

one or more nitrogen-containing ashless dispersants or dispersant viscosity modifiers such that the formulation contains at least one nitrogen-containing dispersant and optionally at least one dispersant viscosity modifier or polymeric material, wherein {the weight percent nitrogen derived from one or more nitrogen-containing ashless dispersants and nitrogen-containing dispersant viscosity modifiers} plus {0.1 times the weight percent of any aromatic carbon provided by the following aromatic containing materials: polymeric materials, dispersants, and dispersant viscosity modifiers} is at least 0.07;

wherein the lubricant composition comprises a nitrogen-containing dispersant viscosity modifier;

and

at least about 0.05 percent by weight of a polyalkylene oxide.

21. The lubricant composition of claim **20** wherein the nitrogen derived from one or more nitrogen-containing ashless dispersants is at least 0.07 weight percent.

22. The lubricant composition of claim **20**, further comprising at least one additional additive selected from the group consisting of detergents, metal salts of phosphorus acids, viscosity modifiers, antioxidants, corrosion inhibitors, antiwear agents, pour point depressants, and anti-foam agents.

23. (canceled)

24. The lubricant composition of claim **20** wherein the oil of lubricating viscosity comprises an API Group II or Group III or Group IV oil or a mixture thereof.

25. A method for reducing accumulation of high-aqueous content sludge in a sump-lubricated diesel engine lubricated with a lubricating oil formulation that contains at least 0.08 weight percent nitrogen derived from one or more nitrogen-containing ashless dispersants, said method comprising:

including in said lubricant at least about 0.05 percent by weight of a polyalkylene oxide.

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