

A LUBRICATING OIL COMPOSITION

FIELD OF THE INVENTION

The present invention relates to lubricating oil compositions, more especially to automotive lubricating oil compositions for use in piston engines, especially gasoline (spark-ignited) and diesel (compression-ignited) crankcase lubrication, such compositions being referred to as crankcase lubricants. In particular, although not exclusively, the present invention relates to use of ashless detergent additives with good copper corrosion properties in lubricating oil compositions where corrosion is a concern.

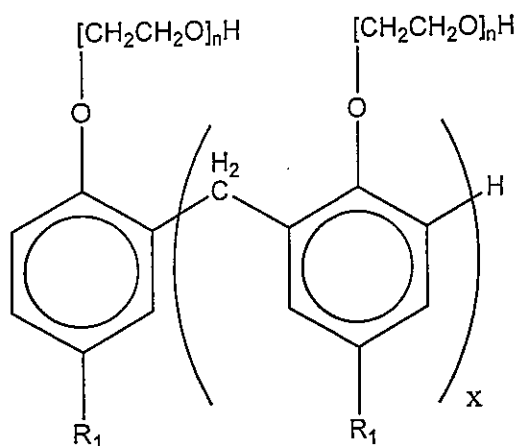
BACKGROUND OF THE INVENTION

A crankcase lubricant is an oil used for general lubrication in an internal combustion engine where an oil sump is situated generally below the crankshaft of the engine and to which circulated oil returns. It is well known to include additives in crankcase lubricants for several purposes.

Among the additives that are and have been commonly included are metal-containing detergents. These are additives that reduce formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines; they have acid-neutralising properties and are capable of keeping finely-divided solids in suspension. They are based on metal salts of acidic organic compounds, sometimes referred to as soaps. Generally, a metal detergent comprises a polar head with a long hydrophobic tail, the polar head comprising the metal salt.

Lubricant specifications are becoming, or have become, more exacting such as in limiting the amount of metal, expressed as sulfated ash. There is therefore considerable incentive to provide detergents that are free of metal, so-called "ashless" detergents.

RD 417045 describes ethoxylated methylene-bridged alkyl phenols as detergents that are metal free, which may for example be represented by the structural formula:



wherein the "n" of the ethoxylated groups is an integer such as in the range of 1 to 20. The compounds are described as being made by the acid-catalysed reaction of an alkylated phenol with paraformaldehyde to give a methylene-bridged phenol, with subsequent ethoxylation using ethylene oxide. Products made according to this disclosure comprise undesirably high levels of non-oxyalkylated (i.e. $n = 0$) content, undesirably high levels of di- and poly-oxyalkylated (i.e. $n \geq 2$) content and consequently low levels of mono-oxyalkylated (i.e. $n = 1$) content. Products with high levels of $n \geq 2$ have inferior oil solubility, resulting in increased levels of haze and sediment. When included within fully-formulated oils, products with high levels of $n \geq 2$ also confer inferior deposit control properties. Products with high levels of $n = 0$ confer inferior copper corrosion in fully-formulated oils.

In this specification, the abbreviation 'n=0' is used to denote non-oxyalkylation; the abbreviation 'n=1' is used to denote mono-oxyalkylation; and the abbreviation 'n $\geq$ 2' is used to denote poly-oxyalkylation which includes di-oxyalkylation, tri-oxyalkylation, tetra-oxyalkylation etc.

EP-B-0 032 617 describes lubricants that contain similar additives to those described in RD 417045 (including an additive marketed under the trade name "Prochinor GR77") for controlling or eliminating emulsion-sludge formation. Preferably, n is from 2 to 10, which is most preferably obtained by ethoxylation using ethylene oxide, and also prefers a molecular weight of 4,000 to 6,000.

Neither of the above prior art references describes the benefits of maximising $n = 1$ content, minimising $n = 0$ content and/or minimising $n \geq 2$ content. Neither of the above prior art references describes the effect of the additives on copper corrosion or on deposit control.

SUMMARY OF THE INVENTION

The present invention provides a lubricating oil composition that exhibits superior deposit control properties whilst minimising copper corrosion. In the lubricating oil composition, the value of n in the oil-soluble oxyalkylated detergent is controlled.

In accordance with a first aspect, the present invention provides a lubricating oil composition comprising or made by admixing

(A) an oil of lubricating viscosity; and

(B) as an additive component, an oil-soluble mixture of oxyalkylated hydrocarbyl phenol condensates, wherein oxyalkyl groups prepared from phenolic functional groups have the formula $-(R'O)_n-$ where R' is an ethylene, propylene or butylene group, and n is independently from 0 to 10;
wherein less than 45, preferably less than 30, mole % of the phenolic functional groups of the condensates are non-oxyalkylated (i.e. $n = 0$); and
more than 55 mole % of the phenolic functional groups of the condensates are mono-oxyalkylated (i.e. $n = 1$).

According to a second aspect, the present invention provides a method of making additive component (B) as defined in the first aspect, the method comprising forming an oxyalkylated hydrocarbyl phenol aldehyde condensate via the steps of (1) condensation of a hydrocarbyl phenol with an aldehyde, in the presence of an acid or base catalyst, to form a hydrocarbyl phenol-aldehyde condensate, and (2) oxyalkylating said condensate in the presence of a base catalyst, preferably a sodium salt, with 0.5 to less than 3, preferably less than 2.5, preferably less than 2.0, equivalents of ethylene carbonate, propylene carbonate or butylene carbonate for each equivalent of phenolic functional groups within the condensate.

According to a third aspect, the present invention provides a method of making an additive component (B) as defined in the first aspect, the method including the steps of forming an oxyalkylated hydrocarbyl phenol-aldehyde condensate via the steps of (1) oxyalkylating a hydrocarbyl phenol in the presence of a base catalyst, preferably a sodium salt, with 0.5 to 3, preferably to less than 2.5, preferably less than 2.0, equivalents of ethylene carbonate, propylene carbonate or butylene carbonate and (2) condensation in the presence of an acid or base catalyst of said oxyalkylated hydrocarbyl phenol with an aldehyde.

According to a fourth aspect, the present invention provides an additive component (B) as defined in the first aspect made by or obtainable by the method of the second or third aspects.

According to a fifth aspect, the present invention provides the use of additive component (B) as defined in the first or fourth aspects to improve the deposit control properties whilst not adversely affecting the copper corrosion properties of the lubricant.

According to a sixth aspect, the present invention provides a method of lubricating surfaces of an internal combustion chamber during its operation by:

- (i) providing, in a minor amount, one or more additives (B) as defined in the first aspect in a major amount of an oil of lubricating viscosity to make a lubricant;
- (ii) providing the lubricant to the crankcase of the internal combustion engine;
- (iii) providing a hydrocarbon fuel in the combustion chamber of the engine, and
- (iv) combusting the fuel in the combustion chamber.

In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

“active ingredient” or “(a.i.)” refers to additive material that is not diluent or solvent;

“comprising” or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof. The expressions

“consists of” or “consists essentially of” or cognates may be embraced within “comprises” or cognates, wherein “consists essentially of” permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

“hydrocarbyl” means a chemical group of a compound that contains only hydrogen and carbon atoms and that is bonded to the remainder of the compound directly via a carbon atom;

“oil-soluble” or “oil-dispersible”, or cognate terms, used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible, or are capable of being suspended in the oil in all proportions. These do mean, however, that they are, for example, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired;

“major amount” means in excess of 50 mass % of a composition;

“minor amount” means less than 50 mass % of a composition;

“TBN” means total base number as measured by ASTM D2896;

“phosphorus content” is measured by ASTM D5185;

“sulfur content” is measured by ASTM D2622; and

“sulfated ash content” is measured by ASTM D874.

Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

Furthermore, the constituents of this invention may be isolated or be present within a mixture and remain within the scope of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The features of the invention relating, where appropriate, to each and all aspects of the invention, will now be described in more detail as follows:

OIL OF LUBRICATING VISCOSITY (A)

The oil of lubricating viscosity (sometimes referred to as “base stock” or “base oil”) is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). Also, a base oil is useful for making concentrates as well as for making lubricants therefrom.

A base oil may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof. It may range in viscosity from light distillate mineral oils to heavy lubricating oils such as gas engine oil, mineral lubricating oil, motor vehicle oil and heavy duty diesel oil. Generally the viscosity of the oil ranges from 2 to 30, especially 5 to 20, mm^2s^{-1} at 100°C.

Natural oils include animal and vegetable oils (e.g. castor and lard oil), liquid petroleum oils and hydrorefined, solvent-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

Synthetic lubricating oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g. polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenols (e.g. biphenyls, terphenyls, alkylated polyphenols); and

alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogues and homologues thereof.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g. phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g. butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols, and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Unrefined, refined and re-refined oils can be used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. 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. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined 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 re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for approval of spent additive and oil breakdown products.

Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be an oil derived from Fischer-Tropsch synthesised hydrocarbons made from synthesis gas

containing H_2 and CO using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed.

Base oil may be categorised in Groups I to V according to the API EOLCS 1509 definition.

When the oil of lubricating viscosity is used to make a concentrate, it is present in a concentrate-forming amount (e.g., from 30 to 70, such as 40 to 60, mass %) to give a concentrate containing for example 1 to 90, such as 10 to 80, preferably 20 to 80, more preferably 20 to 70, mass % active ingredient of an additive or additives, being component (B) above, optionally with one or more co-additives. The oil of lubricating viscosity used in a concentrate is a suitable oleaginous, typically hydrocarbon, carrier fluid, e.g. mineral lubricating oil, or other suitable solvent. Oils of lubricating viscosity such as described herein, as well as aliphatic, naphthenic, and aromatic hydrocarbons, are examples of suitable carrier fluids for concentrates.

Concentrates constitute a convenient means of handling additives before their use, as well as facilitating solution or dispersion of additives in lubricants. When preparing a lubricant that contains more than one type of additive (sometime referred to as "additive components"), each additive may be incorporated separately, each in the form of a concentrate. In many instances, however, it is convenient to provide a so-called additive "package" (also referred to as an "adpack") comprising one or more co-additives, such as described hereinafter, in a single concentrate.

The oil of lubricating viscosity may be provided in a major amount, in combination with a minor amount of additive component (B) as defined herein and, if necessary, one or more co-additives, such as described hereinafter, constituting a lubricant. This preparation may be accomplished by adding the additive directly to the oil or by adding it in the form of a concentrate thereof to disperse or dissolve the additive. Additives may be added to the oil by any method known to those skilled in the art, either before, at the same time as, or after addition of other additives.

Preferably, the oil of lubricating viscosity is present in the lubricant in an amount of greater than 55 mass %, more preferably greater than 60 mass %, even more preferably greater than 65 mass %, based on the total mass of the lubricant. Preferably, the oil of lubricating viscosity is present in an amount of less than 98 mass %, more preferably less than 95 mass %, even more preferably less than 90 mass %, based on the total mass of the lubricant.

The lubricants of the invention may be used to lubricate mechanical engine components, particularly in internal combustion engines, e.g. spark-ignited or compression-ignited two- or four-stroke reciprocating engines, by adding the lubricant thereto. Preferably, they are crankcase lubricants.

The lubricating oil compositions of the invention comprise defined components that may or may not remain the same chemically before and after mixing with an oleaginous carrier. This invention encompasses compositions which comprise the defined components before mixing, or after mixing, or both before and after mixing.

When concentrates are used to make the lubricants, they may for example be diluted with 3 to 100, e.g. 5 to 40, parts by mass of oil of lubricating viscosity per part by mass of the concentrate.

The lubricants of the present invention may contain low levels of phosphorus, namely not greater than 0.12 mass %, preferably up to 0.08 mass %, more preferably up to 0.06 mass % of phosphorus, expressed as atoms of phosphorus, based on the total mass of the lubricant.

Typically, the lubricants may contain low levels of sulfur. Preferably, the lubricant contains up to 0.4, more preferably up to 0.3, most preferably up to 0.2, mass % sulfur, expressed as atoms of sulfur, based on the total mass of the lubricant.

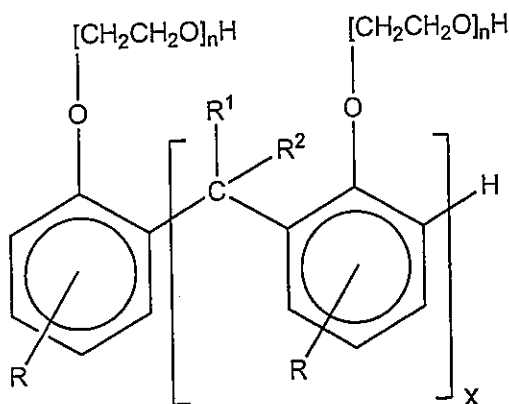
Typically, the lubricant may contain low levels of sulfated ash. Preferably, the lubricant contains less than 1.0, preferably less than 0.8, more preferably less than 0.5, mass % sulfated ash, based on the total mass of the lubricant.

Suitably, the lubricant may have a total base number (TBN) of 5 or more, preferably 7 or more, such as up to 16, preferably 8 to 16. This basicity may originate from metal bases such as overbased detergents or non-metal bases such as nitrogen bases, examples of which are dispersants, anti-oxidants (e.g. alkylated diphenylamine and phenylene diamine) and quaternary ammonium salts, or combinations thereof. Suitably, up to 30%, preferably up to 40%, more preferably up to 50%, even more preferably up to 60% of the TBN in the lubricant originates from non-metal bases.

ADDITIVE COMPONENT (B)

It has been found that the use of additive component (B) comprising less than 45 mole % of $n = 0$ in a lubricant reduces copper corrosion more than the use of additive component (B) comprising 45 mole% or more of $n = 0$. It has also been found that when additive component (B) having a low mole % of $n \geq 2$ content is used in a lubricant, the lubricant has significantly advantageous deposit control properties.

The oxyalkylated condensates in (B) are preferably represented by the following general structural formula:



wherein

x is 1 to 50, preferably 1 to 40, more preferably 1 to 30;

R^1 and R^2 are H, hydrocarbyl groups having 1 to 12 carbon atoms, or hydrocarbyl groups having 1 to 12 carbon atoms and at least one heteroatom; and

R is a hydrocarbyl group having 9 to 100, preferably 9 to 70, preferably 9 to 50, preferably 9 to 30, preferably 9 to 20 and most preferably 9 to 15 carbon atoms.

In the above formula, R is preferably in the para position in relation to the $-O-[CH_2CH_2O]_nH$ group.

In the oxyalkylated condensates in (B), less than 45, preferably less than 35, and more preferably less than 30, mole % of the phenolic functional groups of the condensates are non-oxyalkylated (i.e. $n = 0$).

In the oxyalkylated condensates in (B), more than 55, preferably more than 60, preferably more than 70, more preferably more than 80, even more preferably more than 90, and most preferably more than 95, mole % of the phenolic functional groups of the condensates are mono-oxyalkylated (i.e. $n = 1$).

Advantageously, in the oxyalkylated condensates in (B), less than 5 mole % of the phenolic functional groups of the condensates are poly-oxyalkylated (i.e. $n \geq 2$), which includes di-oxyalkylation, tri-oxyalkylation, tetra-oxyalkylation etc.

Preferably, the mixture has a number average molecular weight (M_n), as measured by GPC, in the range of 1000 to less than 4000, such as to 3000. Advantageously, the mixture has a weight average molecular weight (M_w), as measured by GPC, in the range of 1100 to less than 6000, preferably less than 4000, such as 3500; advantageously, M_w/M_n is in the range of 1.10-1.60.

Preferably, the mixture has a number average degree of polymerization of 4-20, such as 5-15, and more preferred 6-10.

In the above general formula, R is preferably, independently, a branched chain alkyl group having 9 to 30 carbon atoms, preferably 9 to 15 carbon atoms, more preferably 12 to 15 carbon atoms.

The oxyalkylated condensate mixtures of the invention are preferably made by oxyalkylating a hydrocarbyl phenol condensate with ethylene carbonate (which is preferred), propylene carbonate or butylene carbonate.

Without wishing to be bound by any theory, it is believed that oxyalkylation begins at the terminal units of the condensate polymer and progressively moves towards the centre of the polymer, generating more mono-oxyalkyl ($n = 1$) content. However, steric factors inhibit reaction with central units and then further reaction can occur with terminal units to confer the di- and poly-oxyalkyl (i.e. $n \geq 2$) content.

Use of a carbonate for the oxyalkylation reaction is found to give rise to much better control of the "n" value and quantity, as required in this invention, in comparison with use of ethylene oxide or propylene oxide as described in the prior art. Furthermore, an appropriate choice of catalyst can provide a product consisting essentially entirely of mono-oxyalkyl (i.e. $n = 1$) content. Sodium salts are preferred, especially the hydroxide and carboxylates, such as stearate.

Suitably, additive component (B) is present in the amount of 0.1 to 10, such as 0.1 to 5, such as 0.1 to 2, mass % based on the total lubricant mass.

CO-ADDITIVES

Co-additives, with representative effective amounts in lubricants that may also be present, different from additive component (B), are listed below. All the values listed are stated as mass percent active ingredient.

<u>Additive</u>	<u>Mass %</u> (Broad)	<u>Mass %</u> (Preferred)
Ashless Dispersant	0.1 – 20	1 – 8
Metal Detergents	0.1 – 15	0.2 – 9
Friction modifier	0 – 5	0 – 1.5
Corrosion Inhibitor	0 – 5	0 – 1.5
Metal Dihydrocarbyl Dithiophosphate	0 – 10	0 – 4
Anti-Oxidants	0 – 5	0.01 – 3
Pour Point Depressant	0.01 – 5	0.01 – 1.5
Anti-Foaming Agent	0 – 5	0.001 – 0.15
Supplement Anti-Wear Agents	0 – 5	0 – 2
Viscosity Modifier (1)	0 – 6	0.01 – 4
Mineral or Synthetic Base Oil	Balance	Balance

(1) Viscosity modifiers are used only in multi-graded oils.

The final lubricant, typically made by blending the or each additive into the base oil, may contain from 5 to 25, preferably 5 to 18, typically 7 to 15, mass % of the co-additives, the remainder being oil of lubricating viscosity.

The above mentioned co-additives are discussed in further detail as follows; as is known in the art, some additives can provide a multiplicity of effects, for example, a single additive may act as a dispersant and as an oxidation inhibitor.

A dispersant is an additive whose primary function is to hold solid and liquid contaminations in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. For example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use of the lubricant, thus preventing sludge flocculation and precipitation or deposition on metal parts of the engine.

Dispersants are usually “ashless”, as mentioned above, being non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing, and hence ash-forming materials. They comprise a long hydrocarbon chain with a polar head, the polarity being derived from inclusion of e.g. an O, P, or N atom. The hydrocarbon is an

oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric backbone.

A preferred class of olefin polymers is constituted by polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C₄ refinery stream.

Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants is constituted by hydrocarbon-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine. Particularly preferred are the reaction products of polyalkylene polyamines with alkenyl succinic anhydrides, such as described in US-A-3,202,678; -3,154,560; -3,172,892; -3,024,195; -3,024,237, -3,219,666; and -3,216,936, that may be post-treated to improve their properties, such as borated (as described in US-A-3,087,936 and -3,254,025) fluorinated and oxylated. For example, boration may be accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from boron oxide, boron halides, boron acids and esters of boron acids.

Preferably, the dispersant, if present, is a succinimide dispersant derived from a polyisobutene of number average molecular weight in the range of 1000 to 3000, preferably 1500 to 2500, and of moderate functionality. The succinimide is preferably derived from highly reactive polyisobutene.

Metal detergents are metal salts as mentioned above. The salts may contain a substantially stoichiometric amount of the metal when they are usually described as normal or neutral salts and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. Large amounts of a metal base can be included by reaction of 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 neutralised detergent as an outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically of from 250 to 500 or more.

Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates 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 in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium.

Particularly preferred metal detergents are neutral and overbased alkali or alkaline earth metal detergents having a TBN of from 50 to 450, preferably a TBN of 50 to 250. Highly preferred detergents include alkaline earth metal salicylates, particularly magnesium and calcium, especially, calcium salicylates.

The weight ratio of the additive component (B) in the lubricating oil composition to any metal detergents is preferably in the range of 0.1 to 4, preferably 0.1 to 3, preferably 0.1 to 2, or most preferably 0.2 to 1.6. Preferred examples of metal detergents are calcium salicylate, magnesium salicylate, calcium sulfonate, magnesium sulfonate, calcium phenate and mixtures thereof.

Friction modifiers include glyceryl monoesters of higher fatty acids, for example, glyceryl mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; oxazoline compounds; and alkoxyated alkyl-substituted mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

Other known friction modifiers comprise oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. Suitable oil-soluble organo-molybdenum compounds have a molybdenum-sulfur core. As examples there may be mentioned dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates. The molybdenum compound is dinuclear or trinuclear.

One class of preferred organo-molybdenum compounds useful in all aspects of the present invention is tri-nuclear molybdenum compounds of the formula $\text{Mo}_3\text{S}_k\text{L}_n\text{Q}_z$ and mixtures thereof

wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compounds soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through to 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

The molybdenum compounds may be present in a lubricating oil composition at a concentration in the range 0.1 to 2 mass %, or providing at least 10 such as 50 to 2,000 ppm by mass of molybdenum atoms.

Preferably, the molybdenum from the molybdenum compound is present in an amount of from 10 to 1500, such as 20 to 1000, more preferably 30 to 750, ppm based on the total weight of the lubricant. For some applications, the molybdenum is present in an amount of greater than 500 ppm.

Anti-oxidants are sometimes referred to as oxidation inhibitors; they increase the resistance of the lubricant to oxidation and may work by combining with and modifying peroxides to render them harmless, by decomposing peroxides, or by rendering an oxidation catalyst inert. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth.

They may be classified as radical scavengers (e.g. sterically-hindered phenols, secondary aromatic amines, and organo-copper salts); hydroperoxide decomposers (e.g., organosulfur and organophosphorus additives); and multifunctionals (e.g. zinc dihydrocarbyl dithiophosphates, which may also function as anti-wear additives, and organo-molybdenum compounds, which may also function as friction modifiers and anti-wear additives).

Examples of suitable antioxidants are selected from copper-containing antioxidants, sulfur-containing antioxidants, aromatic amine-containing antioxidants, hindered phenolic antioxidants, dithiophosphates derivatives, metal thiocarbamates, and molybdenum-containing compounds.

Dihydrocarbyl dithiophosphate metals salts are frequently used as antiwear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, zinc molybdenum, manganese, nickel or copper. Zinc salts are most commonly used in lubricants such as in amounts of 0.1 to 10, preferably 0.2 to 2, mass %, based upon the total mass of the lubricant. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with P_2S_5 , and then neutralising the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reaction with mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one acid are entirely secondary in character and the hydrocarbyl groups on the other acids are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralisation reaction.

Anti-wear agents reduce friction and excessive wear and are usually based on compounds containing sulfur or phosphorous or both, for example that are capable of depositing polysulfide films on the surfaces involved. Noteworthy are the dihydrocarbyl dithiophosphates, such as the zinc dialkyl dithiophosphates (ZDDPs) discussed herein.

Examples of ashless anti-wear agents include 1,2,3-triazoles, benzotriazoles, thiadiazoles, sulfurised fatty acid esters, and dithiocarbamate derivatives.

Rust and corrosion inhibitors serve to protect surfaces against rust and/or corrosion. As rust inhibitors there may be mentioned non-ionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids.

Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the oil will flow or can be poured. Such additives are well known. Typical of these additive are C_8 to C_{18} dialkyl fumarate/vinyl acetate copolymers and polyalkylmethacrylates.

Additives of the polysiloxane type, for example silicone oil or polydimethyl siloxane, can provide foam control.

A small amount of a demulsifying component may be used. A preferred demulsifying component is described in EP-A-330,522. It is obtained by reacting an alkylene oxide with an adduct obtained by reaction of a bis-epoxide with a polyhydric alcohol. The demulsifier should be used at a level not exceeding 0.1 mass % active ingredient. A treat rate of 0.001 to 0.05 mass % active ingredient is convenient.

Viscosity modifiers (or viscosity index improvers) impart high and low temperature operability to a lubricant. Viscosity modifiers that also function as dispersants are also known and may be prepared as described above for ashless dispersants. In general, these dispersant viscosity modifiers are functionalised polymers (e.g. interpolymers of ethylene-propylene post grafted with an active monomer such as maleic anhydride) which are then derivatised with, for example, an alcohol or amine.

The lubricant may be formulated with or without a conventional viscosity modifier and with or without a dispersant viscosity modifier. Suitable compounds for use as viscosity modifiers are generally high molecular weight hydrocarbon polymers, including polyesters. Oil-soluble viscosity modifying polymers generally have weight average molecular weights of from 10,000 to 1,000,000, preferably 20,000 to 500,000, which may be determined by gel permeation chromatography or by light scattering.

EXAMPLES

The invention will now be particularly described in the following examples which are not intended to limit the scope of the claims hereof.

Example 1 - Preparation of methylene-bridged alkyl phenol

A mixture of 95% para-substituted, branched dodecylphenol (1910g), alkyl benzene sulfonic acid catalyst (19.1g) and toluene (574g) was heated to 110°C over 60 minutes in a 5L reactor under a blanket of nitrogen gas which remained throughout the reaction process. An aqueous formaldehyde solution (37%, 497g) was added stepwise over 2 hours and 30 minutes. The temperature was increased to 120°C and the contents of the reactor maintained at this

temperature for 1 hour and 30 minutes. The contents were cooled to 90°C and an aqueous NaOH solution (50%, 42g) added over 35 minutes. The contents of the reactor were heated to 130°C over 25 minutes, kept at this temperature for 2 hours and toluene stripped therefrom by vacuum distillation. The product was an alkylphenol-formaldehyde condensate in the form of a methylene-bridged alkylphenol in which x was from 0 to 22 or more, Mn (by GPC) = 1600, Mw = 2100, and residual monomer of dodecylphenol < 1%.

Example 2 - Preparation of ethoxylated methylene-bridged alkyl phenol

Xylene (573g) was added to Example 1 (2004g), and then ethylene carbonate (1.02 equivalents per hydroxyl group, 645g) at 90°C over 35 minutes. The contents of the reactor were heated to reflux (150-160°C). The ethylene carbonate was consumed over 4 hours, then xylene was stripped by vacuum distillation. The mixture had a molecular weight, as measured by GPC, of Mn = 1700, Mw = 2300, and residual monomer of dodecylphenol < 0.1%. ¹³C NMR analysis of the mixture showed that it had the following properties with regard to the parameter n:

n	mole %
0	1
1	96
≥2	3

The temperature was lowered to 110°C and group I 150 neutral oil added (2278g) and mixed for 1 hour to make an ethoxylated methylene-bridged alkylphenol mixture at 50% active ingredient (4556g).

Example 3

Heavy duty diesel lube oil formulation A was prepared containing ashless dispersant, metal containing detergent, zinc dialkyl dithiophosphate anti-wear agent, supplementary antioxidant, viscosity modifier and flow improver in a base oil. Heavy duty diesel lube oil formulation B (sulfated ash content = 1.0%, TBN = 12.3) was prepared with the same amount of all the additives except that 1.5 wt% active ingredient of the ethoxylated methylene bridged alkyl phenol mixture of Example 2 was added in place of 1.5 wt% of base oil. The weight

ratio of the ashless detergent of Example 2 relative to the metal containing detergents in Heavy duty diesel lube oil formulation B was 1.2 on an active ingredient basis.

Both products were tested in an OM501LA heavy duty diesel deposit test and the merits produced are compared in Table I.

Table I

	Piston Merits
Heavy duty diesel formulation A	21.7
Heavy duty diesel formulation B	31.4

Clearly, Heavy duty diesel formulation B containing the ashless detergent of Example 2 exhibited significantly enhanced deposit control capability relative to Heavy duty diesel formulation A which contained only ash-containing detergents.

Example 4

Passenger car diesel lube oil formulation C was prepared containing ashless dispersant, metal containing detergent, zinc dialkyl dithiophosphate anti-wear agent, supplementary antioxidant, viscosity modifier and flow improver in a base oil. Passenger car diesel lube oil formulation D (sulfated ash content = 0.5%, TBN = 7.7) was prepared with the same amount of all the additives except that 0.5 wt% active ingredient of the ethoxylated methylene bridged alkyl phenol mixture of Example 2 was added in place of 0.5 wt% of base oil (and the viscosity modifier level was reduced slightly). The weight ratio of the ashless detergent of Example 2 relative to the metal containing detergents in Passenger car diesel lube oil formulation D was 0.6 on an active ingredient basis.

Both products were tested in a VW TDI passenger car diesel deposit test and the merits produced are compared in Table II.

Table II

	Piston Merits
Passenger car diesel formulation C	59
Passenger car diesel formulation D	65

Clearly, both Heavy duty diesel formulation B and Passenger car diesel formulation D containing the ashless detergent of Example 2 exhibited significantly enhanced deposit control capability relative to Heavy duty diesel formulation A and passenger car diesel formulation C which contained only ash-containing detergents.

Examples 5-6 and Comparative Example 1

The procedure of Example 2 was repeated with different amounts of the ethylene carbonate reagent to produce ethoxylated methylene-bridged alkylphenol mixtures of formula (I) with varying amounts of oxyalkyl moieties as shown in Table III.

Example 7

Heavy duty diesel lube oil formulation E was prepared containing ashless dispersant, metal containing detergent, zinc dialkyl dithiophosphate anti-wear agent, supplementary antioxidant, viscosity modifier and flow improver in a base oil. Heavy duty diesel lube oil formulation F (sulfated ash content = 1.0, TBN = 11.1) was prepared with the same amount of all the additives except that 1.8 wt% active ingredient of the ethoxylated methylene bridged alkyl phenol mixture of Examples 2, 5, 6 and Comparative Example 1 was added in place of 1.8 wt% of base oil. The weight ratio of the ashless detergent in relation to the metal containing detergents in Heavy duty diesel lube oil formulation D was 1.3 on an active ingredient basis.

All the above formulated products were tested for copper corrosion using the High Temperature Corrosion Bench Test ('HTCBT', ASTM D6594). The copper corrosion results are expressed in parts per million Cu, where a lower result is superior (≤ 20 ppm is considered a pass).

The results of the High Temperature Corrosion Bench Test ('HTCBT') are as follows:

Table III

Example	Equivalents of EC	Mole % n=1	Mole % n=0	Mole % n $\geq$ 2	Cu (ppm)
Comparative Example 1	0.58	55	45	0	91.6
Example 6	0.75	75	25	0	43.4
Example 5	0.90	87	12	2	44.7
Example 2	1.02	96	1	3	18.2

EC = ethylene carbonate used in preparation

The results clearly show that a low level of non-oxyalkylated group (i.e. n=0) is required to maintain passing copper corrosion performance.

Example 8 - Preparation of highly capped hydroxyethyl methylene bridged alkyl phenol

The procedure of Example 1 was repeated, on a smaller scale (branched dodecyl phenol – 400g; alkylbenzene sulfonic acid catalyst – 4g; aqueous formaldehyde solution (37%) - 104g), except that the 50% aqueous NaOH was replaced by an equal mass percentage of 50% aqueous KOH (10g). Xylene (120g) was added to the intermediate that was produced (418g), and then ethylene carbonate (2 equivalents per hydroxyl group, 270g) at 90°C over 30 minutes. The contents of the reactor were heated to reflux (150-160°C). Reaction continued for 4 hours, when it was determined that the reaction was not completed and temperature was decreased. The next day, heating was resumed (165°C) for a further 8 hours, at which point the reaction was determined to be completed. Xylene was stripped by vacuum distillation, leaving a viscous orange-red liquid. The temperature was reduced to 120°C and it was determined that, after analytical samples removal, the weight of product was 475g. The mixture had a molecular weight, as measured by GPC, of Mn = 2250, Mw = 3900. ¹³C NMR analysis of the mixture showed that it had the following properties with regard to parameter n:

n	mole %
0	0
1	45
$\geq$ 2	55

Group I 150 neutral oil was added (475g) and mixed for 1 hour to make an ethoxylated methylene-bridged alkylphenol mixture at 50% active ingredient (950g).

Example 9 (Performance impact of higher capping)

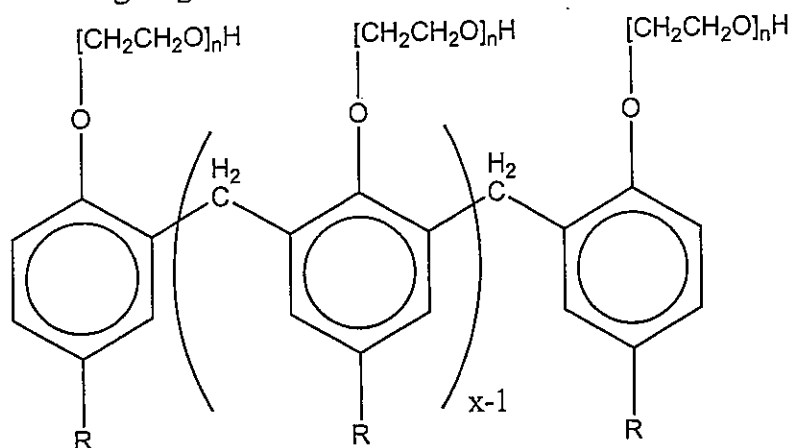
Heavy duty diesel lube oil formulation G was prepared containing ashless dispersant, metal containing detergent, zinc dialkyl dithiophosphate anti-wear agent, supplementary antioxidant, viscosity modifier and flow improver in a base oil. Heavy duty diesel formulation H was prepared with the same amount of all additives except that 1.6 wt% active ingredient of Example 2 was added in place of 1.6 wt% base oil. Heavy duty diesel lube oil formulation I was prepared with the same amount of all the additives except that 1.6 wt% active ingredient of Example 8 was substituted for the 1.6 wt% active ingredient of Example 2. The weight ratio of the ashless detergent relative to the metal containing detergents in all Heavy duty diesel lube oil formulations was 1.3.

All three formulations were tested in the Thermo-oxidation Engine Oil Simulation Test ("TEOST" 33C ; (ASTM 6335) and the results are compared in Table IV.

Table IV

Example	Equivalents of EC	Mole % n=1	Mole % n=0	Mole % n $\geq$ 2	Deposits (mg)
Formulation G	-	-	-	-	38
Formulation H	1.02	96	1	3	22.5
Formulation I	2.0	45	0	55	43

Quantitative ^{13}C NMR was used to determine the $n = 0$, $n = 1$ and $n \geq 2$ contents reported herein. For comparing the contents of $n = 0$ and $n = 1$ in partially ethoxylated oligomers, the following diagram can be used:

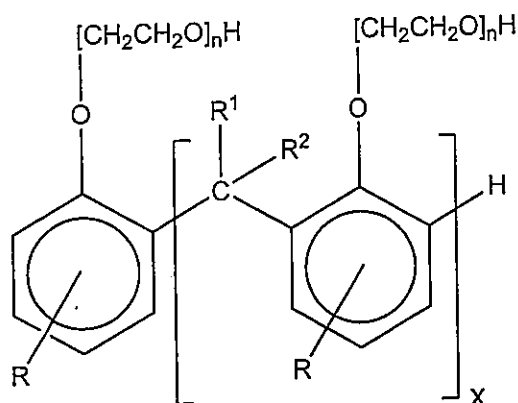


For the progression from $n = 0$ to $n = 1$, carbons A, B and C experience chemical shifts from 150, 147 and 116 ppm to 154, 152 and 110 ppm, respectively.

The region between 60 – 76 ppm is the chemical shift range for all of the carbons of the (poly-)ethoxylated groups. The internal (mono-)hydroxyethyl carbons ($n = 1$) are found at 75 and 61.4 ppm, whereas the external (mono-)hydroxyethyl carbons (also $n = 1$) are found at 69 and 60.7 ppm. On addition of one or more ethoxy units (i.e. $n \geq 2$), these same carbon signals shift to broad peaks at 72, 70 and 61.1 ppm. In order to determine the $n \geq 2$ content, it is possible to subtract the sum of the integrated values of the two peaks at 75 and 69 ppm from the sum of the integrated values of the three peaks at 61.4, 61.1 and 60.7 ppm. Additionally, the proportion of $n = 1$ to $n \geq 2$ can be directly compared (i.e., the sum of the integrated values of the two peaks at 61.4 and 60.7 ppm versus the integral of the peak at 61.1 ppm) provided the resolution of the NMR makes these peaks discernible.

Claims

1. A lubricating oil composition comprising or made by admixing:
 - (A) an oil of lubricating viscosity; and
 - (B) as an additive component, an oil-soluble mixture of oxyalkylated hydrocarbyl phenol condensates wherein oxyalkyl groups prepared from phenolic functional groups have the formula $-(R'O)_n-$ where R' is an ethylene, propylene or butylene group; and n is independently from 0 to 10; less than 45, preferably less than 30, mole % of the phenolic functional groups of the condensates are non-oxyalkylated; and more than 55 mole % of the phenolic functional groups of the condensates are mono-oxyalkylated.
2. The composition as claimed in claim 1, wherein the condensates are represented by the following general structural formula:



wherein:

- x is 1 to 50, preferably 1 to 40, more preferably 1 to 30;
- R^1 and R^2 are H, hydrocarbyl groups having 1 to 12 carbon atoms, or hydrocarbyl groups having 1 to 12 carbon atoms and at least one heteroatom; and
- R is a hydrocarbyl group having 9 to 100, preferably 9 to 70, most preferably, 9 to 50, carbon atoms.
3. The composition as claimed in claim 2, wherein $R^1 = H$, $R^2 = H$ and R is in the para position in relation to the $-O-[CH_2CH_2O]_nH$ group.

4. The composition as claimed in any one of the preceding claims, wherein additive component (B) includes less than 1 mole%, preferably less than 0.5 mole% and most preferably less than 0.1 mole% of unreacted alkyl phenol.
5. The composition as claimed in any one of the preceding claims, wherein more than 60, preferably more than 70, preferably more than 80, preferably more than 90, or most preferably more than 95, mole % of the phenolic functional groups of additive component B are mono-oxyalkylated (i.e. $n = 1$).
6. The composition as claimed in any one of the preceding claims, wherein less than 5 mole % of the phenolic functional groups of additive component B are poly-oxyalkylated (i.e. $n \geq 2$), such as di-oxyalkylated, tri-oxyalkylated and tetra-oxyalkylated.
7. The composition as claimed in any one of claims 2 to 6, wherein R is independently a branched chain alkyl group, preferably having from 9 to 15 carbon atoms.
8. The composition as claimed in any one of the preceding claims, further including one or more other additive components different from (B).
9. The composition as claimed in any one of the preceding claims, wherein the other additive components, different from (B), are selected from one or more ashless dispersants, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers such as organo-molybdenum compounds, demulsifiers, anti-foaming agents and viscosity modifiers.
10. The composition as claimed in claim 8 or claim 9 having a TBN of 5 or more as measured by ASTM D2896, preferably a TBN of 8 to 16.

11. A method of making additive component (B) as defined in any one of the preceding claims, the method comprising forming an oxyalkylated hydrocarbyl phenol aldehyde condensate by the steps of (1) condensation of a hydrocarbyl phenol with an aldehyde, in the presence of an acid or base catalyst, to form a hydrocarbyl phenol-aldehyde condensate, and (2) oxyalkylating said condensate in the presence of a base catalyst, preferably a sodium salt, with 0.5 to less than 3, preferably less than 2.5, preferably less than 2.0, equivalents of ethylene carbonate, propylene carbonate or butylene carbonate for each equivalent of phenolic functional groups within the condensate.
12. A method of making an additive component (B) as defined in any one of the preceding claims, the method including the steps of forming an oxyalkylated hydrocarbyl phenol-aldehyde condensate by the steps of (1) oxyalkylating a hydrocarbyl phenol in the presence of a base catalyst, preferably a sodium salt, with 0.5 to 3, preferably to less than 2.5, preferably less than 2.0, equivalents of ethylene carbonate, propylene carbonate or butylene carbonate, and (2) condensation in the presence of an acid or base catalyst of said oxyalkylated hydrocarbyl phenol with an aldehyde.
13. The method of making an additive component (B) as defined in claim 11 or claim 12, wherein the aldehyde is formaldehyde and the carbonate is ethylene carbonate.
14. An additive component (B) as defined in any one of claims 1 to 7 made by or obtainable by the method of any one of claims 11 to 13.
15. Use of additive component (B) as defined in any one of claims 1 to 7 or 14 to improve the deposit control properties of a lubricant whilst not adversely affecting its copper corrosion properties; preferably when compared to a lubricant not including additive component (B); or preferably when compared to a lubricant including additive component (B) wherein less than 55 mole% of the phenolic functional groups are mono-oxyalkylated.
16. A method of lubricating surfaces of an internal combustion engine during its operation by:

providing, in a minor amount, one or more additives (B) as defined in any of claims 1 to 7 in a major amount of an oil of lubricating

viscosity to make a lubricant, to improve the deposit control properties of the lubricant whilst not adversely affecting its copper corrosion properties;

providing the lubricant to the crankcase of the internal combustion engine;

providing a hydrocarbon fuel in the combustion chamber of the engine, and

combusting the fuel in the combustion chamber.