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(54) Title: COMPOSITION CONTAINING A BLOCK COPOLYMER AND A METHOD OF LUBRICATING AN INTERNAL COMBUSTION ENGINE

(57) **Abstract**: The invention provides a lubricating composition containing an oil of lubricating viscosity and a block copolymer. The block copolymer may contain (a) a hydrophobic first block having C1-30 alkyl (meth)acrylic units, wherein at least 50 wt % of the C1-30 alkyl (meth)acrylic units are C12-15 alkyl (meth)acrylic units, and up to 50 wt % of the C1-30 alkyl (meth)acrylic units are C16 20 alkyl (meth)acrylic units, with the proviso that alkyl groups of the C1-30 alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and (b) a second block having (meth)acrylic units further having a heteroatom-containing group providing a polar group. The invention further relates to a method of lubricating an internal combustion engine by lubricating the engine with the lubricating composition. The invention further relates to the use of the block copolymer as an emulsifier and/or pour point depressant.

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TITLE

Composition Containing a Block Copolymer and a Method of Lubricating an Internal Combustion Engine

FIELD OF INVENTION

[0001] The invention provides a lubricating composition containing an oil of lubricating viscosity and a block copolymer. The invention further relates to a method of lubricating an internal combustion engine by lubricating the engine with the lubricating composition. The invention further relates to the use of the block copolymer as an emulsifier and/or pour point depressant.

BACKGROUND OF THE INVENTION

[0002] Lubricants are often exposed to contaminant amounts of water. The contaminant amounts of water are believed to be caused by ingress of water through equipment seals during operation, or from combustion by-products that pass into the crankcase via blow-by. The water may form a second layer in the lubricant. Typically to reduce the formation of the second layer emulsifiers and/or dispersants are employed. If the water concentration becomes high enough, an emulsion results. If the emulsion is unstable, the contaminant water may then cause additional difficulties such as corrosion. The corrosion may be from copper or lead bearings, or iron.

[0003] In addition to the need for an emulsifier, lubricant base oils may also contain waxy components. Waxes may agglomerate and cause accumulation of crystals in a lubricant. When this occurs, problems arising include reduced low temperature oil pumpability, poorer cold temperature properties or reduced fuel economy. Accordingly, in one embodiment it may also be desirable to employ a pour point depressant that reduces wax agglomeration.

[0004] In flexible fuel vehicles (FFVs) the internal combustion engine is designed to run on gasoline or a blend of up to 85% ethanol (E85). Except for a few engine and fuel system modifications, they are identical to gasoline-only models. Traditionally, dispersants are designed to stabilise contaminants in the engine oil of gasoline-fuelled cars. Fuelling with E85 introduces the potential to transform the engine oil into a milky emulsion. In order to overcome the formation of an unstable milky emulsion, it would be desirable to employ an emulsifier.

[0005] International publication WO2006/047393 discloses linear and star RAFT polymers as viscosity index improvers in a variety of lubricants. The RAFT polymers may have a variety of architectures including diblock copolymers. All of polymers are derived from C_{12-15} alkyl (meth)acrylates. There is no disclosure or teaching of linear or star polymers having emulsifier and/or pour point depressant properties.

[0006] US Patent Application 2006/0189490 discloses a lubricating composition containing base oil and at least one additive having friction-modifying properties. The additive is a linear diblock copolymer which includes hydrophobic segments P and polar segments D, said hydrophobic segments being obtained by polymerisation of monomer compositions which comprises 0 to 40 % of C_{1-5} alkyl (meth)acrylates, 50 to 100 % of C_{6-30} alkyl (meth)acrylates, and 0 to 50 % of a polar group containing ester, thioester or amide functionality. All of the examples disclose C_{12-15} alkyl (meth)acrylates. There is no disclosure or teaching of linear or star polymers having emulsifier and/or pour point depressant properties.

SUMMARY OF THE INVENTION

[0007] The inventors of this invention have discovered that a lubricating composition containing a block copolymer and method as disclosed herein is capable of providing acceptable levels of at least one of (i) emulsifying properties, and (ii) pour point depressant properties. In one embodiment the lubricating composition containing the block copolymer provides both emulsifying properties and pour point depressant properties.

[0008] As used herein, the term “polar” in the state of the art is used in the ordinary sense of the word and is also known to mean hydrophilic.

[0009] In one embodiment the invention provides a lubricating composition comprising an oil of lubricating viscosity and a diblock copolymer, wherein the diblock copolymer comprises:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, wherein at least 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block.

[0010] The second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block, may also be described as a second block having (meth)acrylic units further having a heteroatom group providing a polar group.

[0011] In one embodiment the invention provides a lubricating composition comprising an oil of lubricating viscosity and a diblock copolymer, wherein the diblock copolymer comprises:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, wherein at least 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block.

[0012] In one embodiment the invention provides a diblock copolymer product (and optionally a lubricating composition) obtained/obtainable by a process comprising:

(1) contacting:

(i) a free radical initiator;

(ii) a chain transfer agent (typically containing a thiocarbonyl thio group useful in RAFT polymerisation processes); and

(iii) one or more C_{1-30} alkyl (meth)acrylic monomer units, wherein at least 50 wt % of the C_{1-30} alkyl (meth)acrylic monomer units contain C_{12-15} alkyl (meth)acrylic units, and up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8, to form a polymer;

wherein the process of step (1) is typically a controlled radical or other living polymerisation process with living characteristics (for instance a controlled radical polymerisation process); and at least about 50 wt % of the polymer chains from step (1) contain a reactive end group capable of reacting with a polyvalent coupling agent;

(2) optionally contacting the polymer of step (1) with a polymerisation inhibitor;

(3) contacting the polymer of step (1) or step (2) with one or more (meth)acrylic units typically at least 50 wt % or at least 75 wt % of the said units further containing a heteroatom-containing group; and

(4) optionally mixing the polymer of step (3) with an oil of lubricating viscosity to form a lubricating composition.

[0013] In different embodiments the C_{16-20} alkyl (meth)acrylic units may be C_{16-18} alkyl (meth)acrylic units, or C_{18-20} alkyl (meth)acrylic units. The C_{16-20} alkyl (meth)acrylic units may also contain up to 10 wt % (or typically up to 5 wt %) of C_{14} alkyl (meth)acrylic units. In one embodiment the C_{16-20} alkyl (meth)acrylic units may be in the form of a mixture of (meth)acrylic compounds having alkyl groups containing 16 to 20, or 16 to 18 carbon atoms.

[0014] In the process described above, the first step of the process may be performed in the presence of a mineral oil, synthetic oil, hexane, toluene, tetrahydrofuran, or other known polymerisation solvents.

[0015] In one embodiment the invention provides a diblock copolymer product (and optionally a lubricating composition) obtained/obtainable by a process comprising:

(1) contacting:

(i) a free radical initiator;

(ii) a chain transfer agent (typically containing a thiocarbonyl thio group useful in RAFT polymerisation processes); and

(iii) with one or more (meth)acrylic units typically at least 50 wt % or at least 75 wt % of the said units further having a heteroatom-containing group, wherein the process of step (1) is typically a controlled radical or other living polymerisation process with living characteristics; and at least about 50 wt % of the polymer chains from step (1) contain a reactive end group capable of reacting with a polyvalent coupling agent;

(2) optionally contacting the polymer of step (1) with a polymerisation inhibitor;

(3) contacting the polymer of step (1) or step (2) with one or more C_{1-30} alkyl (meth)acrylic monomer units, wherein at least 50 wt % of the C_{1-30} alkyl (meth)acrylic monomer units contain C_{12-15} alkyl (meth)acrylic units, and up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8, to form a polymer; and

(4) optionally mixing the polymer of step (3) with an oil of lubricating viscosity to form a lubricating composition.

[0016] In the process described above, the first step of the process may be performed in the presence of a solvent such as toluene or tetrahydrofuran.

[0017] The processing temperatures, pressures and reagents are known to a person skilled in the art of controlled radical polymerisation techniques. References describing such materials include WO2006/047393 and the various references disclosed herein below in the description of the diblock copolymer.

[0018] In one embodiment the invention provides block copolymer obtained (or obtainable) by the process described above.

[0019] In one embodiment the invention provides a method of lubricating a flexible fuel vehicle (flex fuel vehicle or FFV) internal combustion engine comprising supplying to the engine a lubricating composition comprising an oil of lubricating viscosity and a block copolymer, wherein the block copolymer comprises:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block.

[0020] A person skilled in the art will appreciate that the flexible fuel vehicle may be fuelled with gasoline typically containing 5 wt % to 85 wt %, or 10 wt % up to 85 wt %, or 15 wt % to up to 85 wt % alcohol. The alcohol may for instance be ethanol.

[0021] The hydrophobic first block may contain 0 wt % to 5 wt % of a hydrophilic monomer (i.e., units derived from a monomer with a polar group such as a monomer containing a heteroatom group derived from a nitrogen or oxygen containing group. Monomers of this type are discussed in more detail below. In one embodiment the hydrophobic first block may contain 0 wt % a hydrophilic monomer.

[0022] In one embodiment the invention provides a method of lubricating an internal combustion engine comprising supplying to the engine a lubricating composition comprising an oil of lubricating viscosity and a block copolymer, wherein the block copolymer comprises:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, wherein at least 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block.

[0023] In one embodiment the invention provides for the use of a block copolymer comprising:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block providing a polar group such that the block copolymer may be an emulsifier and/or pour point depressant.

[0024] In one embodiment the invention provides for the use of a block copolymer comprising:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, wherein at least 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block such that the block copolymer may be an emulsifier and/or pour point depressant.

[0025] Typically the block copolymer may be an emulsifier and/or pour point depressant in an internal combustion engine.

[0026] Pour point depressant properties typically occur when the block copolymer contains C_{16-20} alkyl (meth)acrylic units.

[0027] Emulsifier properties may occur for any block copolymer composition of the present invention.

[0028] Emulsifier and pour point depressant properties typically occur when the diblock block copolymer contains C_{16-20} alkyl (meth)acrylic units, and C_{12-15} alkyl (meth)acrylic units.

[0029] The internal combustion engine may be operated on gasoline, diesel, biofuels, ethanol, or mixtures thereof. In one embodiment the internal combustion engine may be operated on a mixture of gasoline and ethanol. The internal combustion engine may be referred to as a flexible fuel vehicle engine.

[0030] Typically the block copolymer disclosed herein may be a linear diblock copolymer.

[0031] In one embodiment the lubricating composition may be further characterised as having at least one of (i) a sulphur content of 0.8 wt % or less, (ii) a phosphorus content of 0.2 wt % or less, or (iii) a sulphated ash content of 2 wt % or less.

[0032] In one embodiment the lubricating composition may be further characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.1 wt % or less, and (iii) a sulphated ash content of 1.5 wt % or less.

[0033] In one embodiment the lubricating composition further includes at least one of a friction modifier, a viscosity modifier, an antioxidant, an overbased detergent, a succinimide dispersant, a pour point depressant, or mixtures thereof.

[0034] In one embodiment the lubricating composition further includes a viscosity modifier and an overbased detergent.

[0035] In one embodiment the lubricating composition further includes an overbased detergent and a succinimide dispersant.

[0036] In one embodiment the invention provides a method for lubricating an engine oil comprising supplying to the engine a lubricating composition as disclosed herein.

[0037] The block copolymer may be used at 0.01 wt % to 0.5 wt %, or 0.05 to 0.3 wt % of the lubricating composition disclosed herein.

DETAILED DESCRIPTION OF THE INVENTION

[0038] The present invention provides a lubricating composition and a method for lubricating a mechanical device as disclosed above. Typically the mechanical device may be an internal combustion engine.

Block Copolymer

[0039] As used herein the term “(meth)acrylic units” includes both acrylic and methacrylic units and the units are derived from an appropriate monomer. The (meth)acrylic units typically include methacrylates, acrylates, methacrylamides, acrylamides, or mixtures thereof.

[0040] As described hereinafter the molecular weight of the block copolymer has been determined using known methods, such as GPC analysis using polystyrene standards. Methods for determining molecular weights of polymers are well known. The methods are described for instance: (i) P.J. Flory, “Principles of Polymer Chemistry”, Cornell University Press 91953), Chapter VII, pp 266-315; or (ii) “Macromolecules, an Introduction to Polymer Science”, F. A. Bovey and F. H. Winslow, Editors, Academic Press (1979), pp 296-312.

[0041] The block copolymer may be a diblock, a triblock, or a higher block copolymer.

[0042] The diblock copolymer may have a AB composition, where A is a hydrophobic unit, and B is a hydrophilic unit.

[0043] The triblock copolymer may have ABA or BAB, ABA', or BAB', where A and B are defined above, and A' and B' represent hydrophobic and hydrophilic units different from A and B respectively.

[0044] Each block may be a tapered copolymer, a random copolymer, a sequential copolymer, or may have a random or sequential distribution of two or more monomer units.

[0045] The weight average molecular weight of the block copolymer may be in the range of 1000 to 400,000, or 1000 to 150,000, or 15,000 to 100,000.

[0046] The weight ratio of the second block to the first block may be in the range of 1:2 to 1:100, or 1:4 to 1:30, or 1:6 to 1:18.

[0047] The length of the first block to the second block may have a ratio of 10:1 to 1:10, or 6:1 to 1:2.

[0048] The C_{1-30} alkyl (meth)acrylic units may be derived from an alkyl (meth)acrylate.

[0049] The alkyl (meth)acrylate includes for example compounds derived from saturated alcohols, such as methyl methacrylate, butyl methacrylate, 2-methylpentyl (meth)acrylate, 2-propylheptyl (meth)acrylate, 2-butyloctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, nonyl (meth)acrylate, isooctyl (meth)acrylate, isononyl (meth)acrylate, 2-tert-butylheptyl (meth)acrylate, 3-isopropylheptyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)-acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate, hexadecyl (meth)acrylate, 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate, 5-ethyloctadecyl (meth)acrylate, 3-isopropyloctadecyl-(meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate, cetyleicosyl (meth)acrylate, stearyleicosyl (meth)acrylate, docosyl (meth)acrylate and/or eicosyltetratriacontyl (meth)acrylate; (meth)-acrylates derived from unsaturated alcohols, such as oleyl (meth)acrylate; and cycloalkyl (meth)acrylates, such as 3-vinyl-2-butylcyclohexyl (meth)acrylate or bornyl (meth)acrylate.

[0050] The alkyl (meth)acrylates with long-chain alcohol-derived groups may be obtained, for example, by reaction of a (meth)acrylic acid (by direct esterification) or methyl methacrylate (by transesterification) with long-chain fatty alcohols, in which reaction a mixture of esters such as (meth)acrylate with alcohol groups of various chain lengths is generally obtained. These fatty alcohols include Oxo Alcohol® 7911, Oxo Alcohol® 7900 and Oxo Alcohol® 1100 of Monsanto; Alphanol® 79 of ICI; Nafol® 1620, Alfol® 610 and Alfol® 810 of Condea (now Sasol); Epal® 610 and Epal® 810 of Ethyl Corporation; Linevol® 79, Linevol® 911 and Dobanol® 25 L of Shell AG; Lial® 125 of Condea Augusta, Milan; Dehydad® and Lorol® of Henkel KGaA (now Cognis) as well as Linopol® 7-11 and Acropol® 91 of Ugine Kuhlmann.

[0051] In one embodiment the block copolymer may be a methacrylate polymer.

[0052] The hydrophobic first block may contain 70 wt % or more, or 80 wt % or more of the C_{1-30} alkyl (meth)acrylic units containing C_{12-15} alkyl (meth)acrylic units.

[0053] The hydrophobic first block may contain up to 30 wt %, or up to 20 wt % of the C_{1-30} alkyl (meth)acrylic units containing C_{16-20} alkyl (meth)acrylic units.

[0054] In one embodiment the hydrophobic first block contains C_{1-30} alkyl (meth)acrylic units, wherein at least 70 wt % of the C_{1-30} alkyl (meth)acrylic units may be C_{12-15} alkyl (meth)acrylic units, and up to 30 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8 (or at least 10 carbon atoms).

[0055] In one embodiment the hydrophobic first block contains C_{1-30} alkyl (meth)acrylic units, wherein at least 80 wt % of the C_{1-30} alkyl (meth)acrylic units may be C_{12-15} alkyl (meth)acrylic units, and up to 20 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8 (or at least 10 carbon atoms).

[0056] In one embodiment the hydrophobic first block contains C_{1-30} alkyl (meth)acrylic units, wherein at least 50 wt % to 99 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and 1 up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8 (or at least 10 carbon atoms).

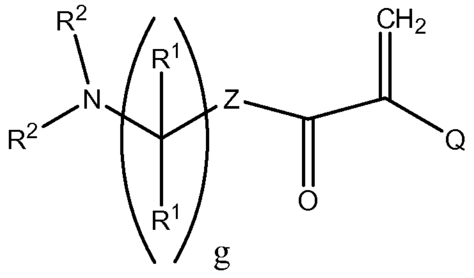
[0057] In one embodiment the hydrophobic first block contains C_{1-30} alkyl (meth)acrylic units, wherein at least 75 wt % to 95 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and 5 up to 25 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8 (or at least 10 carbon atoms).

[0058] In one embodiment the hydrophobic first block contains C_{1-30} alkyl (meth)acrylic units, wherein at least 80 wt % to 95 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and 1 up to 20 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8 (or at least 10 carbon atoms).

[0059] The second block having (meth)acrylic units have a heteroatom-containing group providing the polar group, with the heteroatom including sulphur, nitrogen, non-carbonyl oxygen, phosphorus, or mixtures thereof. In one embodiment the heteroatom may be nitrogen. The term "non-carbonyl oxygen" is not meant to exclude the presence of a carbonyl oxygen, but rather to indicate that if such is present , there will also be a heteroatom that is not a carbonyl oxygen (that is, neither an oxygen atom of an aldehyde, ketone or either oxygen atoms of a carboxylic acid or ester).

[0060] In one embodiment the copolymer of the invention further includes a heteratom group derived from a nitrogen or oxygen containing group. The group may be derived from a nitrogen or oxygen containing compound capable of being incorporated during copolymerisation.

[0061] The nitrogen or oxygen containing group may be derived from an aminoalkyl (meth)acrylamide or a nitrogen containing (meth)acrylate monomer that may be represented by the formula:



wherein

Q is hydrogen or methyl and, in one embodiment, Q is methyl;

Z is an N-H group or an NR^2 group or O (oxygen);

each R^2 is independently hydrogen or a hydrocarbyl group containing 1 to 8, or 1 to 4 carbon atoms;

each R^1 is independently hydrogen or a hydrocarbyl group containing 1 to 2 carbon atoms and, in one embodiment, each R^1 is hydrogen; and

g is an integer in ranges including 1 to 6, or 1 to 3.

[0062] Examples of suitable nitrogen-containing compounds capable of being incorporated into the copolymer include N,N-dimethylacrylamide, N-vinyl carbonamides (such as, N-vinyl-formamide, N-vinylacetoamide, N-vinyl propionamides, N-vinyl hydroxyacetoamide, vinyl pyridine, N-vinyl imidazole, N-vinyl pyrrolidinone, N-vinyl caprolactam, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminobutylacrylamide, dimethylaminopropyl methacrylate, dimethylaminopropyl acrylate, dimethylaminopropylacrylamide, dimethylaminopropylmethacrylamide, dimethylaminoethylacrylamide or mixtures thereof.

[0063] In one embodiment the heteratom group derived from a nitrogen containing group may include dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl methacrylate, dimethylaminopropyl acrylate, dimethylaminopropylacrylamide, dimethylaminopropylmethacrylamide, nitriles of (meth)acrylic acid and other nitrogen-containing (meth)acrylates, such as N-(methacryloyloxyethyl)diisobutyl ketimine, N-(methacryloyloxyethyl)dihexadecyl ketimine, methacryloylamidoacetonitrile, 2-methacryloyloxyethylmethylcyanamide, cyanomethyl methacrylate, or mixtures thereof.

[0064] Examples of suitable non-carbonyl oxygen containing compounds capable of being incorporated into the copolymer include hydroxyalkyl (meth)acrylates such as 3-hydroxypropyl methacrylate, 3,4-dihydroxybutyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2,5-dimethyl-1,6-hexanediol (meth)acrylate, 1,10-decanediol (meth)acrylate, carbonyl-containing methacrylates such as 2-carboxyethyl methacrylate, carboxymethyl methacrylate, oxazolidinylethyl methacrylate, N-(methacryloyl-oxy)formamide, acetonyl methacrylate, N-methacryloylmorpholine, N-methacryloyl-2-pyrrolidinone, N-(2-methacryloyloxyethyl)-2-pyrrolidinone, N-(3-methacryloyloxypropyl)-2-pyrrolidinone, N-(2-methacryloyloxypentadecyl)-2-pyrrolidinone, N-(3-methacryloyloxyheptadecyl)-2-pyrrolidinone; glycol dimethacrylates such as 1,4-butanediol methacrylate, 2-butoxyethyl methacrylate, 2-ethoxyethoxymethyl methacrylate, 2-ethoxyethyl methacrylate, or mixtures thereof.

[0065] Other examples of suitable non-carbonyl oxygen containing compounds capable of being incorporated into the copolymer include methacrylates of ether alcohols, such as tetrahydrofurfuryl methacrylate, vinyloxyethoxyethyl methacrylate, methoxyethoxyethyl methacrylate, 1-butoxypropyl methacrylate, 1-methyl-(2-vinyloxy)ethyl methacrylate, cyclohexyloxymethyl methacrylate, methoxymethoxyethyl methacrylate, benzyloxymethyl methacrylate, furfuryl methacrylate, 2-butoxyethyl methacrylate, 2-ethoxyethoxymethyl methacrylate, 2-ethoxyethyl methacrylate, allyloxymethyl methacrylate, 1-ethoxybutyl methacrylate, methoxymethyl methacrylate, 1-ethoxyethyl methacrylate, ethoxymethyl methacrylate and ethoxylated (meth)-acrylates which typically have 1 to 20, or 2 to 8, ethoxy groups, or mixtures thereof.

[0066] The block copolymer may be obtained/obtainable from controlled radical or other living polymerisation techniques such as RAFT (Reversible Addition Fragmentation Transfer), ATRP (Atom Transfer Radical Polymerisation), nitroxide-mediated and anionic. These polymerisation techniques are known to a person skilled in the art.

[0067] Anionic polymerisation processes may be useful when the heteroatom of the second block contains a nitrogen heteroatom (from an amine) when steps are taken to quench the amine during polymerisation. Such techniques are known to a person skilled in the art.

[0068] More detailed descriptions of polymerisation mechanisms and related chemistry is discussed for nitroxide-mediated polymerisation (Chapter

10, pages 463 to 522) of in the Handbook of Radical Polymerization, edited by Krzysztof Matyjaszewski and Thomas P. Davis, 2002, published by John Wiley and Sons Inc (hereinafter referred to as "Matyjaszewski et al.").

[0069] In one embodiment the controlled radical polymerisation process employed to prepare the block copolymer may be a RAFT process. A detailed description of RAFT processes is described in WO2006/047393 (see whole document for reagents, and reference to linear polymers) or US Patent Application 2006/0189490 (see paragraphs [0128] to [0131].

[0070] In one embodiment the controlled radical polymerisation process employed to prepare the block copolymer may be an ATRP process. In ATRP polymerisation, groups that may be transferred by a radical mechanism include halogens (from a halogen-containing compound) or various ligands. A more detailed review of groups that may be transferred is described in US Patent 6,391,996, or paragraphs 61 to 65 of US Patent Application 2005/038146. Another detailed description of ATRP processes is described in US Patent Application 2006/0189490 (see paragraphs [0102] to [0126]).

[0071] More detailed descriptions of polymerisation mechanisms and related chemistry is discussed for ATRP (Chapter 11, pages 523 to 628) and RAFT (Chapter 12, pages 629 to 690) in Matyjaszewski et al.

[0072] In one embodiment the controlled radical polymerisation process may be a RAFT process.

[0073] In RAFT polymerisation, chain transfer agents are important. A more detailed review of suitable chain transfer agents is found in paragraphs 66 to 71 of US Patent Application US 2005/038146.

[0074] In one embodiment a suitable RAFT chain transfer agent includes 2-Dodecylsulphanylthiocarbonylsulphanyl-2-methyl-propionic acid butyl ester, cumyl dithiobenzoate or mixtures thereof.

Oils of Lubricating Viscosity

[0075] The lubricating composition comprises an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined and re-refined oils and mixtures thereof.

[0076] Unrefined oils are those obtained directly from a natural or synthetic source generally without (or with little) further purification treatment.

[0077] 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. Purification techniques are known in the art and include solvent extraction, secondary distillation, acid or base extraction, filtration, percolation and the like.

[0078] Re-refined oils are also known as reclaimed or reprocessed oils, and are obtained by processes similar to those used to obtain refined oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

[0079] Natural oils useful in making the inventive lubricants include animal oils, vegetable oils (e.g., castor oil), 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 and oils derived from coal or shale or mixtures thereof.

[0080] Synthetic lubricating oils are useful and include hydrocarbon oils such as polymerised and interpolymerised olefins (typically hydrogenated) (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), poly(1-decenes), and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulphides and the derivatives, analogs and homologs thereof or mixtures thereof.

[0081] Other synthetic lubricating oils include polyol esters (such as Prolube®3970), diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be 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.

[0082] Oils of lubricating viscosity may also be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulphur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulphur content $\leq$0.03 wt %, and $\geq$90 wt % saturates, viscosity index 80-120); Group III (sulphur content $\leq$0.03 wt %, and $\geq$90 wt % saturates, viscosity index $\geq$120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity includes an API Group I, Group II, Group III, Group IV, Group V oil or mixtures thereof. Often the oil of lubricating viscosity is an API Group I, Group II, Group III, Group IV oil or mixtures thereof.

[0083] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt % the sum of the amount of the compound of the invention and the other performance additives.

[0084] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention comprising the additives disclosed herein above is in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

Other Performance Additives

[0085] The composition optionally includes other performance additives. The other performance additives comprise at least one of metal deactivators, viscosity modifiers, detergents, friction modifiers, antiwear agents, corrosion inhibitors, dispersants, dispersant viscosity modifiers, extreme pressure agents, antioxidants, foam inhibitors, demulsifiers, emulsifiers (other than the block copolymer of the invention), pour point depressants (other than the block copolymer of the invention), seal swelling agents and mixtures thereof. Typically, fully-formulated lubricating oil will contain one or more of these performance additives.

[0086] In one embodiment the lubricating composition of the invention further includes at least one of a friction modifier, a viscosity modifier, an antioxidant, an overbased detergent, a succinimide dispersant, or mixtures thereof.

[0087] In one embodiment the lubricating composition of the invention further includes at least one of a viscosity modifier, an antioxidant, an overbased detergent, a succinimide dispersant, or mixtures thereof.

Detergents

[0088] In one embodiment the lubricating composition further includes known neutral or overbased detergents. Suitable detergent substrates include phenates, sulphur containing phenates, sulphonates, salixarates, salicylates, carboxylic acid, phosphorus acid, mono- and/or di- thiophosphoric acids, alkyl phenols, sulphur coupled alkyl phenol compounds, or saligenins. Various overbased detergents and their methods of preparation are described in greater detail in numerous patent publications, including WO2004/096957 and references cited therein. The detergent substrate may be salted with a metal such as calcium, magnesium, potassium, sodium, or mixtures thereof.

[0089] In one embodiment the overbased detergent is selected from the group consisting of phenates, sulphur containing phenates, sulphonates, salixarates, salicylates, and mixtures thereof. Typically the selected overbased detergent include calcium or magnesium phenates, sulphur containing phenates, sulphonates, salixarates, saliginens, salicylates, or mixtures thereof.

[0090] In one embodiment the detergent may be a calcium salicylate. In one embodiment the detergent may be a calcium sulphonate. In one embodiment the invention the detergent may be a mixture of a calcium sulphonate and a calcium salicylate.

[0091] In one embodiment the detergent may be a calcium phenate. In one embodiment the detergent may be a calcium sulphonate. In one embodiment the invention the detergent may be a mixture of a calcium sulphonate and a calcium phenate.

[0092] When the lubricating composition is not lubricating a 2-stroke marine diesel engine the detergent may be present (on an oil free basis i.e., an actives basis) at 0 wt % to 10 wt %, or 0.1 wt % to 8 wt %, or 1 wt % to 4 wt % of the lubricating composition. When the lubricating composition is lubricating a 2-stroke marine diesel engine the amount of detergent (on an oil free basis i.e., an actives basis)may be 0 wt % to 40 wt %, or 2 wt % to 35 wt %, or 5 wt % to 30 wt % of the lubricating composition.

Dispersants

[0093] Dispersants are often known as ashless-type dispersants because, prior to mixing in a lubricating oil composition, they do not contain ash-forming metals and they do not normally contribute any ash forming metals when added to a lubricant and polymeric dispersants. Ashless type dispersants are characterised by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides. Examples of N-substituted long chain alkenyl succinimides include polyisobutylene succinimide with number average molecular weight of the polyisobutylene substituent in the range 350 to 5000, or 500 to 3000. Succinimide dispersants and their preparation are disclosed, for instance in US Patent 3,172,892 or US Patent 4,234,435. Succinimide dispersants are typically the imide formed from a polyamine, typically a poly(ethyleneamine).

[0094] In one embodiment the invention further includes at least one dispersant which is a polyisobutylene succinimide derived from a polyisobutylene with number average molecular weight in the range 350 to 5000, or 500 to 3000. The polyisobutylene succinimide may be used alone or in combination with other dispersants.

[0095] In one embodiment the invention further includes at least one dispersant derived from polyisobutylene succinic anhydride, an amine and zinc oxide to form a polyisobutylene succinimide complex with zinc. The polyisobutylene succinimide complex with zinc may be used alone or in combination.

[0096] Another class of ashless dispersant includes Mannich bases. Mannich dispersants are the reaction products of alkyl phenols with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). The alkyl group typically contains at least 30 carbon atoms.

[0097] The dispersants may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are boron, urea, thiourea, dimercaptothiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

[0098] The dispersant (typically a polyisobutylene succinimide) may have a high total base number or the dispersant may have a high total acid number. Generally dispersants with a high TAN number have a carbonyl to nitrogen ratio of 1 or higher, in one aspect 1.2 or higher, in another aspect 1.4 or higher and in yet another aspect 1.45 or higher, for example 1.5. Generally dispersants with a high TBN number have a carbonyl to nitrogen ratio of less than 1, in one aspect 0.94 or lower, in another aspect 0.88 or lower and in another aspect 0.8 or lower, for instance 0.77. The carbonyl to nitrogen ratio is to be calculated on a molar basis, that is, the ratio of moles of carbonyl functionality (e.g., -C(O)O-) to the moles of nitrogen functionality (e.g., amine nitrogens). In one embodiment the dispersant may be in a mixture of (i) a dispersant with a carbonyl to nitrogen ratio of 1 or higher; and (ii) a dispersant with a carbonyl to nitrogen ratio of less than 1.

[0099] The dispersant may be present (on an oil free basis i.e., an actives basis) at 0 wt % to 20 wt %, or 0.1 wt % to 15 wt %, or 0.1 wt % to 10 wt %, or 1 wt % to 6 wt % of the lubricating composition.

Antioxidants

[0100] Antioxidant compounds are known and include for example, sulphurised olefins, alkylated diphenylamines (typically di-nonyl diphenylamine, octyl diphenylamine, di-octyl diphenylamine), hindered phenols, molybdenum compounds (such as molybdenum dithiocarbamates), or mixtures thereof. Antioxidant compounds may be used alone or in combination. The antioxidant may be present in ranges (on an oil free basis i.e., an actives basis) of 0 wt % to 20 wt %, or 0.1 wt % to 10 wt %, or 1 wt % to 5 wt %, of the lubricating composition.

[0101] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group may be further substituted with a hydrocarbyl group (typically linear or branched alkyl) and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba.

A more detailed description of suitable ester-containing hindered phenol antioxidant chemistry is found in US Patent 6,559,105.

[0102] In one embodiment the lubricating composition further includes a molybdenum compound.

[0103] The molybdenum compound is selected from the group consisting of molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, amine salts of molybdenum compounds, and mixtures thereof.

[0104] Suitable examples of molybdenum dithiocarbamates which may be used as an antioxidant include commercial materials sold under the trade names such as Molyvan 822™, Molyvan™ A and Molyvan 855™ from R. T. Vanderbilt Co., Ltd., and Adeka Sakura-Lube™ S-100, S-165 S-515, S-600 and S-710 from Adeka ; and mixtures thereof.

[0105] When present, the molybdenum compound may provide 5 ppm to 1000 ppm, or 20 ppm to 300 ppm of molybdenum to the lubricating composition.

Viscosity Modifiers

[0106] Viscosity modifiers include hydrogenated copolymers of maleic anhydride-(alpha olefin) copolymers, styrene-butadiene, ethylene-propylene copolymers, polyisobutenes, hydrogenated styrene-isoprene polymers, hydrogenated isoprene polymers, polymethacrylates, polyacrylates, polyalkyl styrenes, hydrogenated alkenyl arene conjugated diene copolymers, polyolefins, esters of maleic anhydride-styrene copolymers.

Dispersant Viscosity Modifiers

[0107] Dispersant viscosity modifiers (often referred to as DVM), include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalized with an acylating agent such as maleic anhydride and an amine; polymethacrylates functionalised with an amine, or esterified styrene-maleic anhydride copolymers reacted with an amine.

Antiwear Agents

[0108] In one embodiment the lubricating composition further includes an antiwear agent.

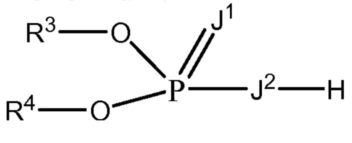
[0109] The additional antiwear agent may be either ashless or ash-forming. Typically ashless antiwear agents do not contain metal, whereas ash-forming do contain metal.

[0110] The antiwear agent may be present (on an oil free basis i.e., an actives basis) in ranges including 0 wt % to 15 wt %, or 0 wt % to 10 wt %, or 0.05 wt % to 5 wt %, or 0.1 wt % to 3 wt % of the lubricating composition.

[0111] In one embodiment the lubricating composition further includes a phosphorus-containing antiwear agent. Typically the phosphorus-containing antiwear agent may be present in an amount to deliver the ranges of phosphorus described below in the subject matter under the sub-heading "Industrial Application".

[0112] Examples of suitable antiwear agents include phosphate esters, sulphurised olefins, sulphur-containing anti-wear additives including metal dihydrocarbyldithiophosphates (such as primary or secondary zinc dialkyldithiophosphates, or molybdenum dialkyldithiophosphates), molybdenum thiocarbamate-containing compounds including thiocarbamate esters, alkylene-coupled thiocarbamates, and bis(S-alkyldithiocarbamyl) disulphides.

[0113] Examples of suitable zinc dialkyldithiophosphates include those disclosed in PCT Application US07/073428 (entitled "Method of Lubricating an Internal Combustion Engine and Improving the Efficiency of the Emissions Control System of the Engine") or in PCT Application US07/073426 (entitled "Lubricating Oil Composition and Method of Improving Efficiency of Emissions Control System"). Both applications claim priority from July 17, 2006. The zinc dialkyldithiophosphates or zinc dialkylphosphates may in one embodiment be defined as a zinc salt of a mixture of phosphorus-containing compounds represented by the formula:



wherein in formula, J^1 and J^2 are independently S or O, and R^3 and R^4 may be independently hydrocarbyl groups, the average total number of carbon atoms in R^3 plus R^4 for the mixture of phosphorus-containing compounds being at least 9.5; wherein R^3 and R^4 are characterised in that (i) 4 to 70 mole percent of such groups contain 2 to 4 carbon atoms and (ii) 30 to 96 mole percent such groups contain 5 to 12 carbon atoms; and wherein, in less than 8 mole percent of the molecules of the formula in the mixture of phosphorus-containing compounds, each of R^3 and R^4 contain 2 to 4 carbon atoms and in greater than 11 mole percent of the molecules of the formula in said mixture R^3 has 2 to 4 carbon atoms and R^4 has 5 to 12 carbon atoms; and wherein, within the formula, the average total number of hydrogen atoms in R^3 and R^4 on carbon atoms located beta to the O atoms is at least 7.25.

[0114] The dithiocarbamate-containing compounds may be prepared by reacting a dithiocarbamate acid or salt with an unsaturated compound. The dithiocarbamate containing compounds may also be prepared by simultaneously reacting an amine, carbon disulphide and an unsaturated compound. Generally, the reaction occurs at a temperature of 25 °C to 125 °C. US Patents 4,758,362 and 4,997,969 describe dithiocarbamate compounds and methods of making them.

[0115] Examples of suitable olefins that may be sulphurised to form an sulphurised olefin include propylene, butylene, isobutylene, pentene, hexane, heptene, octane, nonene, decene, undecene, dodecene, undecyl, tridecene, tetradecene, pentadecene, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof. In one embodiment, hexadecene, heptadecene, octadecene, octadecenene, nonodecene, eicosene or mixtures thereof and their dimers, trimers and tetramers are especially useful olefins. Alternatively, the olefin may be a Diels-Alder adduct of a diene such as 1,3-butadiene and an unsaturated ester, such as butylacrylate.

[0116] Another class of sulphurised olefin includes fatty acids and their esters. The fatty acids are often obtained from vegetable oil or animal oil and typically contain 4 to 22 carbon atoms. Examples of suitable fatty acids and their esters include triglycerides, oleic acid, linoleic acid, palmitoleic acid or mixtures thereof. Often, the fatty acids are obtained from lard oil, tall oil, peanut oil, soybean oil, cottonseed oil, sunflower seed oil or mixtures thereof. In one embodiment fatty acids and/or ester are mixed with olefins.

Extreme Pressure Agents

[0117] Extreme Pressure (EP) agents that are soluble in the oil include sulphur- and chlorosulphur-containing EP agents, chlorinated hydrocarbon EP agents and phosphorus EP agents. Examples of such EP agents include chlorinated wax; organic sulphides and polysulphides such as dibenzyldisulphide, bis–(chlorobenzyl) disulphide, dibutyl tetrasulphide, sulphurised methyl ester of oleic acid, sulphurised alkylphenol, sulphurised dipentene, sulphurised terpene, and sulphurised Diels-Alder adducts; phosphosulphurised hydrocarbons such as the reaction product of phosphorus sulphide with turpentine or methyl oleate; phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite; dipentylphenyl phosphite, dioleyl phosphite, di-2-ethylhexyl phosphite, didodecyl phosphite, di C_{12-14} alkyl phosphite, tridecyl phosphite, distearyl phosphite and polypropylene substituted phenol phosphite; metal thiocarbamates such as zinc dioctyldithiocarbamate and barium heptylphenol diacid; amine salts of alkyl and dialkylphosphoric acids, including, for example, the amine salt of the reaction product of a dialkyldithiophosphoric acid with propylene oxide; and mixtures thereof.

Friction Modifiers

[0118] In one embodiment the lubricating composition further includes a friction modifier, or mixtures thereof. Typically the friction modifier may be present (on an oil free basis i.e., an actives basis) in ranges including 0 wt % to 10 wt %, or 0.05 wt % to 8 wt %, or 0.1 wt % to 4 wt %.

[0119] Examples of suitable friction modifiers include long chain fatty acid derivatives of amines, esters, or epoxides; fatty imidazolines such as condensation products of carboxylic acids and polyalkylene-polyamines; amine salts of alkylphosphoric acids; fatty alkyl tartrates; fatty alkyl tartrimides; or fatty alkyl tartramides.

[0120] Friction modifiers may also encompass materials such as fatty alkyl tartrates; fatty alkyl tartrimides, sulphurised fatty compounds and olefins, molybdenum dialkyldithiophosphates, molybdenum dithiocarbamates, sunflower oil or monoester of a polyol and an aliphatic carboxylic acid (all these friction modifiers may also be described as antioxidants or antiwear agents).

[0121] In one embodiment the friction modifier friction modifier is selected from the group consisting of long chain fatty acid derivatives of amines, esters, or epoxides; fatty alkyl tartrates; fatty alkyl tartrimides; and fatty alkyl tartramides.

[0122] In one embodiment the friction modifier may be a long chain fatty acid ester (previously described above as an ashless antiwear agent). In one embodiment the long chain fatty acid ester may be a mono-ester, e.g., a monoglyceride, and in one embodiment the long chain fatty acid ester may be a (tri)glyceride.

Other Additives

[0123] Other performance additives such as corrosion inhibitors include those described in paragraphs 5 to 8 of US Application US05/038319 (filed on October 25, 2004 McAtee and Boyer as named inventors), octylamine octanoate, condensation products of dodecenyl succinic acid or anhydride and a fatty acid such as oleic acid with a polyamine. In one embodiment the corrosion inhibitors include the Synalox® corrosion inhibitor. The Synalox® corrosion inhibitor is typically a homopolymer or copolymer of propylene oxide. The Synalox® corrosion inhibitor is described in more detail in a product brochure with Form No. 118-01453-0702 AMS, published by The Dow Chemical Company. The product brochure is entitled "SYNALOX Lubricants, High-Performance Polyglycols for Demanding Applications."

[0124] Metal deactivators including derivatives of benzotriazoles (typically tolyltriazole), dimercaptothiadiazole derivatives, 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, or 2-alkyldithiobenzothiazoles; foam inhibitors including copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers; pour point depressants including esters of maleic anhydride-styrene, polymethacrylates, polyacrylates or polyacrylamides may be useful. Foam inhibitors that may be useful in the compositions of the invention include copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

[0125] Pour point depressants that may be useful in the compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene copolymers, fumarate ester-vinyl acetate copolymers, polyalkyl(meth)acrylates, polyalkylacrylates or polyalkylacrylamides.

Industrial Application

[0126] In one embodiment the mechanical device is an internal combustion engine.

[0127] In one embodiment the internal combustion engine may be a diesel fueled engine, a gasoline fueled engine, a natural gas fueled engine or a mixed gasoline/alcohol fueled engine. In one embodiment the internal combustion engine may be a diesel fueled engine and in one embodiment a gasoline fueled engine.

[0128] The internal combustion engine may be a 2-stroke or 4-stroke engine. Suitable internal combustion engines include marine diesel engines, aviation piston engines, low-load diesel engines, and automobile and truck engines.

[0129] As used herein the components of the internal combustion engine include all of the parts of the engine derived from metal lubricated by an engine lubricant. This includes for example, cylinder liners, camshafts, pistons, bearings, oil coolers etc.

[0130] In one embodiment the internal combustion engine contains components ferric (i.e., ferrous) components. The ferric components include Fe, FeO, Fe_3O_4 or other materials containing iron.

[0131] In one embodiment the internal combustion engine contains components of an aluminium-alloy. The aluminium-alloy includes aluminium silicates, aluminium oxides, or other ceramic materials. In one embodiment the aluminium-alloy is an aluminium-silicate surface.

[0132] The lubricating composition for an internal combustion engine may be suitable for any engine lubricant irrespective of the sulphur, phosphorus or sulphated ash (ASTM D-874) content. The sulphur content of the engine oil lubricant may be 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less, or 0.3 wt % or less. In one embodiment the sulphur content may be in the range of 0.001 wt % to 0.5 wt %, or 0.01 wt % to 0.3 wt %. The phosphorus content may be 0.2 wt % or less, or 0.1 wt % or less, or 0.085 wt % or less, or even 0.06 wt % or less, 0.055 wt % or less, or 0.05 wt % or less. In one embodiment the phosphorus content may be 100 ppm to 1000 ppm, or 200 ppm to 600 ppm. The total sulphated ash content may be 2 wt % or less, or 1.5 wt % or less, or 1.1 wt % or less, or 1 wt % or less, or 0.8 wt % or less, or 0.5 wt % or less. In one embodiment the sulphated ash content may be 0.05 wt % to 0.9 wt %, or 0.1 wt % to 0.2 wt % to 0.45 wt %.

[0133] In one embodiment the lubricating composition may be an engine oil, wherein the lubricating composition may be characterised as having (i) a sulphur content of 0.5 wt % or less, (ii) a phosphorus content of 0.08 wt % or less, and (iii) a sulphated ash content of 1.5 wt % or less.

[0134] In one embodiment the lubricating composition may be suitable for a 2-stroke or a 4-stroke marine diesel internal combustion engine. In one embodiment the marine diesel combustion engine is a 2-stroke engine.

[0135] The block copolymer of the invention may also be used in a variety of lubricants requiring emulsifiers and/or pour point depressants. The block copolymer of the invention may be an emulsifier and/or pour point depressant in driveline devices, industrial gears, hydraulic devices, off-highway mobile equipment such as farm tractors, greases, metalworking fluids and fuels. For each of these devices the lubricant formulation may, as a person skilled in the art will appreciate, change due to the different additives and treat rates commonly employed in each lubricant type. None the less, the block copolymer is believed to function as an emulsifier and/or pour point depressant.

[0136] Driveline devices include gearboxes, axle gears, traction drive transmissions, automatic transmissions or manual transmissions.

[0137] Automatic transmissions include continuously variable transmissions (CVT), infinitely variable transmissions (IVT), Torroidal transmissions, continuously slipping torque converted clutches (CSTCC), stepped automatic transmissions or dual clutch transmissions (DCT).

[0138] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

EXAMPLES

[0139] Preparative Example 1 (EX1): is a diblock copolymer of (C_{12-15}-alkyl methacrylate and 2-ethylhexylmethacrylate)-b-dimethylaminoethyl methacrylate. The diblock copolymer is prepared by charging reagents into a 4-necked flask equipped with a nitrogen inlet, thermocouple and a heating mantle. The reagents added include 99.2 g of C_{12-15}-alkyl methacrylate, 48 g of 2-ethylhexylmethacrylate, 5.04 g of a chain transfer agent (dodecyl-trithiocarbonate butyl ester), 0.87 g of Trigonox®21 initiator and 41.48 g of PAO-4 diluent oil. The flask is stirred and purged with nitrogen for 30 minutes. The nitrogen flow rate is 0.028 m^3/hr (or 1 SCFH). The flask is then heated to 90 °C and the nitrogen flow is reduced to 0.014 m^3/hr (or 0.5 SCFH) and held for 150 minutes. The flask is then charged with 12.8 g of dimethylaminoethyl methacrylate. The flask is held for a further 3 hours at 90 °C, before cooling. The product is a viscous liquid.

[0140] Preparative Example 2 (EX2): is a diblock copolymer of (C_{12-15}-alkyl methacrylate and 2-ethylhexylmethacrylate)-b-dimethylaminoethyl methacrylate. 111.6 g of C_{12-15}-alkyl methacrylate, 54 g of 2-ethylhexylmethacrylate, and 0.97 g of Trigonox®21 initiator are blended to form a blend. About one third of the blend is charged into a 4-necked flask equipped with a nitrogen inlet, thermocouple and a heating mantle. 5.67 g of a chain transfer agent (dodecyl-trithiocarbonate butyl ester) is then added to the flask.

[0141] The flask is stirred and purged with nitrogen for 30 minutes. The nitrogen flow rate is 0.028 m^3/hr (or 1 SCFH). The flask is then heated to 80 °C and the nitrogen flow is reduced to 0.014 m^3/hr (or 0.5 SCFH) and the remaining two thirds of the blend is added over a period of 90 minutes. The flask is maintained at 80 °C and held for 150 minutes. The flask is then charged with 14.4 g of dimethylaminoethyl methacrylate. The flask is held for a further 150 minutes at 80 °C, before cooling. The product is a viscous liquid.

[0142] Preparative Example 3 (EX3): is a diblock copolymer of (C_{12-15}-alkyl methacrylate and C_{16-18}-alkyl methacrylate)-b-dimethylaminoethyl methacrylate. 1500 g of C_{12-15}-alkyl methacrylate, 260 g of C_{16-18}-alkyl methacrylate (the C_{16-18}-alkyl methacrylate also contains up to 5 wt % C_{14}-alkyl methacrylate and up to 2 wt % C_{20}-alkyl methacrylate), and 3 g of Trigonox®21 initiator are blended to form a blend. About one third of the blend is charged into a 4-necked flask equipped with a nitrogen inlet, thermocouple and a heating mantle. 17.5 g of a chain transfer agent (dodecyl-trithiocarbonate butyl ester) is then added to the flask.

[0143] The flask is stirred and purged with nitrogen for 30 minutes. The nitrogen flow rate is 0.056 m^3/hr (or 2 SCFH). The flask is then heated to 80 °C and the nitrogen flow is reduced to 0.014 m^3/hr (or 0.5 SCFH) and the remaining two thirds of the blend is added over a period of 90 minutes. The flask is maintained at 80 °C and held for 15 hours. The flask is then charged with 240 g of dimethylaminoethyl methacrylate. The flask is held for at 90 °C for 2 hours. Three separate charges (each 1 g) of Trigonox®21 initiator are added over a period of 5 hours. The product is a viscous liquid before dilution with diluent oil to form a 40 % polymer mixture in oil.

[0144] Preparative Example 4 (EX4): is a diblock copolymer prepared by a process similar to EX3, except the final polymer is a block copolymer of (C_{12-15}-alkyl methacrylate and C_{16-18}-alkyl methacrylate)-b-(dimethylaminoethyl methacrylate and methylmethacrylate). The methyl methacrylate is added concurrently with dimethylaminoethyl methacrylate. The ratio of the weight percent of C_{12-15}-alkyl methacrylate to C_{16-18}-alkyl methacrylate is 85:15 (the C_{16-18}-alkyl methacrylate also contains up to 5 wt % C_{14}-alkyl methacrylate and up to 2 wt % C_{20}-alkyl methacrylate). The ratio of the weight percent of dimethylaminoethyl methacrylate to methylmethacrylate is 91:9. The ratio weight percent of hydrophobic block to the second block containing a polar group is 87:13. The product is a viscous liquid before dilution with diluent oil to form a 50 % polymer mixture in oil.

[0145] Comparative Preparative Example 1 (CP1): is a random polymer of C_{12-15}-alkyl methacrylate, 2-ethylhexylmethacrylate, and dimethylaminoethyl methacrylate. The random polymer is prepared by charging reagents into a 4-necked flask equipped with a nitrogen inlet, thermocouple and a heating mantle. The reagents added include 99.2 g of C_{12-15}-alkyl methacrylate, 48 g of 2-ethylhexylmethacrylate, 12.8 g of dimethylaminoethyl methacrylate, 5.04 g of a chain transfer agent (dodecyl-trithiocarbonate butyl ester), 0.87 g of Trigonox®21 initiator and 41.48 g of PAO-4 diluent oil. The flask is then heated to 90 °C as is described in EX1.

[0146] In the following lubricant examples and comparative lubricant examples, the listed amount of the products from the preparative example or comparative preparative example, as the case may be, includes the amount of diluent oil reported to be added or included therein.

[0147] Comparative Lubricant Example 1 (CLC1) is a SAE 5W-30 engine lubricant.

[0148] Comparative Lubricant Example 2 (CLC2) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.05 wt % of the product of CP1.

[0149] Comparative Lubricant Example 3 (CLC3) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.12 wt % of the product of CP1.

[0150] Comparative Lubricant Example 4 (CLC4) is a oil mixture of 80 wt % of ExxonMobil Group II EHC™-45, with viscosity of 4.6 mm^2/s at 100 °C and 20 wt % of ExxonMobil Group II EHC™-60, with viscosity of 6.0 mm^2/s at 100 °C.

[0151] Lubricant Example 1 (LC1) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.05 wt % of the product of EX1.

[0152] Lubricant Example 2 (LC2) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.12 wt % of the product of EX1.

[0153] Lubricant Example 3 (LC3) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.05 wt % of the product of EX2.

[0154] Lubricant Example 4 (LC4) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.12 wt % of the product of EX2.

[0155] Lubricant Example 5 (LC5) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.07 wt % of the product of EX3.

[0156] Lubricant Example 6 (LC6) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.16 wt % of the product of EX3.

[0157] Lubricant Example 7 (LC7) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.06 wt % of the product of EX4.

[0158] Lubricant Example 8 (LC8) is a 5W-30 engine lubricant similar to CLC1, except it further contains 0.15 wt % of the product of EX4.

[0159] Lubricant Example 9 (LC9) is similar to CLC4, except it contains 0.26 wt % of the product of EX2.

[0160] Lubricant Example 10 (LC10) is similar to CLC4, except it contains 0.35 wt % of the product of EX3.

[0161] Lubricant Example 11 (LC11) is similar to CLC4, except it contains 0.35 wt % of the product of EX4.

Testing

[0162] Lubricant examples LC1 to LC8 and comparative Lubricant examples CLC1 to CLC3 are evaluated in the following ASTM tests D445, D4684-07 and D5985-02. The lubricants are also evaluated in Chrysler's FFV emulsion stability test.

[0163] ASTM D445 relates to measurement of kinematic viscosity (units mm^2/s) at 100 °C.

[0164] ASTM D4684-07 (Mini-Rotary Viscometer or MRV) relates to the low-temperature pumpability of an engine lubricating oil. Yield stress and low-shear-rate viscosity are measured after cooling at controlled rates over a period exceeding 45 hour to a final test temperature between -10 °C and -40 °C. The units are Centipoise (cP) or mPa-s.

[0165] D5985-02 covers the determination of pour point of petroleum products by an automatic instrument that continuously rotates the test specimen against a suspended detection device during cooling of the test specimen.

[0166] The Chrysler FFV emulsion stability test involves the steps of combining 10 volume % E85 fuel, 10% water, and 80% fully formulated engine oil and mixing them in a Waring blender. The resultant emulsion is stored in graduated cylinders at 0 °C and room temperature (25 °C) for 24 hours. At the end of the test, the volume percent oil (% oil), percent emulsion (% emul), and percent water (% H_2O) are recorded. Typically, a formulated oil is considered to pass the FFV test if %H_2O at both 0°C and room temperature is zero.

[0167] The results obtained for the tests described above are as follows:

Test	D445	D4684-07 (at -35 °C)
CLC1	10.33	32400
CLC2	10.62	30900
CLC3	10.60	32300
LC1	n/m	n/m
LC2	n/m	n/m
LC3	10.54	30500
LC4	10.54	31300
LC5	10.45	44500
LC6	10.43	66000
LC7	10.65	36300
LC8	10.66	46500

	Chrysler FFV at 0 °C			Chrysler FFV at 25 °C		
	% oil	% emul	% H_2O	% oil	% emul	% H_2O
CLC1	86	0	14	85	0	15
CLC2	87	0	13	84	0	16
CLC3	88	0	12	84	0	15
LC1	n/m	n/m	n/m	12	88	0
LC2	n/m	n/m	n/m	3	97	0
LC3	18	82	0	52	48	0
LC4	6	94	0	15	85	0
LC5	7	94	0	3	97	0
LC6	23	77	0	1	99	0
LC7	9	91	0	40	60	0
LC8	5	95	0	26	74	0

Footnote to the tables:

n/m indicates a data point not measured

[0168] Examples CLC4 and LC9 to LC11 are analysed for pour point performance by the methodology of ASTM method D5985-02. The results obtained are as follows:

Example	Pour Point (°C)	No Flow Point (°C)
CLC4	-18	-19.9
LC9	-18	-21
LC10	-30	-30.1
LC11	-30	-30.1

[0169] Overall the results obtained for the block copolymer of the present invention indicate that the polymer has emulsifying properties and/or pour point depressant properties.

[0170] 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. The products formed thereby, including the products formed upon employing lubricating 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 lubricating composition prepared by admixing the components described above.

[0171] Each of the documents referred to above is incorporated herein by reference. 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 may be used together with ranges or amounts for any of the other elements. Multiple groups represented by the same symbol in the formulae described above, may be the same or different.

[0172] As used herein the "C_{1-30} alkyl (meth)acrylic units" relate to product formed by the polymerisation of C_{1-30} alkyl (meth)acrylic monomer. The C_{1-30} alkyl (meth)acrylic units may then be used to form the block(s) as described herein above. Reference to the percentage of C_{1-30} alkyl (meth)acrylic units is considered as a mole percent.

[0173] 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:

(i) 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);

(ii) 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 sulphoxy);

(iii) 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; and

(iv) heteroatoms, including sulphur, 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.

[0174] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

What is claimed is:

1. A method of lubricating an internal combustion engine comprising supplying to the engine a lubricating composition comprising an oil of lubricating viscosity and a block copolymer, wherein the block copolymer comprises:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block.

2. The method of claim 1, wherein the internal combustion engine is a flexible fuel vehicle engine.

3. The method of any preceding claim 1 to 2, wherein the block copolymer comprises:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, wherein at least 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units further having a heteroatom group providing a polar group.

4. The method of any preceding claim 1 to 3, wherein the block copolymer comprises:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, wherein at least 70 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and up to 30 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block.

5. The method of any preceding claim 1 to 3, wherein the block copolymer comprises:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, wherein at least 80 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and up to 20 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block.

6. The method of any preceding claim 1 to 5, wherein the heteroatom-containing group of the second block contains sulphur, nitrogen, non-carbonyl oxygen, phosphorus, or mixtures thereof.

7. The method of any preceding claim 1 to 6, wherein the heteroatom-containing group of the second block contains nitrogen.

8. The method of any preceding claim 1 to 7, wherein the heteroatom-containing group is derived from a nitrogen containing monomer selected from the group consisting of dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminopropyl methacrylate, dimethylaminopropyl acrylate, dimethylaminopropylacrylamide, dimethylaminopropylmethacrylamide, and mixtures thereof.

9. The method of any preceding claim 1 to 8, wherein the block copolymer is a methacrylate polymer.

10. The method of any preceding claim 1 to 9, wherein the block copolymer is a linear diblock copolymer.

11. The method of any preceding claim 1 to 10, wherein the block copolymer is obtained/obtainable from a controlled radical polymerisation process or other living polymerisation process.

12. The method of claim 11, wherein the controlled radical or other living polymerisation process is one of RAFT (Reversible Addition Fragmentation Transfer), ATRP (Atom Transfer Radical Polymerisation), nitroxide-mediated or anionic.

13. The method of claim 12, wherein the controlled radical polymerisation process is a RAFT process.

14. A lubricating composition comprising an oil of lubricating viscosity and a block copolymer comprising:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, wherein at least 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block.

15. The use of a block copolymer as an emulsifier and/or pour point depressant in a lubricant, said polymer comprising:

(a) a hydrophobic first block having C_{1-30} alkyl (meth)acrylic units, wherein at least 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{12-15} alkyl (meth)acrylic units, and up to 50 wt % of the C_{1-30} alkyl (meth)acrylic units are C_{16-20} alkyl (meth)acrylic units, with the proviso that alkyl groups of the C_{1-30} alkyl (meth)acrylic units have an average total number of carbon atoms of at least 8; and

(b) a second block having (meth)acrylic units which further have a non-carbonyl heteroatom-containing group providing a polar group to such units, whereby said second block exhibits greater hydrophilicity than does the hydrophobic first block.

16. The use of the block copolymer of claim 15 as an emulsifier and a pour point depressant.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/063046

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M145/14 C10M149/02 C10M149/06 C10M151/02 C10M153/02
ADD. C10N30/04 C10N40/25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/056739 A1 (ARKEMA INC [US]; SCHMIDT SCOTT CHARLES [US]; CALLAIS PETER ANTHONY [US) 23 June 2005 (2005-06-23) paragraphs [0037], [0087], [0088], [0091], [0092]; claims 1,14	1,3-14
X	EP 0 265 254 A2 (DU PONT [US]) 27 April 1988 (1988-04-27) claims 4,5; table 1	14
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X	US 4 985 160 A (HENRY CYRUS P [US] ET AL) 15 January 1991 (1991-01-15) claim 16; example 26	14
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 January 2010	29/01/2010

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 080 794 A (AUSCHRA CLEMENS [DE] ET AL) 27 June 2000 (2000-06-27) claim 1 -----	1-16
X	US 2006/189490 A1 (DARDIN ALEXANDER [DE] ET AL) 24 August 2006 (2006-08-24) cited in the application claims 1,7,17; table 1 -----	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

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