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(54) Title: LUBRICATING OIL, HAVING IMPROVED FUEL ECONOMY RETENTION PROPERTIES

(57) Abstract

A lubricating oil composition which exhibits improved fuel economy and fuel economy retention, contains the combination of (a) a dithiocarbarmate of the formula $R^1(R^2)N\text{–}C(:S)\text{–}S\text{–}(CH_2)_n\text{–}S\text{–}(:S)C\text{–}N(R^2)R^1$ where R^1 and R^2 independently represent alkyl groups having 1 to 20 carbon atoms and n is an integer from 1 to 4; and (b) an oil soluble trinuclear friction modifying molybdenum compound, the two components functioning to provide an improvement in the friction reducing properties of the composition.

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LUBRICATING OIL HAVING IMPROVED FUEL ECONOMY RETENTION PROPERTIES

This invention relates to lubricating oil composition particularly useful for internal combustion engines such as passenger car engines. More particularly, the invention relates to lubricating oil compositions which exhibit improvements in fuel economy and fuel economy retention.

The use of molybdenum compounds as fuel economy additives or friction reducing agents in lubricating oil compositions is known in the art and is illustrated, for example, in US-A-4,501,678 and -4,479,883, the former describing the combination of dinuclear, but not trinuclear, Mo compounds in combination with dithiocarbamates.

It is now surprisingly found, according to this invention, that the use of certain molybdenum compounds, namely trinuclear molybdenum compounds, in combination with a dithiocarbamate provides a significant increase in fuel economy as well as fuel economy retention as observed by coefficient of friction studies for lubricating oil compositions containing these two additives.

In a first aspect, this invention provides a lubricating oil composition exhibiting improved fuel economy and fuel economy retention properties which comprises an oil of lubricating viscosity; (a) 0.05 to 10, preferably 0.1 to 1.5, mass% of an oil-soluble dithiocarbamate of the formula $R^1(R^2)N\text{-}C(:S)\text{-}S\text{-}(CH_2)_n\text{-}S\text{-}(:S)C\text{-}N(R^2)R^1$ where R^1 and R^2 independently represent alkyl groups having 1 to 20 carbon atoms and n is an integer from 1 to 4; and (b) an oil-soluble trinuclear molybdenum compound, for example of the formula $Mo_3S_kL_n$ where k is 4 to 10, n is 1 to 4 and L represents an organic ligand having sufficient carbon atoms to render the trinuclear molybdenum compound oil-soluble, the compound being present in such an amount so as to provide 10 to 1000 ppm by weight of molybdenum in the composition.

In a second aspect, this invention provides a method of making a lubricating oil composition which comprises admixing (or blending) an oil of lubricating viscosity and (a) and (b) as defined in the first aspect of the invention.

In a third aspect, this invention provides a method of lubricating a spark-ignited engine or a compression-ignited engine which comprises supplying to the engine a lubricating oil composition according to the first aspect of the invention.

In a fourth aspect, this invention provides the use of a lubricating oil composition according to the first aspect of the invention for improving the fuel economy and fuel economy retention properties of an internal combustion engine.

The features of the invention will now be discussed in more detail as follows:

(b) Oil-soluble trinuclear molybdenum compound

L may be independently selected from the group of:

$-X-R$, $-(X^1)(X^2)CR$, $-(X^1)(X^2)CYR$, $-(X^1)(X^2)CN(R^1)(R^2)$, or $-(X^1)(X^2)P(OR^1)(OR^2)$

and mixtures thereof, and perthio derivatives thereof, wherein X, X^1, X^2 and Y are independently selected from the group of oxygen and sulfur, and wherein R^1, R^2, and R are independently selected from the group consisting of H and organo groups that may be the same or different. Preferably, the organo groups are hydrocarbyl groups such as alkyl (e.g., in which the carbon atom attached to the remainder of the ligand is primary, secondary or tertiary), aryl, substituted aryl and ether groups. More preferably, all ligands are the same.

Importantly, the organo groups of the ligands have a sufficient number of carbon atoms to render the compounds soluble in oil. The compounds' oil solubility may be influenced by the number of carbon atoms in the ligands. In the compounds (b) in the present invention, the total number of carbon atoms present among all of the organo groups of the compounds' ligands typically will be at least 21, e.g. 21 to 800, such as at least 25, at least 30 or at least 35. For example, the number of carbon atoms in each alkyl group will generally range between 1 to 100, preferably 1 to 40 and more preferably between 3 and 20. Preferred ligands include dialkyldithiophosphate ("ddp"), xanthates, thioxanthates, dialkylphosphate, dialkyldithiocarbamate ("dtc"), and carboxylate and of these the dtc is more preferred, particularly when the alkyl group contains 8 to 18 carbon atoms.

Multidentate organic ligands containing at least two of the above functionalities are also capable of binding to at least one of the trinuclear cores and serving as ligands. Without wishing to be bound by any theory, it is believed that one or more trinuclear molybdenum cores may be bound or interconnected by means of at least one of these multidentate ligands. Such structures fall within the scope of the compounds (b). This includes the case of a multidentate ligand having multiple connections to one core.

Those skilled in the art will realize that formation of the compounds (b) will require selection of appropriate ligands having suitable charge to balance the corresponding core's charge.

The term "hydrocarbyl" denotes a substituent having carbon atoms directly attached to the remainder of the ligand and is predominantly hydrocarbyl in character within the context of this invention. Such substituents include the following: (1) hydrocarbon substituents, that is, aliphatic (for example alkyl or alkenyl), alicyclic (for example cycloalkyl or cycloalkenyl) substituents, aromatic-, aliphatic- and alicyclic-substituted aromatic nuclei and the like, as well as cyclic substituents wherein the ring is completed through another portion of the ligand (that is, any two indicated substituents may together form an alicyclic group); (2) substituted hydrocarbon substituents, that is those containing nonhydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbyl character of the substituent. Those skilled in the art will be aware of suitable groups (e.g., halo, (especially chloro and fluoro), amino, alkoxyl, mercapto, alkylmercapto, nitro, nitroso and sulfoxy,); (3) hetero substituents, that is, substituents which, while predominantly hydrocarbon in character within the context of this invention, contain atoms other than carbon present in a chain or ring otherwise composed of carbon atoms.

Generally, the trinuclear molybdenum-containing compounds (b) can be prepared by reacting a suitable molybdenum source, with a ligand source and, optionally, with a sulfur abstracting agent. This may be carried out in a suitable liquid medium which may be aqueous or organic. Oil-soluble or -dispersible trinuclear molybdenum compounds can be prepared, for example, by reacting in the appropriate solvent(s) $(M^1)_2Mo_3S_{13}.n(H_2O)$, wherein n varies between 0 and 2 and includes non-stoichiometric values, with a suitable ligand source such as a tetraalkylthiuram disulfide. Other oil-soluble or -dispersible trinuclear molybdenum compounds can be formed by reacting $(M^1)_2Mo_3S_{13}.n(H_2O)$, wherein n varies between 0 and 2 and includes nonstoichiometric values, a ligand source such as tetraalkylthiuram disulfide, dialkyldithiocarbamate, or dialkyldithiophosphate, and a sulfur abstracting agent such as cyanide ions, sulfite ions, or substituted phosphines. Alternatively, a trinuclear molybdenum-sulfur halide salt such as $[M^1]_2[Mo_3S_7A_6]$, wherein A = Cl, Br, or I, may be reacted with a ligand source such as a dialkyldithiocarbamate or dialkyldithiophosphate in the appropriate solvent(s) to form an oil-soluble or dispersible trinuclear molybdenum compound. In the above formulae, M^1 is a counter ion such as NH_4. The trinuclear molybdenum compounds are related by the number of sulfur atoms in the molybdenum core. Within the disclosed range, the number of the sulfur atoms in the core may be altered by the addition of sulfur abstractors such as cyanide and substituted phosphines, or sulfur donators such as elemental sulfur and organic trisulfides to the trinuclear molybdenum compounds.

Preferred trinuclear molybdenum compounds for use in the compositions of this invention are those of the formula $Mo_3S_7((alkyl)_2dtc)_4$ where the alkyl group has 8 to 18 carbon atoms, preferably being a “coco” alkyl chain which is a mixture of chains of varying even numbers of carbon atoms from typically a C_8 to C_{18} alkyl group, mainly C_{10}, C_{12} and C_{14} alkyl groups derived from coconut oil.

The preferred amount of trinuclear molybdenum compound (b) is that which will provide 50 to 750, most preferably 150 to 500, ppm by weight of molybdenum in the composition of the invention.

International Patent Application No PCT/IB97/01656 describes trinuclear molybdenum compounds, their preparation, and their use in lubricating oil compositions.

(a) Oil-soluble dithiocarbamate

Preferably n is 1 and R^1 and R^2 are each butyl, when the compound is 4,4'-methylene-bis(dibutyldithiocarbamate), such as sold as "Vanlube 7723" by Vanderbilt Chemical Co. It has been found that use of the defined dithiocarbamate in combination with the trinuclear Mo compound provides to the composition enhanced fuel economy retention characteristics not obtained with chemically similar thiocarbamate compounds known to be lubricating oil additives, such as zinc diamyl dithiocarbamate (e.g. "Vanlube AZ") and 1,2-dicarboxyethyl dithiocarbamate having alkyl groups with four carbon atoms (e.g. "Vanlube 732").

The preferred amount of the dtc of this invention is 0.1 to 1.5 mass % of the lubricating oil composition.

Oil of lubricating viscosity

Natural oils useful as basestocks in this invention as the oil of lubricating viscosity include animal oils and vegetable oils (e.g., castor or lard oil) liquid petroleum oils and hydrorefined, solvent-treated or acid-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.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by, for example esterification or etherification, are a class of known synthetic lubricating oils useful as basestocks in this invention. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-poly isopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500 to1000, diethyl ether of polypropylene glycol having a molecular weight of 1000 to1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3 to C_8 fatty acid esters and C_{13} Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils useful in this invention 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, sebasic 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.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants; they include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tertbutylphenyl) silicate, hexa-(4-methyl-2-pentoxy) disiloxane, poly(methyl) siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined oils can be used in the lubricants 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 an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improved 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. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

Concentrates, compositions and uses

The compositions of this invention are principally applicable in the formulation of crankcase lubricating oils for passenger car engines such as spark-ignited and compression-ignited engines, for example four-stroke engines. Further additives may be incorporated in the compositions to enable them to meet particular requirements. Examples of such additives (or co-additives) are listed below and are typically used in such amounts so as to provide their normal attendant functions. Typical amounts for individual additives are also set forth below. All the values listed are stated as mass percent active ingredient in the total lubricating oil composition.

ADDITIVE	MASS % (Broad)	MASS % (Preferred)
Ashless Dispersant	0.1 - 20	1 - 8
Metal Detergents	0.1 - 15	0.2 - 9
Corrosion Inhibitors	0 - 5	0 - 1.5
Metal Dihydrocarbyl Dithiophosphate	0.1 - 6	0.1 - 4
Supplemental Anti-oxidant	0 - 5	0.01 - 3
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Anti-foaming Agent	0 - 5	0.001 - 0.15
Supplemental Anti-wear Agents	0 - 5	0 - 2
Friction Modifier	0 - 5	0 - 1.5
Viscosity Modifier	0.01 - 6	0 - 4

The individual additives may be incorporated into a basestock, constituting the oil of lubricating viscosity, in any convenient way. Thus, each of the components can be added directly to the basestock by dispersing or dissolving it in the basestock at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature.

In the preparation of lubricating oil compositions, it is common practice to introduce additive(s) therefor in the form of concentrates of the additive(s) in 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 lubricating oil compositions. When preparing a lubricating oil composition that contains more than one type of additive, 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 two or more additives in a single concentrate. Preferably, all the additives except for the viscosity modifier and the pour point depressant are blended into a concentrate for subsequent use to make the composition.

A concentrate may contain 1 to 90, such as 10 to 80, preferably 20 to 80, more preferably 20 to 70, mass % active ingredient of the additive or additives.

A concentrate is conveniently made in accordance with the method described in US-A-4,938,880 which describes making a pre-mix of ashless dispersant and metal detergents that is pre-blended at a temperature of at least about 200°C. Thereafter, the pre-mix is cooled to at least 85°C and the additional components are added.

Lubricating oil compositions may be prepared by adding to the oil of lubricating viscosity a mixture of an effective minor amount of at least one additive and, if necessary, one or more co-additives such as described herein. This preparation may be accomplished by adding the additive directly to the oil or by adding it in the form of a concentrate thereof (which is preferred, as stated above) to disperse or dissolve the additive. Additives my be added to the oil by any method known to those skilled in the art, either prior to, contemporaneously with, or subsequent to addition of other additives.

The terms “oil-soluble” or “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 instance, 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.

The lubricating oil compositions may be used to lubricate mechanical engine components, particularly of an internal combustion engine, by adding the lubricating oil thereto.

The lubricating compositions and concentrates comprise defined components that may or may not remain the same chemically before and after mixing with the oil of lubricating viscosity. This invention encompasses compositions and concentrates which comprise the defined components before mixing, or after mixing, or both before and after mixing. That is to say, the various components of the composition, essential as well as optimal and customary, may react under the conditions of formulation, storage, or use, and the invention also provides the product obtainable or obtained as a result of any such reaction.

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

The final crankcase lubricating oil composition may employ from 2 to 20, preferably 4 to 15, mass % of the concentrate, the remainder being base stock.

The aforementioned co-additives will now be described in further detail as follows:

Ashless dispersants maintain in suspension oil insolubles resulting from oxidation of the oil during wear or combustion. They are particularly advantageous for preventing the precipitation of sludge and the formation of varnish, particularly in gasoline engines.

Ashless dispersants comprise an oil soluble polymeric hydrocarbon backbone bearing one or more functional groups that are capable of associating with particles to be dispersed. Typically, the polymer backbone is functionalized by amine, alcohol, amide, or ester polar moieties, often via a bridging group. The ashless dispersant may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon substituted mono and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

The oil soluble polymeric hydrocarbon backbone of these dispersants is typically derived from an olefin polymer or polyene, especially polymers comprising a major molar amount (i.e., greater than 50 mole %) of a C_2 to C_{18} olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a C_2 to C_5 olefin. The oil-soluble polymeric hydrocarbon backbone may be a homopolymer (e.g., polypropylene or polyisobutylene) or a copolymer of two or more of such olefins (e.g., copolymers of ethylene and an alpha-olefin such as propylene or butylene, or copolymers of two different alpha-olefins). Other copolymers include those in which a minor molar amount of the copolymer monomers, for example, 1 to 10 mole %, is an α,ω-diene, such as a C_3 to C_{22} non-conjugated diolefin (for example, a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene).

The viscosity modifier (VM) functions to impart high and low temperature operability to a lubricating oil. The VM used may have that sole function, or may be multifunctional.

Multifunctional viscosity modifiers that also function as dispersants are also known. Suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene and higher alpha-olefins, polymethacrylates, polyalkylmethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, inter polymers of styrene and acrylic ester, and partially hydrogenated copolymers of styrene/isoprene, styrene/butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene and isoprene/divinylbenzene.

Metal-containing or ash-forming detergents may be present and these function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with long hydrophobic tail, with the polar head comprising a metal salt of an acid organic compound. The salts may contain a substantially stoichiometric amount of the metal in which they are usually described as normal or neutral salts, and would typically have a total base number (TBN), as may be measured by ASTM D-2896 of from 0 to 80. It is possible to include large amounts of a metal base by reacting an excess of a metal compound such as an oxide or hydroxide with an acid gas such as carbon dioxide. The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g., carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically from 250 to 450 or more.

Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and nephthenates and other oil-soluble carboxylates of a metal, particularly the alkali, e.g., sodium, potassium, lithium and magnesium. Preferred are neutral or overbased calcium and magnesium phenates and sulfonates.

Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2, mass %, based upon the total weight of the lubricating oil composition. They may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others 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 neutralization reaction.

Oxidation inhibitors or antioxidants reduce the tendency of basestocks to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, ashless oil-soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil soluble copper compound as described in US-A-4,867,890, and molybdenum-containing compounds.

Rust inhibitors selected from the group consisting of nonionic polyoxyalkylene polyols and esters thereof, polyoxyalkylene phenols, and anionic alkyl sulfonic acids may be used.

Copper- and lead- bearing corrosion inhibitors may be used, but are typically not required with the formulation of the present invention. Typically such compounds are the thiadiazole polysulfides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Derivatives of 1,3,4-thiadiazoles such as those described in US-A-2,719,125; -2,719,126; and -3,087,932; are typical. Other similar material are described in US-A-3,821,236; -3,904,537; -4,097,387; 4,107,059; -4,136,043; -4,188,299; and -4,193,882. Other additives are the thio and polythio sulfenamides of thiadiazoles such as those described in GB-B-1,560,830.

Benzotriazoles derivatives also fall within this class of additives. When these compounds are included in the lubricating composition, they are preferably present in an amount not exceeding 0.2 mass % active ingredient.

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 reacting 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.

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

Foam control can be provided by many compounds including an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

The words “comprises” or “comprising”, or cognate words, when used in this specification, are taken to specify the presence of stated features, but do not preclude the presence or addition of one or more other features or groups thereof.

Examples

The invention is further illustrated by the following examples which are not to be considered as limitative of its scope.

Friction measurements were made using a high frequency reciprocating rig (HFRR) after an accelerated aging of the test oils in which air and NO_2 are added to a 30 ml sample of test oil containing soluble iron, the sample being in a test tube in a silicone oil bath. Aging conditions were 2.2 ml/min. NO_2 and 26 ml/min. air, 155°C oil bath temperature and 40 ppm soluble Fe (ferric acetylacetonate) in chloroform. These aging laboratory conditions have been demonstrated to give a correlation relative to the Sequence IIIE engine test. The HFRR parameters were 100°C oil temperature, 400 g. load, 20 Hz stroke frequency and 1 mm stroke length. The disks were 650 Hv, AISI 52100 steel, polished to 0.05 micron Ra roughness.

Example 1

A lubricating oil composition was prepared composed of the following (percentages are mass % active ingredient):

1.925% - dispersant formed by reacting a neo acid functionalized ethylene (45%) 1-butene copolymer of Mn 3500 with a polyalkylene polyamine having 7 N atoms per mole, as disclosed in US-A-5,696,064
0.001% - silicone antifoam (45% vol. solution in mineral oil)
0.672% - calcium C_{24} alkyl benzene sulfonate (TBN 400)
0.3% - C_8 hindered alkylphenol antioxidant
0.7% - nonyldiphenylamine antioxidant
0.56% - zinc dialkyldithiophosphate antiwear additive
0.407% - $Mo_3S_7((coco)_2dtc)_4$ - anti-friction additive (trinuclear Mo) (provides 500 ppm Mo in the oil composition)
0.20% - copper salt of polyisobutenyl succinic anhydride - antioxidant
0.34% - borated polyisobutenyl (Mn 950) succinimide dispersant
0.40% - olefin copolymer viscosity modifier
1.00% - 4,4'-methylene-bis(dibutyldithiocarbamate), "Vanlube 7723"
Balance - mineral oil basestock of lubricating viscosity

Example 2 (Comparison)

Another lubricating oil composition was prepared having the same ingredients as that of Example 1 except the "Vanlube 7723" was replaced with "Vanlube AZ", which is zinc diamyldithiocarbamate.

Example 3 (Comparison)

Another lubricating oil composition was prepared having the same ingredients as that of Example 1 except that the "Vanlube 7723" was replaced by "Vanlube 732", which is 1,2-dicarboethoxyethyl dithiocarbamate having C_4 alkyl groups.

A comparison of friction data for these three lubricating oil compositions is reported below.

Coefficient of Friction			Hours of Aging at 155°C
Ex. 1	Ex. 2	Ex. 3	
.115	.130	.103	0
.088	.083	.080	22
.080	.095	.082	30
.085	.136	.135	46

The data show the superior friction retention of the composition of Example 1 due to the combination of the trinuclear molybdenum compound and the dithiocarbamate of this invention. The results at 30 hours are significant.

CLAIMS:

1. A lubricating oil composition exhibiting improved fuel economy and fuel economy retention properties which comprises, or is made by admixing, an oil of lubricating viscosity; (a) 0.05 to 10 mass % of a dithiocarbamate of the formula $R^1(R^2)N-C(:S)-S-(CH_2)_n-S-(:S)C-N(R^2)R^1$ where R^1 and R^2 independently represent alkyl groups having from 1 to 20 carbon atoms and n is an integer from 1 to 4; and (b) an oil-soluble trinuclear molybdenum , for example of the formula $Mo_3S_kL_n$ where k is 4 to 10, n is 1 to 4 and L represents an organic ligand having sufficient carbon atoms to render the trinuclear molybdenum compound oil-soluble, the compound being present in such an amount as to provide 10 to 1000 ppm by wright of molybdenum in the composition.

2. The composition as claimed in claim 1 wherein n is 1 and R^1 and R^2 represent butyl groups.

3. The composition as claimed in claim 1 or claim 2 wherein L represents a coco alkyl group.

4. The composition as claimed in any of the preceding claims further comprising a dispersant, an antiwear additive, an antioxidant and a viscosity modifier in such amounts as to provide their normal attendant functions.

5. The composition as claimed in any preceding claim wherein there is present 50 to 750, preferably 150 to 500, ppm by weight of molybdenum in the oil composition.

6. The composition as claimed in any preceding claim wherein there is present 0.1 to 1.5 mass % of the dithiocarbamate.

7. A method of making a lubricating oil composition which comprises blending an oil of lubricating viscosity and (a) and (b) as defined in claim 1.

8. A method of lubricating a spark-ignited engine or a compression-ignited engine which comprises supplying to the engine a lubricating oil composition as claimed in any of claims 1 to 6.

9. The use of a lubricating oil composition as claimed in any of claims 1 to 6 for improving the fuel economy and fuel enconomy retention properties of an internal combustion engine.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/EP 99/01520

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C10M163/00 //(C10M163/00,135:18,159:18),C10N10:12,C10N30:06,
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)
IPC 6 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 383 931 A (RYU YUMI P ET AL) 17 May 1983 see examples 13,14; table III see column 5, line 36 - line 57 ---	1-9
A	US 4 501 678 A (KATAYAMA TAKAO ET AL) 26 February 1985 cited in the application see example 9; table I see column 1, line 49 - line 65 ---	1-9
A	US 4 978 464 A (COYLE CATHERINE L ET AL) 18 December 1990 see the whole document --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

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Date of the actual completion of the international search 1 July 1999	Date of mailing of the international search report 13/07/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Rotsaert, L

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INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/EP 99/01520

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

.formation on patent family members

Inte onal Application No

PCT/EP 99/01520

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