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Office de la Propriété Intellectuelle du Canada

Innovation, Science and
Economic Development Canada
Canadian Intellectual Property Office

CA 2732190 C 2018/06/19

(11)(21) **2 732 190**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(22) **Date de dépôt/Filing Date:** 2011/02/22
(41) **Mise à la disp. pub./Open to Public Insp.:** 2011/08/23
(45) **Date de délivrance/Issue Date:** 2018/06/19
(30) **Priorité/Priority:** 2010/02/23 (EP10154430.2)

(51) **Cl.Int./Int.Cl.** *C10M 143/12* (2006.01)
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(54) Titre : COMPOSITIONS D'HUILE LUBRIFIANTE COMPORTANT DES COMPOSANTS ADDITIFS AMELIORANT L'INDICE DE VISCOSITE
(54) Title: LUBRICATING OIL COMPOSITIONS INCLUDING VISCOSITYINDEX IMPROVER ADDITIVE COMPONENTS

(57) Abrégé/Abstract:

A lubricating oil composition comprising: (A) an oil of lubricating viscosity in a major amount, comprising a Group III base stock; (B) as an additive component in a minor amount, a viscosity index improver comprising a linear or star-shaped polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers; and, wherein the lubricating oil composition is contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of a biofuel or a decomposition product thereof and mixtures thereof.

ABSTRACT

A lubricating oil composition comprising: (A) an oil of lubricating viscosity in a major amount, comprising a Group III base stock; (B) as an additive component in a minor amount, a viscosity index improver comprising a linear or star-shaped polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers; and, wherein the lubricating oil composition is contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of a biofuel or a decomposition product thereof and mixtures thereof.

LUBRICATING OIL COMPOSITIONS INCLUDING VISCOSITYINDEX IMPROVER ADDITIVE COMPONENTS

FIELD OF THE IVNENTION

The present invention relates to automotive lubricating oil compositions, more especially to automotive lubricating oil compositions for use in gasoline (spark-ignited) and diesel (compression-ignited) internal combustion engines fuelled at least in part with a biofuel, especially compression-ignited internal combustion engines fuelled at least in part with a biodiesel fuel and spark-ignited internal combustion engines fuelled at least in part with bioethanol fuel, crankcase lubrication, such compositions being referred to as crankcase lubricants.

In particular, although not exclusively, the present invention relates to automotive lubricating oil compositions, preferably having low levels of phosphorus and also low levels of sulfur and/or sulfated ash, which exhibit improved anti-oxidant properties during operation of the engine which is fuelled with a biofuel; and to the use of additives in such compositions for improving the anti-oxidant properties of the lubricating oil composition.

BACKGROUND OF THE INVENTION

A crankcase lubricant is an oil used for general lubrication in an internal combustion engine where an oil sump is situated generally below the crankshaft of the engine and to which circulated oil returns. The contamination or dilution of the crankcase lubricant in internal combustion engines, especially engines fuelled at least in part with a biofuel, is a concern.

Biodiesel fuels include components of low volatility which are slow to vaporize after injection of the fuel into the engine. Typically, an unburnt portion of the biodiesel and some of the resulting partially combusted decomposition products become mixed with the lubricant on the cylinder wall and are washed down into the oil sump, thereby contaminating the crankcase lubricant. The biodiesel fuel in the contaminated lubricant may form further decompositions products, due to the extreme conditions during lubrication of the engine. It has been found that the presence of biodiesel fuel and the decomposition products thereof in the crankcase lubricant promotes the oxidation of the lubricant. Moreover, it has been found that this problem is significantly worse in diesel engines which employ a late post-injection of fuel into the cylinder (e.g. light duty, medium duty and passenger car diesel engines) to regenerate an exhaust gas after-treatment device.

Exhaust gas after-treatment devices, such as a diesel particulate filter (DPF), require periodical regeneration to remove the build up of soot and to prevent them from having a detrimental effect on engine performance. One way to create conditions for initiating and sustaining regeneration of a DPF involves elevating the temperature of the exhaust gases entering the DPF to burn the soot. As a diesel engine runs relatively cool and lean, this may be achieved by adding fuel into the exhaust gases optionally in combination with the use of an oxidation catalyst located upstream of the DPF. Heavy duty diesel (HDD) engines, such as those in trucks, typically employ a late post-injection of fuel directly into the exhaust system outside of the cylinder, whilst light duty and medium duty diesel engines typically employ a late post-injection of fuel directly into the cylinder during an expansion stroke. Surprisingly, it has been found that the oxidation of the lubricant increases significantly in a diesel engine fuelled at least in part with biodiesel when the engine employs a late post-injection of fuel directly into the cylinder. Although only theory, it is believed this increased oxidation of the lubricant is due to more biodiesel being absorbed by the lubricant on the more exposed cylinder wall, thereby increasing contamination of the lubricant in the sump.

A similar increase in the oxidation of the lubricant has also been found to occur in spark-ignited internal combustion engines fuelled at least in part with an alcohol based fuel (e.g. bioethanol) due to the presence of the alcohol based fuel and the decomposition products thereof in the crankcase lubricant.

Oxidation of the lubricant typically yields corrosive acids and an undesirable increase in viscosity, thereby shortening the useful life of the lubricant. Accordingly, lubricants with improved antioxidant properties need to be identified.

SUMMARY OF THE INVENTION

The present invention is based on the discovery that a lubricating oil composition can be formulated which exhibits significantly improved antioxidant properties in the presence of a biofuel.

In accordance with a first aspect, the present invention provides a lubricating oil composition comprising:

(A) an oil of lubricating viscosity in a major amount, comprising a Group III base stock;

(B) as an additive component in a minor amount, an oil-soluble or oil-dispersible viscosity index improver comprising a linear or star-shaped polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers; and,

wherein the lubricating oil composition is contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of a biofuel or a decomposition product thereof and mixtures thereof.

Preferably, the lubricating oil composition according to the present invention is a crankcase lubricant.

It has unexpectedly been found that the inclusion of a viscosity index improver comprising a linear or star-shaped polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers, in a lubricating oil composition, particularly one including a Group III base stock, improves the antioxidant properties of the lubricant, in use, in the lubrication of an internal combustion engine which is fuelled at least in part with a biofuel. In particular, the inclusion of such a viscosity index improver in a lubricating oil composition comprising a Group III base stock provides, in use, a positive credit in terms of reduced oxidation of the lubricant and/or may promote the useful life of the lubricant.

According to a second aspect, the present invention provides a method of lubricating a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel, comprising operating the engine with a lubricating oil composition comprising: (A) an oil of lubricating viscosity in a major amount, comprising a Group III base stock; and, (B) as an additive component in a minor amount, an oil-soluble or oil-dispersible viscosity index improver comprising a linear or star-shaped polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers.

According to a third aspect, the present invention provides the use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel, of an oil-soluble or oil-dispersible viscosity index improver comprising a linear or star-shaped polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers, as an additive component in a minor amount, in a lubricating oil composition, to reduce and/or inhibit oxidation of the lubricating oil composition, during operation of the engine. Preferably, the lubricating oil composition comprises a major amount of an oil of lubricating viscosity comprising a Group III base stock.

According to a fourth aspect, the present invention provides a method of reducing and/or inhibiting the oxidation of a lubricating oil composition in the lubrication of a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel, the method comprising lubricating the engine with a lubricating oil composition comprising an oil of lubricating viscosity in a major amount and an oil-soluble or oil-dispersible viscosity index improver, as an additive component in a minor amount, comprising a linear or star-shaped polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers, as an additive component in a minor amount, and operating the engine. Preferably, the oil of lubricating viscosity comprises a Group III base stock.

According to a fifth aspect, the present invention provides the use, in the lubrication of a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel, of a lubricating oil composition comprising: (A) an oil of lubricating viscosity in a major amount, comprising a Group III base stock; and, (B) as an additive component in a minor amount, an oil-soluble or oil-dispersible viscosity index improver comprising a linear or star-shaped polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers, to reduce and/or inhibit oxidation of the lubricating oil composition, during operation of the engine.

According to a sixth aspect, the present invention provides a spark-ignited or compression-ignited internal combustion engine comprising a crankcase containing a lubricating oil composition comprising: (A) an oil of lubricating viscosity in a major amount, comprising a Group III base stock; and, (B) as an additive component in a minor amount, an oil-soluble or oil-dispersible viscosity index improver comprising a linear or star-shaped polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers, wherein the engine is fuelled at least in part with a biofuel.

Preferably, the lubricating oil compositions as defined in the second to sixth aspects of the invention are each independently contaminated with at least 0.3 mass %, based on the total mass of the lubricating oil composition, of a biofuel or a decomposition product thereof and mixtures thereof.

Preferably, the viscosity index improver comprises a linear or star-shaped, at least partially hydrogenated, polymer which is derivable, at least in part, from the polymerisation of one or more conjugated diene monomers.

Preferably, the spark-ignited internal combustion engine is fuelled at least in part with an alcohol based fuel, especially an ethanol based fuel such as bioethanol fuel.

Preferably, the compression-ignited internal combustion engine is fuelled at least in part with a biodiesel fuel.

Preferably, the engine of the second to sixth aspects comprises a compression-ignited internal combustion engine.

Preferably, the biofuel of each aspect of the invention is biodiesel.

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

> "active ingredients" or "(a.i.)" refers to additive material that is not diluent or solvent;
>
> "alcohol based fuel" refers to a fuel including an alcohol, such as methanol, ethanol, propanol and butanol, especially ethanol. The term "alcohol based fuel" embraces pure alcohol based fuel (i.e. pure ethanol) and also alcohol based fuel blends comprising, for example, a mixture of an alcohol and petroleum gasoline;
>
> "ethanol based fuel" refers to a fuel including ethanol and is otherwise defined in the same way as "alcohol based fuel";
>
> "biofuel" refers to a fuel that is produced from renewable biological resources and includes biodiesel fuel and bioalcohol fuel as defined herein. The term biofuel as used herein also embraces an "alcohol based fuel" as defined herein, such as "ethanol based fuel", irrespective of the source of the alcohol (i.e. the alcohol may be derived from a renewable biological source and or a non-renewable source, such as petroleum). Preferably, the term "biofuel" means a fuel derived solely from a renewable biological resource e.g. biodiesel fuel or bioalchohol fuel;
>
> "biodiesel fuel" refers to a fuel derived from a renewable biological resource (e.g. derivable from a natural oil/fat, such as vegetable oils or animal fats) comprising at least one alkyl ester, typically a mono-alkyl ester, of a long chain fatty acid. The term "biodiesel fuel" embraces pure biodiesel fuel (i.e. B100 as defined by ASTM D6751-08 (USA) and EN 14214 (Europe)) and

also biodiesel fuel blends comprising a mixture of biodiesel fuel and another fuel, such as petroleum diesel fuel;

"bioalcohol fuel" refers to fuel including an alcohol derived from a renewable biological resource (e.g. fermented sugar) and is otherwise defined in the same way as "alcohol based fuel";

"bioethanol fuel" refers to fuel including ethanol derived from a renewable biological resource and is otherwise defined in the same way as "ethanol based fuel". The term "bioethanol fuel" embraces pure bioethanol fuel (i.e. pure bioethanol E100) and also bioethanol fuel blends comprising, for example, a mixture of an bioethanol and petroleum gasoline;

"petroleum diesel fuel" refers to a diesel fuel produced from petroleum;

"bioethanol" refers to ethanol derived from a renewable biological resource;

"cold cranking simulator" ("CCS") is a measure of the cold-cranking characteristics of crankcase lubricants and is measured by ASTM D5293-92;

"comprising" or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof. The expressions "consists of" or "consists essentially of" or cognates may be embraced within "comprises" or cognates, wherein "consists essentially of" permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

"hydrocarbyl" means a chemical group (i.e. substituent) of a compound that contains hydrogen and carbon atoms and that is bonded to the remainder of the compound directly via a carbon atom. The group may contain one or more atoms other than carbon and hydrogen provided they do not affect the essentially hydrocarbyl nature of the group. 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 non-hydrocarbon 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, sulfoxy, etc.).

“halo” or “halogen” includes fluoro, chloro, bromo and iodo;

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

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

“minor amount” means less than 50 mass % of a composition, expressed in respect of the stated additive and in respect of the total mass of all the additives present in the composition, reckoned as active ingredient of the additive or additives;

"ppm" means parts per million by mass, based on the total mass of the lubricating oil composition;

"Shear Stability Index" ("SSI") is measured by ASTM D6278-98 (known as the Kurt-Orban (KO) or DIN bench test). SSI measures the ability of the polymer used as a viscosity index improver in crankcase lubricants to maintain thickening power during use and it is indicative of the resistance of the polymer to degradation under service conditions;

"KV100" means kinematic viscosity at 100°C as measured by ASTM D445;

"TBN" means total base number as measured by ASTM D2896;

"phosphorus content" is measured by ASTM D5185;

"sulfur content" is measured by ASTM D2622; and,

"sulfated ash content" is measured by ASTM D874.

All percentages reported are mass % on an active ingredient basis, i.e., without regard to carrier or diluent oil, unless otherwise stated.

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

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

DETAILED DESCRIPTION OF THE INVENTION

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

OIL OF LUBRICATING VISCOSITY (A)

The oil of lubricating viscosity (sometimes referred to as "base stock" or "base oil") is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil is useful for making concentrates as well as for making lubricating oil compositions therefrom, and may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

The oil of lubricating viscosity comprises a Group III base stock. The base stock groups are defined in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Typically, the base stock will have a viscosity preferably of 3-12, more preferably 4-10, most preferably 4.5-8, mm^2/s (cSt) at 100°C.

Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes base stocks as follows:

a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1.

d) Group IV base stocks are polyalphaolefins (PAO).

e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

Table E-1: Analytical Methods for Base Stock

Property	Test Method
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulphur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

Preferably, the oil of lubricating viscosity comprises greater than or equal to 10 mass %, more preferably greater than or equal to 20 mass %, even more preferably greater than or equal to 25 mass %, even more preferably greater than or equal to 30 mass %, even more preferably greater than or equal to 40 mass %, even more preferably greater than or equal to 45 mass % of a Group III base stock, based on the total mass of the oil of lubricating viscosity. Even more preferably, the oil of lubricating viscosity comprises greater than 50 mass %, preferably greater than or equal to 60 mass %, more preferably greater than or equal to 70 mass %, even more preferably greater than or equal to 80 mass %, even more preferably greater than or equal to 90 mass % of a Group III base stock, based on the total mass of the oil of lubricating viscosity. Most preferably, the oil of lubricating viscosity consists essentially of a Group III base stock. In some embodiments the oil of lubricating viscosity consists solely of Group III base stock. In the latter case it is acknowledged that additives included in the lubricating oil composition may comprise a carrier oil which is not a Group III base stock.

Other oils of lubricating viscosity which may be included in the lubricating oil composition are detailed as follows:

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

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

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g. phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, 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.

Unrefined, refined and re-refined oils can be used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for approval of spent additive and oil breakdown products.

Other examples of base oil are gas-to-liquid ("GTL") base oils, i.e. the base oil may be an oil derived from Fischer-Tropsch synthesised hydrocarbons made from synthesis gas containing H_2 and CO using a Fischer-Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed.

The oil of lubricating viscosity may also comprise a Group I, Group II, Group IV or Group V base stocks or base oil blends of the aforementioned base stocks.

Preferably, the volatility of the oil of lubricating viscosity or oil blend, as measured by the NOACK test (ASTM D5880), is less than or equal to 16%, preferably less than or equal to 13.5%, preferably less than or equal to 12%, more preferably less than or equal to 10%, most preferably less than or equal to 8%. Preferably, the viscosity index (VI) of the oil of lubricating viscosity is at least 95, preferably at least 110, more preferably at least 120, even more preferably at least 125, most preferably from about 130 to 140.

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

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

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

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

Preferably, the lubricating oil composition of the present invention contains low levels of phosphorus, namely up to 0.12 mass %, preferably up to 0.11 mass %, more preferably not greater than 0.10 mass %, even more preferably up to 0.09 mass %, even more preferably up to 0.08 mass %, even more preferably up to 0.06 mass % of phosphorus, expressed as atoms of phosphorus, based on the total mass of the composition.

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

Typically, the lubricating oil composition may contain low levels of sulphated ash. Preferably, the lubricating oil composition contains up to and including 1.2, more preferably up to 1.1, even more preferably up to 1.0, even more preferably up to 0.8, mass % sulphated ash, based on the total mass of the composition.

Suitably, the lubricating oil composition may have a total base number (TBN) of 4 to 15, preferably 5 to 12. In heavy duty diesel (HDD) engine applications the TBN of the lubricating composition ranges from about 4 to 12, such as 6 to 12. In a passenger car diesel engine lubricating oil composition (PCDO) and a passenger car motor oil for a spark-ignited engine (PCMO), the TBN of the lubricating composition ranges from about 5.0 to about 12.0, such as from about 5.0 to about 11.0.

Preferably, the lubricating oil composition is a multigrade identified by the viscometric descriptor SAE 20WX, SAE 15WX, SAE 10WX, SAE 5WX or SAE 0WX, where X represents any one of 20, 30, 40 and 50; the characteristics of the different viscometric grades can be found in the SAE J300 classification. In an embodiment of each aspect of the invention, independently of the other embodiments, the lubricating oil composition is in the form of an SAE 10WX, SAE 5WX or SAE 0WX, preferably in the form of an SAE 5WX or SAE 0WX, wherein X represents any one of 20, 30, 40 and 50. Preferably X is 20 or 30.

VISCOSITY INDEX IMPROVER (B)

Additive component B comprises a viscosity index improver (or viscosity modifier). Viscosity index improvers for lubricating oil compositions advantageously increase the viscosity of the lubricating oil composition at higher temperatures when used in relatively small amounts (have a high thickening efficiency (TE)), provide reduced lubricating oil resistance to cold engine starting (as measured by "CCS" performance) and resist mechanical degradation and reduction in molecular weight in use (have a high shear stability index (SSI)). It is also preferred that the viscosity index improver displays soot-dispersing characteristics in lubricating oil compositions. These oil-soluble polymers are generally of high molecular weight ($M_n > 50,000$) compared to the base oil and other components. Crankcase lubricating oil compositions conventionally contain viscosity index improvers to improve the viscometric performance of the engine oil, i.e., to provide multigrade oils such as SAE 5W-30, 10W-30 and 10W-40.

Viscosity index improvers useful in the practice of the present invention comprise linear or star-shaped polymers which are derivable, at least in part, from the polymerisation of one or more conjugated diene monomers. Preferably, the linear and star-shaped polymers are at least partially or fully hydrogenated.

Conjugated diene monomers contain two double bonds located in conjugation with each other, generally in a 1,3 relationship. Conjugated dienes containing more than two doudle bonds are also considered within the definition of *"conjugated diene monomers"*, provided at least two of the double bonds are located in conjugation with each other. Preferred conjugated diene monomers useful in the formation of the viscosity index improvers include conjugated dienes containing from 4 to 20 carbon atoms, preferably 4 to 12 carbon atoms, for example, 1,3-butadiene, isoprene, piperylene, 4-methylpenta-1,3-diene, 2-phenyl-1,3-butadiene, 3,4-dimethyl-1,3-hexadiene and 4,5-diethyl-1,3-octadiene. Highly preferred conjugated diene monomers include 1,3-butadiene, isoprene, or mixtures thereof; especially isoprene. Preferred isoprene monomers that may be used as the precursors of the viscosity index improver polymers can be incorporated into the polymer as either 1,4- or 3,4-configuration units, and mixtures thereof. Preferably, the majority of the isoprene is incorporated into the polymer as 1,4-units, such as greater than about 60 mass %, more preferably greater than about 80 mass %, such as about 80 to 100 mass %, most preferably greater than about 90 mass %., such as about 93 mass % to 100 mass %. Preferred butadiene monomers that may be used as the precursors of the viscosity index improver polymers can be incorporated into the polymer as either as either 1,2- or 1,4-configuration units. Preferably, at least about 70 mass %, such as at least about 75 mass %, more preferably at least about 80 mass %, such as at least about 85 mass %, most preferably at least about 90, such as 95 to 100 mass %, of the butadiene is incorporated into the polymer as 1,4- units.

According to a preferred embodiment of the present invention, the viscosity index improver comprises a linear polymer, especially a linear diblock copolymer comprising at least one block derivable predominantly from a vinyl aromatic hydrocarbon monomer and at least one block derivable predominantly from said one or more conjugated diene monomers.

Useful vinyl aromatic hydrocarbon monomers include those containing from 8 to 16 carbon atoms, for example: styrene; alkyl-substituted styrene; alkoxy-substitued styrene; vinyl naphthalene and alkyl-substituted vinyl naphthalene. Typically, the alkyl and alkoxy substituents include 1 to 6 carbon atoms. Highly preferred vinyl aromatic hydrocarbon monomers include styrene, alkyl-substituted styrene, alkoxy-substitued styrene; especially, styrene.

Linear diblock copolymers useful in the practice of the present invention may be represented by the following general formula:

$$A_z\text{-}(B\text{-}A)_y\text{-}B_x$$

wherein:

A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer;

B is a polymeric block derived predominantly from conjugated diene monomer;

x and z are, independently, a number equal to 0 or 1; and

y is a whole number ranging from 1 to about 15.

Also included in the definition of "linear diblock copolymers" are tapered linear block copolymers represented by the following general formula:

$$A\text{-}A/B\text{-}B$$

wherein:

A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer;

B is a polymeric block derived predominantly from conjugated diene monomer; and

A/B is a tapered segment derived from both vinyl aromatic hydrocarbon monomer and conjugated diolefin monomer.

As used herein in connection with polymer block composition, "predominantly" means that the specified monomer or monomer type that is the principle component in that polymer block is present in an amount of at least 85 mass % of the block.

Polymers prepared with diolefins will contain ethylenic unsaturation, and such polymers are preferably hydrogenated. When the polymer is hydrogenated, the hydrogenation may be accomplished using any of the techniques known in the prior art. For example, the hydrogenation may be accomplished such that both ethylenic and aromatic unsaturation is converted (saturated) using methods such as those taught, for example, in U.S. Pat. Nos. 3,113,986 and 3,700,633 or the hydrogenation may be accomplished selectively such that a significant portion of the ethylenic unsaturation is converted while little or no aromatic unsaturation is converted as taught, for example, in U.S. Pat. Nos. 3,634,595; 3,670,054; 3,700,633 and Re 27,145. Any of these methods can also be used to hydrogenate polymers containing only ethylenic unsaturation and which are free of aromatic unsaturation. Preferably, the linear diblock copolymer is hydrogenated wherein at least 50%, preferably at least 70%, more preferably at least 90%, most preferably at least 95 mass % of the original olefinic unsaturation is hydrogenated.

The block copolymers may include mixtures of linear polymers as disclosed above, having different molecular weights and/or different vinyl aromatic contents as well as mixtures of linear diblock copolymers having different molecular weights and/or different vinyl aromatic contents. The use of two or more different polymers may be preferred to a single polymer depending on the rheological properties the product is intended to impart when used to produce formulated engine oil.

The linear polymer, particularly the linear diblock copolymer, may have a number average molecular weight of between 200,000 and 1,500,000. A number average molecular weight of between 350,000 and 900,000 is preferred. The amount of vinyl aromatic content of the copolymer is preferably between 5% and 40% by mass of the copolymer. For such copolymers, number average molecular weights between 85,000 and 300,000 are acceptable. The term "number average molecular weight", as used herein, refers to the number average weight as measured by Gel Permeation Chromatography ("GPC") with a polystyrene standard, subsequent to hydrogenation.

Useful block copolymers include those prepared in bulk, suspension, solution or emulsion. As is well known, polymerization of monomers to produce hydrocarbon polymers may be accomplished using free-radical, cationic and anionic initiators or polymerization catalysts, such as transition metal catalysts used for Ziegler-Natta and metallocene type (also referred to as "single-site") catalysts.

Preferably, the linear diblock copolymer is at least one linear diblock copolymer having a polystyrene block and a block derived from isoprene, butadiene, or a mixture thereof. More preferably, the linear diblock copolymer is at least one linear diblock copolymer selected from hydrogenated styrene/butadiene diblock copolymers and hydrogenated styrene/isoprene diblock copolymers. Preferably, the diblock copolymer has a Shear Stability Index value, determined in accordance with the procedure of ASTM D6278-98 (known as the Kurt-Orban (KO) or DIN bench test), of from 2 to 50%, more preferably from 5 to 50% (30 cycles), and the block of the diblock copolymer derived from diene comprises from 40 to 90 mass % derived from isoprene and from 10 to 60 mass % derived from butadiene.

Diblock copolymer components of the present invention are available as commercial products. Examples of commercially available styrene/hydrogenated isoprene linear diblock copolymers include Infineum SV140™, Infineum SV150™, Infineum SV151™ and Infineum SV160™, available from Infineum USA L.P. and Infineum UK Ltd.; Lubrizol® 7318, available from The Lubrizol Corporation; and Septon 1001™ and Septon 1020™, available from Septon Company of America (Kuraray Group). Suitable styrene/1, 3-butadiene hydrogenated block copolymers are sold under the tradename Glissoviscal™ by BASF.

According to a further preferred embodiment of the present invention, the viscosity index improver comprises at least one star-shaped, at least partially hydrogenated, polymer derivable, at least in part, from the polymerisation of one or more conjugated diene monomers as defined hereinbefore. Suitably, the star-shaped polymer includes multiple arms extending from a central core; the arms being derived from the polymerisation of one or more conjugated diene monomers as defined hereinbefore, and optionally a vinyl aromatic hydrocarbon monomer as defined hereinbefore.

The arms of the star polymer may be a homopolymer derived essentially from the polymerisation of a single conjugated diene monomer as defined herein, such as isoprene or 1,3-butadiene, particularly isoprene.

Alternatively, the arms of the star polymer may be a copolymer derived essentially from the polymerisation of two or more conjugated diene monomers as defined herein, such as an isoprene and 1,3-butadiene copolymer, or a copolymer derived essentially from the polymerisation of one or more conjugated diene monomers as defined herein and a vinyl aromatic hydrocarbon monomer as defined herein, such as an isoprene-styrene copolymer, a butadiene-styrene copolymer or an isoprene-butadiene-styrene copolymer.

As used herein in connection with polymer composition, "derived essentially" permits the inclusion of other substances not materially affecting the characteristics of the polymer to which it applies. Preferably, "derived essentially" means the specified monomer and comonomers, in the case of a copolymer, are present in an amount of at least 90 %, more preferably 95 %, even more preferably greater than 99 % by mass of the polymer.

The arms of the star polymer may also be a block copolymer, preferably a linear block copolymer, more preferably a linear diblock copolymer, such as one represented by the following general formula:

$$A_z\text{-}(B\text{-}A)_y\text{-}B_x$$

wherein:

A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer;

B is a polymeric block derived predominantly from conjugated diene monomer;

x and z are, independently, a number equal to 0 or 1; and

y is a whole number ranging from 1 to about 15.

The arms of the star polymer may also be a tapered linear block copolymer such as one represented by the following general formula:

A-A/B-B

wherein:

A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer;

B is a polymeric block derived predominantly from conjugated diene monomer; and

A/B is a tapered segment derived from both vinyl aromatic hydrocarbon monomer and conjugated diolefin monomer.

Preferably, the arms of the star polymer comprise a hydrogenated isoprene-butadiene copolymer, a hydrogenated styrene-isoprene-butadiene copolymer, a hydrogenated isoprene-styrene copolymer or a hydrogenated butadiene-styrene copolymer.

Most preferably, the arms of the star polymer comprise a linear diblock copolymer as defined herein. Preferably, the linear diblock copolymer comprises at least one block derivable predominantly from a vinyl aromatic hydrocarbon monomer as defined herein and at least one block derivable predominantly from one or more conjugated diene monomers as defined herein. Preferably, the vinyl aromatic hydrocarbon monomer comprises styrene. Preferably, the one or more conjugated diene monomers comprise isoprene, butadiene or a mixture thereof. Most preferably, the linear diblock copolymer is at least partially hydrogenated.

Preferably, the at least one block derivable predominantly from a vinyl aromatic hydrocarbon monomer (e.g. styrene) in the linear diblock copolymer is present in an amount of up to 35 %, even more preferably up to 25 %, most preferably 5 to 25 %, by mass based on the total mass of the linear diblock copolymer.

Preferably, the at least one block derivable from predominantly from one or more conjugated diene monomers is present in an amount of greater than 65 %, even more preferably greater than or equal to 75 %, most preferably 75 to 95 %, by mass based on the total mass of the linear diblock copolymer.

Preferably, the linear diblock copolymer comprises at least one polystyrene block and a block derived from isoprene, butadiene, or a mixture thereof. Highly preferred linear diblock copolymers comprise linear diblock copolymers including at least one linear diblock copolymer selected from hydrogenated styrene/isoprene diblock copolymers, hydrogenated styrene/butadiene diblock copolymers and hydrogenated styrene/isoprene-butadiene diblock copolymers.

Preferably, when the linear diblock copolymer comprises at least one isoprene-butadiene block the block is derived predominantly from 70 to 90 mass % isoprene monomers and 30 to 10 mass % 1,3-butadiene monomers.

The arms of the star polymer typically comprise a copolymer derived from 70 to 90 mass % isoprene monomers and 30 to 10 mass % 1,3-butadiene monomers. More preferably, the arms of the star polymer further include a vinyl aromatic hydrocarbon monomer as defined herein, particularly styrene. A highly preferred copolymer is derived from isoprene monomers, 1,3-butadiene monomers and a vinyl aromatic hydrocarbon monomer, especially styrene. The vinyl aromatic hydrocarbon monomer may be present in an amount of up to 35 mass %, preferably up to 25 mass %, based on the total mass of the copolymer.

Preferably, the arms of the star polymer are formed via anionic polymerization to form a living polymer. Anionic polymerization has been found to provide copolymers having a narrow molecular weight distribution (Mw/Mn), such as a molecular weight distribution of less than about 1.2

As is well known, and disclosed, for example, in U.S. Patent No. 4,116,917, living polymers may be prepared by anionic solution polymerization of a mixture of the conjugated diene monomers in the presence of an alkali metal or an alkali metal hydrocarbon, e.g., sodium naphthalene, as anionic initiator. The preferred initiator is lithium or a monolithium hydrocarbon. Suitable lithium hydrocarbons include unsaturated compounds such as allyl lithium, methallyl lithium; aromatic compounds such as phenyl lithium, the tolyl lithiums, the xylyl lithiums and the naphthyl lithiums, and in particular, the alkyl lithiums such as methyl lithium, ethyl lithium, propyl lithium, butyl lithium, amyl lithium, hexyl lithium, 2-ethylhexyl lithium and n-hexadecyl lithium. Secondary-butyl lithium is the preferred initiator. The initiator(s) may be added to the polymerization mixture in two or more stages, optionally together with additional monomer. The living polymers are olefinically unsaturated.

The solvents in which the living polymers are formed are inert liquid solvents, such as hydrocarbons e.g., aliphatic hydrocarbons such as pentane, hexane, heptane, octane, 2-ethylhexane, nonane, decane, cyclohexane, methylcyclohexane, or aromatic hydrocarbons e.g., benzene, toluene, ethylbenzene, the xylenes, diethylbenzenes, propylbenzenes. Cyclohexane is preferred. Mixtures of hydrocarbons e.g., lubricating oils, may also be used.

The temperature at which the polymerization is conducted may be varied within a wide range, such as from about -50°C to about 150°C, preferably from about 20°C to about 80°C. The reaction is suitably carried out in an inert atmosphere, such as nitrogen, and may optionally be carried out under pressure e.g., a pressure of from about 0.5 to about 10 bars.

The concentration of the initiator used to prepare the living polymer may also vary within a wide range and is determined by the desired molecular weight of the living polymer.

To form the star polymer, the living polymers formed via the foregoing process are reacted in an additional reaction step, with a polyalkenyl coupling agent. Polyalkenyl coupling agents capable of forming star polymers have been known for a number of years and are described, for example, in U.S. Patent No. 3,985,830. Polyalkenyl coupling agents are conventionally compounds having at least two non-conjugated alkenyl groups. Such groups are usually attached to the same or different electron-withdrawing moiety e.g. an aromatic nucleus. Such compounds have the property that at least of the alkenyl groups are capable of independent reaction with different living polymers and in this respect are different from conventional conjugated diene polymerizable monomers such as butadiene, isoprene, etc. Pure or technical grade polyalkenyl coupling agents may be used. Such compounds may be aliphatic, aromatic or heterocyclic. Examples of aliphatic compounds include the polyvinyl and polyallyl acetylene, diacetylenes, phosphates and phosphates as well as dimethacrylates, e.g. ethylene dimethylacrylate. Examples of suitable heterocyclic compounds include divinyl pyridine and divinyl thiophene.

The preferred coupling agents are polyalkenyl aromatic compounds and most preferred are the polyvinyl aromatic compounds. Examples of such compounds include those aromatic compounds, e.g. benzene, toluene, xylene, anthracene, naphthalene and durene, which are substituted with at least two alkenyl groups, preferably attached directly thereto. Specific examples include the polyvinyl benzenes e.g. divinyl, trivinyl and tetravinyl benzenes; divinyl, trivinyl and tetravinyl ortho-, meta- and para-xylenes, divinyl naphthalene, divinyl ethyl benzene, divinyl biphenyl, diisobutenyl benzene, diisopropenyl benzene, and diisopropenyl biphenyl. The preferred aromatic compounds are those represented by the formula A-$(CH{=}CH_2)_x$ wherein A is an optionally substituted aromatic nucleus and x is an integer of at least 2. Divinyl benzene, in particular meta-divinyl benzene, is the most preferred aromatic compound. Pure or technical grade divinyl benzene (containing other monomers e.g. styrene and ethyl styrene) may be used. The coupling agents may be used in admixture with small amounts of added monomers which increase the size of the nucleus, e.g. styrene or alkyl styrene. In such a case, the nucleus can be described as a poly(dialkenyl coupling agent/monoalkenyl aromatic compound) nucleus, e.g. a poly(divinylbenzene/monoalkenyl aromatic compound) nucleus.

The polyalkenyl coupling agent should be added to the living polymer after the polymerization of the monomers is substantially complete, i.e. the agent should be added only after substantially all the monomer has been converted to the living polymers.

The amount of polyalkenyl coupling agent added may vary within a wide range, but preferably, at least 0.5 mole of the coupling agent is used per mole of unsaturated living polymer. Amounts of from about 1 to about 15 moles, preferably from about 1.5 to about 5 moles per mole of living polymer are preferred. The amount, which can be added in two or more stages, is usually an amount sufficient to convert at least about 80 mass % to 85 mass % of the living polymer into star-shaped polymer.

The coupling reaction can be carried out in the same solvent as the living polymerization reaction. The coupling reaction can be carried out at temperatures within a broad range, such as from 0°C to 150°C, preferably from about 20°C to about 120°C. The reaction may be conducted in an inert atmosphere, e.g. nitrogen, and under pressure of from about 0.5 bar to about 10 bars.

The star polymers thus formed are characterized by a dense centre or nucleus of crosslinked poly(polyalkenyl coupling agent) and a number of arms of substantially linear unsaturated polymers extending outwardly from the nucleus. The number of arms may vary considerably, but is typically between about 4 and 25.

The resulting star polymers can then be hydrogenated using any suitable means. A hydrogenation catalyst may be used e.g. a copper or molybdenum compound. Catalysts containing noble metals, or noble metal-containing compounds, can also be used. Preferred hydrogenation catalysts contain a non-noble metal or a non-noble metal-containing compound of Group VIII of the periodic Table i.e., iron, cobalt, and particularly, nickel. Specific examples of preferred hydrogenation catalysts include Raney nickel and nickel on kieselguhr. Particularly suitable hydrogenation catalysts are those obtained by causing metal hydrocarbyl compounds to react with organic compounds of any one of the group VIII metals iron, cobalt or nickel, the latter compounds containing at least one organic compound that is attached to the metal atom via an oxygen atom as described, for example, in U.K. Patent No. 1,030,306. Preference is given to hydrogenation catalysts obtained by causing an aluminium trialkyl (e.g. aluminium diethyl ($Al(Et_3)$) or aluminium triisobutyl) to react with a nickel salt of an organic acid (e.g. nickel diisopropyl salicylate, nickel naphthenate, nickel 2-ethyl hexanoate, nickel di-tert-butyl benzoate, nickel salts of saturated monocarboxylic acids obtained by reaction of olefins having from 4 to 20 carbon atoms in the molecule with carbon monoxide and water in the presence of acid catalysts) or with nickel enolates or phenolates (e.g., nickel acetonylacetonate, the nickel salt of butylacetophenone). Suitable hydrogenation catalysts will be well known to those skilled in the art and the foregoing list is by no means intended to be exhaustive.

The hydrogenation of the star polymer is suitably conducted in solution, in a solvent which is inert during the hydrogenation reaction. Saturated hydrocarbons and mixtures of saturated hydrocarbons are suitable. Advantageously, the hydrogenation solvent is the same as the solvent in which polymerization is conducted. Suitably, at least 50%, preferably at least 70%, more preferably at least 90%, most preferably at least 95% by mass of the original olefinic unsaturation is hydrogenated.

The hydrogenated star polymer may then be recovered in solid form from the solvent in which it is hydrogenated by any convenient means, such as by evaporating the solvent. Alternatively, oil e.g. lubricating oil, may be added to the solution, and the solvent stripped off from the mixture so formed to provide a concentrate. Suitable concentrates contain from about 3 mass % to about 25 mass %, preferably from about 5 mass % to about 15 mass % of the hydrogenated star polymer VI improver.

The star polymers useful in the practice of the present invention can have a number average molecular weight of from about 10,000 to 700,000, preferably from about 30,000 to 500,000. The term "number average molecular weight", as used herein, refers to the number average weight as measured by Gel Permeation Chromatography ("GPC") with a polystyrene standard, subsequent to hydrogenation. It is important to note that, when determining the number average molecular weight of a star polymer using this method, the calculated number average molecular weight will be less than the actual molecular weight due to the three dimensional structure of the star polymer.

In one preferred embodiment, the star polymer of the present invention is derived from about 75 % to about 90 % by mass isoprene and about 10 % to about 25 % by mass butadiene, and greater than 80 % by mass of the butadiene units are incorporated 1,4-addition product. In another preferred embodiment, the star polymer of the present invention comprises amorphous butadiene units derived from about 30 to about 80 % by mass 1,2-, and from about 20 to about 70 % by mass 1,4-incorporation of butadiene. In another preferred embodiment, the star polymer is derived from isoprene, butadiene, or a mixture thereof, and further contains from about 5 to about 35 % by mass styrene units.

Typically, the star polymer has a Shear Stability Index (SSI) of from about 1 % to 35 % (30 cycle). An example of a commercially available star polymer VI improver having an SSI equal to or less than 35 is Infineum SV200™, available from Infineum USA L.P. and Infineum UK Ltd. Other examples of commercially available star polymer VI improver having an SSI equal to or less than 35 include Infineum SV250™, Infineum SV261™ and Infineum SV270™, also available from Infineum USA L.P. and Infineum UK Ltd.

Typically, the viscosity index improver may be provided in an amount of from 0.01 to 20, preferably 1 to 15, mass % based on the mass of the lubricating oil composition.

Optionally, one or both types of VI improvers used in the practice of the invention can be provided with nitrogen-containing functional groups that impart dispersant capabilities to the VI improver. One trend in the industry has been to use such "multifunctional" VI improvers in lubricants to replace some or all of the dispersant. Nitrogen-containing functional groups can be added to a polymeric VI improver by grafting a nitrogen- or hydroxyl- containing moiety, preferably a nitrogen-containing moiety, onto the polymeric backbone of the VI improver (functionalizing). Processes for the grafting of a nitrogen-containing moiety onto a polymer are known in the art and include, for example, contacting the polymer and nitrogen-containing moiety in the presence of a free radical initiator, either neat, or in the presence of a solvent. The free radical initiator may be generated by shearing (as in an extruder) or heating a free radical initiator precursor, such as hydrogen peroxide.

The amount of nitrogen-containing grafting monomer will depend, to some extent, on the nature of the substrate polymer and the level of dispersancy required of the grafted polymer. To impart dispersancy characteristics to both star and linear copolymers, the amount of grafted nitrogen-containing monomer is suitably between about 0.4 and about 2.2 mass %, preferably from about 0.5 to about 1.8 mass %, most preferably from about 0.6 to about 1.2 mass %, based on the total weight of grafted polymer.

Methods for grafting nitrogen-containing monomer onto polymer backbones, and suitable nitrogen-containing grafting monomers are known and described, for example, in U.S. Patent No. 5,141,996, WO 98/13443, WO 99/21902, U.S. Patent No. 4,146,489, U.S. Patent No. 4,292,414, and U.S. Patent No. 4,506,056. (See also *J Polymer Science*, Part A: Polymer Chemistry, Vol. 26, 1189-1198 (1988); *J. Polymer Science*, Polymer Letters, Vol. 20, 481-486 (1982) and *J. Polymer Science*, Polymer Letters, Vol. 21, 23-30 (1983), all to Gaylord and Mehta and Degradation and Cross-linking of Ethylene-Propylene Copolymer Rubber on Reaction with Maleic Anhydride and/or Peroxides; *J. Applied Polymer Science*, Vol. 33, 2549-2558 (1987) to Gaylord, Mehta and Mehta.

ENGINES

The lubricating oil compositions of the invention may be used to lubricate mechanical engine components, particularly in internal combustion engines, e.g. spark-ignited or compression-ignited two- or four- stroke reciprocating engines, by adding the composition thereto. The engines may be conventional gasoline or diesel engines designed to be powered by gasoline or petroleum diesel, respectively; alternatively, the engines may be specifically modified to be powered by an alcohol based fuel or biodiesel fuel. Preferably, the lubricating oil compositions are crankcase lubricants.

Preferably, the lubricating oil composition is for use in the lubrication of a compression-ignited internal combustion engine (diesel engine), especially a compression-ignited internal combustion engine which is fuelled at least in part with a biodiesel fuel. Such engines include passenger car diesel engines and heavy duty diesel engines, for example engines found in road trucks. More preferably, the lubricating oil composition is for use in the lubrication of a passenger car compression-ignited internal combustion engine (i.e. a light duty diesel engine), which is fuelled at least in part with a biodiesel fuel, especially such an engine which employs a late post-injection of fuel into the cylinder. More preferably, the lubricating oil composition is for use in the lubrication of the crankcase of the aforementioned engines.

When the lubricating oil composition, such as a crankcase lubricant, is used in the lubrication of a spark-ignited or compression-ignited internal combustion engine which is fuelled at least in part with a biofuel, the lubricant during operation of the engine becomes contaminated with biofuel and decomposition products thereof. Thus according to a preferred aspect of the present invention, the lubricating oil composition of the present invention comprises at least 0.3, preferably at least 0.5, more preferably at least 1, even more preferably at least 5, even more preferably at least 10, even more preferably at least 15, even more preferably at least 20, mass % of biofuel and/or a decomposition product thereof. Although the lubricating oil composition may comprise up to 50 mass % of biofuel and/or a decomposition product thereof, preferably it includes less than 35, more preferably less than 30, mass % of biofuel and/or a decomposition product thereof.

The biofuel comprises an alcohol based fuel in the case of spark-ignited internal combustion engines, preferably a bioalcohol fuel, especially bioethanol fuel.

The biofuel comprises biodiesel in the case of compression ignited internal combustion engines.

BIOFUELS

Biofuels include fuels that are produced from renewable biological resources and include biodiesel fuel as defined herein and bioethanol fuel which may be derived from fermented sugar. The term biofuel also embraces an "alcohol based fuel", such as "ethanol based fuel", irrespective of the source of the alcohol (i.e. the alcohol may be derived from a renewable biological source or a non-renewable source, such as petroleum).

Alcohol Based Fuels

Alcohol based fuels are employed in spark-ignited internal combustion engines. The alcohol based fuel may include one or more alcohols selected from methanol, ethanol, propanol and butanol. The alcohol may be derived from a renewable biological source or a non-renewable source, such as petroleum. The alcohol based fuel may comprise 100 % by volume of one or more alcohols (i.e. pure alcohol). Alternatively the alcohol based fuel may comprise a blend of an alcohol and petroleum gasoline; suitable blends include 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70, 80, 85, and 90, vol.% of the alcohol, based on the total volume of the alcohol and gasoline blend.

Preferably, the alcohol based fuel comprises an ethanol based fuel. More preferably, the alcohol based fuel comprises a bioalcohol fuel, especially a bioethanol fuel.

The bioethanol fuel comprises ethanol derived from a renewable biological source (i.e. bioethanol), preferably ethanol derived solely from a renewable biological source. The bioethanol may be derived from the sugar fermentation of crops such as corn, maize, wheat, cord grass and sorghum plants. The bioethanol fuel may comprise 100% by volume bioethanol (designated as E100); alternatively, the bioethanol fuel may comprise a blend of bioethanol and petroleum gasoline. The bioethanol fuel blend may have the designation "Exx" wherein xx refers to the amount of E100 bioethanol in vol.%, based on the total volume of the bioethanol fuel blend. For example, E10 refers to a bioethanol fuel blend which comprises 10 volume % E100 bioethanol fuel and 90 volume % of petroleum gasoline. For the avoidance of doubt, the term "bioethanol fuel" includes pure bioethanol fuel (i.e. E100) and bioethanol fuel blends comprising a mixture of bioethanol fuel and petroleum gasoline fuel.

Typically, the bioethanol fuel comprises E100, E95, E90, E85, E80, E75, E70, E65, E60, E55, E50, E45, E40, E35, E30, E25, E20, E15, E10, E8, E6 or E5. Highly preferred blends include E85 (ASTM D5798 (USA)), E10 (ASTM D4806 (USA)) and E5 (EN 228:2004 (Europe)).

Biodiesel Fuels

The biodiesel fuel comprises at least one alkyl ester, typically a mono-alkyl ester, of a long chain fatty acid derivable from vegetable oils or animal fats. Preferably, the biodiesel fuel comprises one or more methyl or ethyl esters of such long chain fatty acids, especially one or more methyl esters.

The long chain fatty acids typically comprise long chains which include carbon, hydrogen and oxygen atoms. Preferably, the long chain fatty acids include from 10 to 30, more preferably 14 to 26, most preferably 16 to 22, carbon atoms. Highly preferred fatty acids include palmitic acid, stearic acid, oleic acid and linoleic acid.

The biodiesel fuel may be derived from the esterification or transesterification of one or more vegetable oils and animal fats, such as corn oil, cashew oil, oat oil, lupine oil, kenaf oil, calendula oil, cotton oil, hemp oil, soybean oil, linseed oil, hazelnut oil, euphorbia oil, pumpkin seed oil, palm oil, rapeseed oil, olive oil, tallow oil, sunflower oil, rice oil, sesame oil or algae oil. Preferred vegetable oils include palm oil, rapeseed oil and soybean oil.

Generally, a pure biodiesel fuel that meets the ASTM D6751-08 standard (USA) or EN 14214 standard (European) specifications is designated as B100. A pure biodiesel fuel may be mixed with a petroleum diesel fuel to form a biodiesel blend which may reduce emissions and improve engine performance. Such biodiesel blends are given a designation "Bxx" where xx refers to the amount of the B100 biodiesel in volume %, based on the total volume of the biodiesel blend. For example, B10 refers to a biodiesel blend which comprises 10 volume % B100 biodiesel fuel and 90 volume % of petroleum diesel fuel. For the avoidance of doubt, the term "biodiesel fuel" includes pure biodiesel fuel (i.e. B100) and biodiesel fuel blends comprising a mixture of biodiesel fuel and petroleum diesel fuel.

Typically, the biodiesel fuel comprises a B100, B95, B90, B85, B80, B75, B70, B65, B60, B55, B50, B45, B40, B35, B30, B25, B20, B15, B10, B8, B6, B5, B4, B3, B2 or

B1. Preferably, the biodiesel fuel comprises a B50 designation or lower, more preferably a B5 to B40, even more preferably B5 to B40, most preferably B5 to B20.

CO-ADDITIVES

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

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

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

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

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

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

Dispersants are usually "ashless", as mentioned above, being non-metallic organic materials that form substantially no ash on combustion, in contrast to metal-containing, and hence ash-forming materials. They comprise a long hydrocarbon chain with a polar head, the polarity being derived from inclusion of e.g. an O, P, or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric backbone.

A preferred class of olefin polymers is constituted by polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C_4 refinery stream.

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

Preferably, the lubricating oil composition includes an oil-soluble boron containing compound, especially a borated dispersant. Preferably, the borated dispersant comprises an ashless nitrogen containing borated dispersant, such as a borated polyalkenyl succinimide, especially a borated polyisobutenyl succinimide.

A detergent is an additive that reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines; it normally has acid-neutralising properties and is capable of keeping finely divided solids in suspension. Most detergents are based on metal “soaps”, that is metal salts of acidic organic compounds.

Detergents generally comprise a polar head with a long hydrophobic tail, the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal when they are usually described as normal or neutral salts and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. Large amounts of a metal base can be included by reaction of an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralised detergent as an outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically of from 250 to 500 or more.

Detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates, and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g. sodium, potassium, lithium, calcium and magnesium. The most commonly-used metals are calcium and magnesium, which may both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium.

Particularly preferred metal detergents are neutral and overbased alkali or alkaline earth metal salicylates having a TBN of from 50 to 450, preferably a TBN of 50 to 250. Highly preferred salicylate detergents include alkaline earth metal salicylates, particularly magnesium and calcium, especially, calcium salicylates. Preferably, the alkali or alkaline earth metal salicylate detergent is the sole detergent in the lubricating oil composition.

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

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

One class of preferred organo-molybdenum compounds useful in all aspects of the present invention is tri-nuclear molybdenum compounds of the formula $Mo_3S_kL_nQ_z$ and mixtures thereof wherein L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compounds soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through to 7, Q is selected from the group of neutral electron donating compounds such as water, amines, alcohols, phosphines, and ethers, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligands' organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

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

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

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

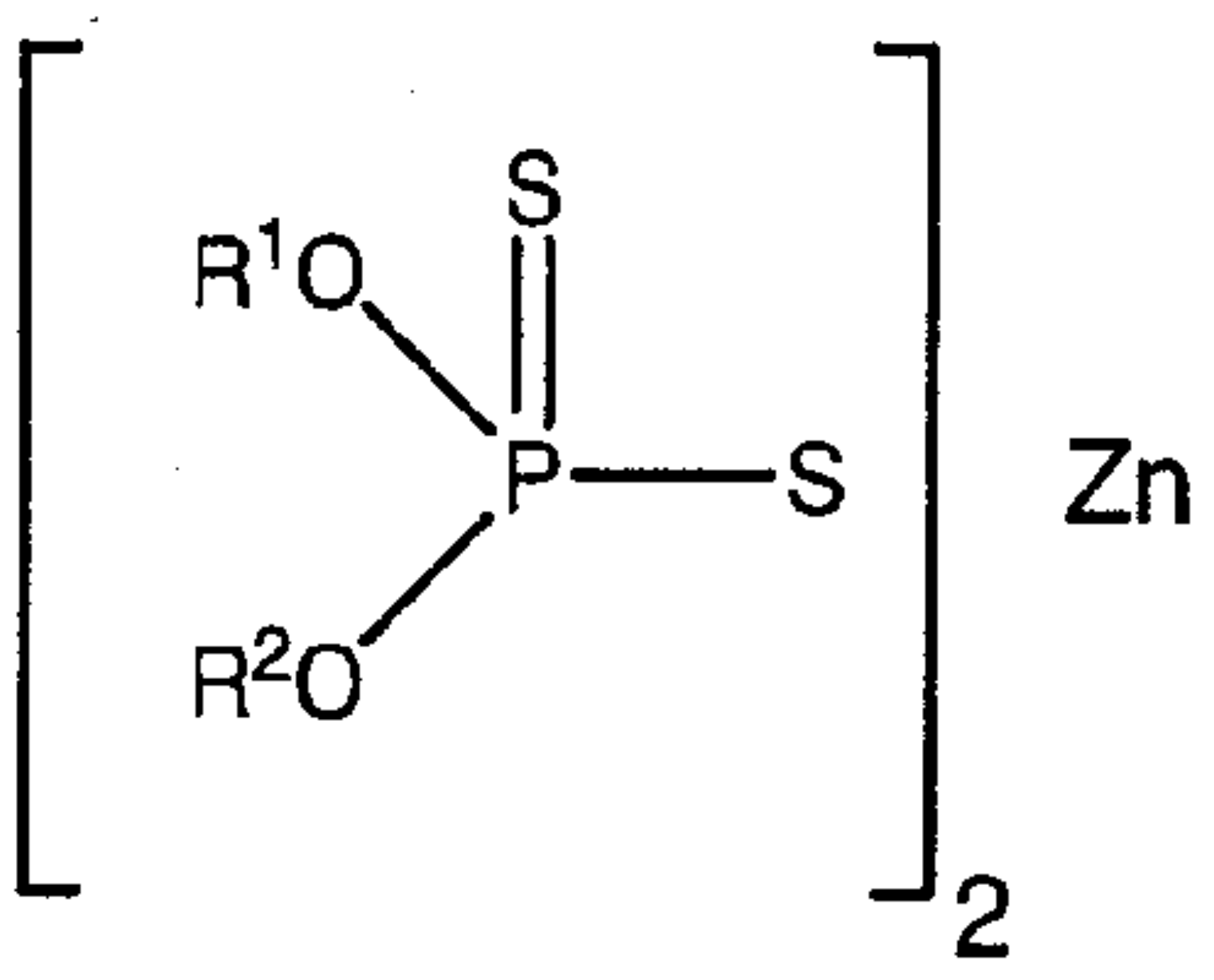
They may be classified as radical scavengers (e.g. sterically hindered phenols, secondary aromatic amines, and organo-copper salts); hydroperoxide decomposers (e.g., organosulfur and organophosphorus additives); and multifunctionals (e.g. zinc dihydrocarbyl dithiophosphates, which may also function as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

Examples of suitable antioxidants are selected from copper-containing antioxidants, sulfur-containing antioxidants, aromatic amine-containing antioxidants, hindered phenolic antioxidants, dithiophosphates derivatives, metal thiocarbamates, and molybdenum-containing compounds. Preferred anti-oxidants are aromatic amine-containing antioxidants, molybdenum-containing compounds and mixtures thereof, particularly aromatic amine-containing antioxidants. Preferably, an antioxidant is present in the lubricating oil composition.

Anti-wear agents reduce friction and excessive wear and are usually based on compounds containing sulfur or phosphorous or both, for example that are capable of depositing polysulfide films on the surfaces involved. Noteworthy are dihydrocarbyl dithiophosphate metal salts wherein the metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel, copper, or preferably, zinc.

Dihydrocarbyl dithiophosphate metal salts may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with P_2S_5 and then neutralizing the formed DDPA with a metal 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 metal salt, any basic or neutral metal compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of metal due to the use of an excess of the basic metal compound in the neutralization reaction.

The preferred dihydrocarbyl dithiophosphate metal salts are zinc dihydrocarbyl dithiophosphates (ZDDP) which are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:



wherein R^1 and R^2 may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and include radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R^1 and R^2 groups are alkyl groups of 2 to 8 carbon atoms, especially primary alkyl groups (i.e. R^1 and R^2 are derived from predominantly primary alcohols). Thus, the radicals may, for example, be ethyl, n-propyl, i-propyl, n-butyl, iso-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylhexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R^1 and R^2) in the dithiophosphoric acid will generally be about 5 or greater. Preferably, the zinc dihydrocarbyl dithiophosphate comprises a zinc dialkyl dithiophosphate.

Preferably, the lubricating oil composition contains an amount of dihydrocarbyl dithiophosphate metal salt that introduces 0.02 to 0.10 mass %, preferably 0.02 to 0.09 mass%, preferably 0.02 to 0.08 mass %, more preferably 0.02 to 0.06 mass % of phosphorus into the composition.

To limit the amount of phosphorus introduced into the lubricating oil composition to no more than 0.10 mass %, the dihydrocarbyl dithiophosphate metal salt should preferably be added to the lubricating oil compositions in amounts no greater than from 1.1 to 1.3 mass % (a.i.), based upon the total mass of the lubricating oil composition.

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

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

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

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

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

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

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

The additives may be incorporated into an oil of lubricating viscosity (also known as a base oil) in any convenient way. Thus, each additive can be added directly to the oil by dispersing or dissolving it in the oil at the desired level of concentration. Such blending may occur at ambient temperature or at an elevated temperature. Typically an additive is available as an admixture with a base oil so that the handling thereof is easier.

When a plurality of additives are employed it may be desirable, although not essential, to prepare one or more additive packages (also known as additive compositions or concentrates) comprising additives and a diluent, which can be a base oil, whereby the additives, with the exception of viscosity modifiers, multifuntional viscosity modifiers and pour point depressants, can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive package(s) into the oil of lubricating viscosity may be facilitated by diluent or solvents and by mixing accompanied with mild heating, but this is not essential. The additive package(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration in the final formulation when the additive package(s) is/are combined with a predetermined amount of oil of lubricating viscosity. Thus, one or more detergents may be added to small amounts of base oil or other compatible solvents (such as a carrier oil or diluent oil) together with other desirable additives to form additive packages containing from 2.5 to 90, preferably from 5 to 75, most preferably from 8 to 60, mass %, based on the mass of the additive package, of additives on an active ingredient basis in the appropriate proportions. The final formulations may typically contain 5 to 40 mass % of the additive package(s), the remainder being oil of lubricating viscosity.

EXAMPLES

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

Oxidative Stability: Hot Surface Oxidation Test

Oxidative stability is measured using the Hot Surface Oxidation Test which determines the Oxidation Induction Time (OIT) of a lubricating oil composition by Pressure Differential Scanning Calorimetry (PDSC).

A measured sample (3 mg) of a lubricating oil composition is placed in a test cell of a Pressure Differential Scanning Calorimeter (Netzsch 204 HPDSC) and the cell pressurised to 100 psi with clean dry air. The cell is then heated at a rate of 40°C per minute until the isothermal test temperature of 210°C is attained and the sample maintained at this temperature for a maximum of 240 minutes. The calorimeter provides a value of the OIT i.e. the time taken for the sample to oxidise; a larger OIT indicates the sample is more stable to oxidation than a sample having a smaller OIT.

Unless otherwise specified, all of the additives described in the Examples are available as standard additives from lubricant additive companies such as Infineum UK Ltd, Lubrizol Corporation and Afton Chemicals Corporation, for example.

Examples

A series of 5W-30 multigrade lubricating oil compositions (0.08% P), as detailed in Table 1, were prepared by admixing a Group III base stock with known additives including an overbased calcium sulphonate detergent (TBN 310), an overbased calcium phenate detergent (TBN 150), a non-borated polyisobutylene derived dispersant, ZDDP and an aminic antioxidant. Comparative Lubricant 1 also included an ethylene-propylene copolymer viscosity index improver (LZ-7077^{TM} available from Lubrizol), Lubricant 1 of the invention included an isopropene-butadiene-styrene copolymer star polymer viscosity index improver (Infineum SV261^{TM} available from Infineum UK Ltd) and Lubricant 2 of the invention included an isoprene-styrene block copolymer viscosity index improver (Infineum SV151^{TM} available from Infineum UK Ltd). The oxidation induction times for each of the lubricants was determined in: (a) the absence of biodiesel fuel; and, (b) in the presence of 10 % B50 biodiesel fuel. The results are also detailed in Table 1.

The results illustrate that each of the lubricants demonstrated comparable oxidation performance in the absence of biodiesel fuel, irrespective of the type of viscosity index improver used in the lubricating oil composition. However, in the presence of biodiesel fuel, the oxidation control is significantly greater for a lubricant that includes a viscosity index improver derived from the polymerisation of one or more conjugated diene monomers (Lubricants 1 and 2 of the invention) compared with an ethylene-propylene copolymer viscosity index improver; the performance difference between the two types of viscosity index improver technologies being approximately 15 %. As expected, the oxidation control for all lubricants fell in the presence of biodiesel fuel compared to the absence of biodiesel fuel.

Table 1

	Comparative Lubricant 1 (mass %)	Comparative Lubricant 1 (mass %)	Lubricant 1 (mass %)	Lubricant 1 (mass %)	Lubricant 2 (mass %)	Lubricant 2 (mass %)
Dispersant	5.50	5.50	5.50	5.50	5.50	5.50
Calcium sulphonate detergent (TBN 310)	0.90	0.90	0.90	0.90	0.90	0.90
Calcium phenate detergent (TBN 150)	2.00	2.00	2.00	2.00	2.00	2.00
Antioxidant	1.00	1.00	1.00	1.00	1.00	1.00
ZDDP	1.0	1.0	1.0	1.0	1.0	1.0
Viscosity modifier Concentrate (LZ-7077)	13.0 (a.i. 6.60)	13.0 (a.i. 6.60)	-	-	-	-
Viscosity modifier Concentrate (SV-261)	-	-	10.7 (a.i. 5.50)	10.7 (a.i. 5.50)	-	-
Viscosity modifier Concentrate (SV-151)	-	-	-	-	15.00 (a.i. 6.0)	15.00 (a.i. 6.0)
B50 Biodiesel	0	10	0	10	0	10
Group III base stock	balance	balance	balance	balance	balance	balance
Oxidation Induction Time (mins)	101.2	67.6	104.5	79.7	108.3	79.9

CLAIMS:

1. A use, for lubricating a compression-ignited internal combustion engine, that is fuelled with biodiesel, of an oil-soluble or oil-dispersible viscosity index improver (B) comprising a linear or star-shaped polymer which is derived from the polymerisation of one or more conjugated diene monomers, as an additive component in a minor amount of from 0.01 to 20 mass % based on the mass of the lubricating oil composition, in a lubricating oil composition, to reduce and/or inhibit oxidation of the lubricating oil composition during operation of the engine, wherein the lubricating oil composition comprises an oil of lubricating viscosity, in a major amount in excess of 50 mass % of the lubricating oil composition, which comprises a Group III base stock, and wherein the lubricating oil composition becomes contaminated with biodiesel during operation of the engine.

2. Use as claimed in claim 1, wherein the one or more conjugated diene monomer(s) is 1,3-butadiene, isoprene, or mixtures thereof.

3. Use as claimed in claim 1 or 2, wherein the viscosity index improver is at least one star-shaped, at least partially hydrogenated, polymer.

4. Use as claimed in claim 3, wherein the star-shaped, at least partially hydrogenated, polymer includes multiple arms extending from a central core, said arms being a homopolymer derived from a single said conjugated diene monomer, or comprising a copolymer derived from two or more of said conjugated diene monomers, or comprising a copolymer derived from one or more of said conjugated diene monomers and from a vinyl aromatic hydrocarbon monomer.

5. Use as claimed in claim 4, wherein said arms of the star-shaped, at least partially hydrogenated, polymer comprise a hydrogenated isoprene-butadiene copolymer.

6. Use as claimed in claim 4, wherein said arms of the star-shaped, at least partially hydrogenated, polymer comprise a hydrogenated styrene-isoprene-butadiene copolymer, a hydrogenated isoprene-styrene copolymer or a hydrogenated butadiene-styrene copolymer.

7. Use as claimed in claim 6, wherein the copolymer of said arms includes up to 35 mass % of the styrene monomer.

8. Use as claimed in claim 7, wherein the copolymer of said arms includes up to 25 mass % of the styrene monomer.

9. Use as claimed in claim 4, wherein said arms of the star-shaped, at least partially hydrogenated, polymer comprise a linear diblock copolymer having at least one block derived predominantly from a vinyl aromatic hydrocarbon monomer and at least one block derived predominantly from one or more of said conjugated diene monomers and said linear diblock copolymer is at least partially hydrogenated.

10. Use as claimed in claim 9, wherein the linear diblock copolymer comprises at least a polystyrene block and a block derived from isoprene, butadiene or a mixture thereof and said linear diblock copolymer is at least partially hydrogenated.

11. Use as claimed in claim 10, wherein the linear diblock copolymer is selected from the group consisting of hydrogenated styrene/butadiene diblock copolymers, hydrogenated styrene/isoprene diblock copolymers and hydrogenated styrene/isoprene-butadiene diblock copolymers.

12. Use as claimed in claim 11, wherein the linear diblock copolymer is a hydrogenated styrene/isoprene-butadiene diblock copolymer.

13. Use as claimed in claim 4, wherein the arms of the star-shaped, at least partially hydrogenated, polymer are a homopolymer derived from isoprene monomers.

14. Use as claimed in any one of claims 4 to 13, wherein the core of the star-shaped, at least partially hydrogenated, polymer is derived from a polyolefinic linking agent.

15. Use as claimed in claim 1 or 2, wherein the viscosity index improver is a linear diblock copolymer comprising at least one block derived predominantly from a vinyl aromatic hydrocarbon monomer and at least one block derived predominantly from said one or more conjugated diene monomers.

16. Use as claimed in claim 15, wherein the linear diblock copolymer comprises at least a polystyrene block and a block derived from isoprene, butadiene or a mixture thereof.

17. Use as claimed in claim 16, wherein the linear diblock copolymer is selected from the group consisting of hydrogenated styrene/butadiene diblock copolymers and hydrogenated styrene/isoprene diblock copolymers.

18. Use as claimed in any one of claims 1 to 17, wherein the lubricating oil composition is contaminated with at least 0.3 mass % of biodiesel, based on the total mass of the lubricating oil composition.

19. Use as claimed in any one of claims 1 to 18, wherein the lubricating oil composition further comprises one or more co-additives in a minor amount of less than 50 mass % of the lubricating oil composition, other than the oil-soluble or oil-dispersible viscosity index improver additive component (B) as defined in any one of claims 1 to 18, selected from the group consisting of ashless dispersants, metal detergents, corrosion inhibitors, antioxidants, pour point depressants, antiwear agents, friction modifiers, demulsifiers, antifoam agents and viscosity modifiers.