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(54) Titre : COMPOSITION LUBRIFIANTE D'UNE CARACTERISTIQUE DE VISCOSITE AMELIOREE A BASSE TEMPERATURE DE FONCTIONNEMENT

(54) Title: LUBRICANT COMPOSITION WITH AN IMPROVED VISCOSITY CHARACTERISTIC AT LOW OPERATING TEMPERATURE

(57) Abrégé/Abstract:
The invention relates to a lubricant composition comprising a comb polymer and a synthetic base oil. The lubricant composition has improved viscosity characteristics at low operating temperatures. The invention also relates to the use of a comb polymer for producing a lubricant having an R-factor of less than or equal to 8, wherein the R-factor is defined as the ratio of the kinematic viscosity at -20°C and the kinematic viscosity at +20°C.

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(54) Title: LUBRICANT COMPOSITION WITH AN IMPROVED VISCOSITY CHARACTERISTIC AT LOW OPERATING TEMPERATURE

(57) Abstract: The invention relates to a lubricant composition comprising a comb polymer and a synthetic base oil. The lubricant composition has improved viscosity characteristics at low operating temperatures. The invention also relates to the use of a comb polymer for producing a lubricant having an R-factor of less than or equal to 8, wherein the R-factor is defined as the ratio of the kinematic viscosity at -20°C and the kinematic viscosity at +20°C.

Lubricant composition with an improved viscosity characteristic at low operating temperature

The invention relates to lubricant compositions for use in industrial applications having improved low temperature viscosity characteristics.

Lubricants for use in industrial applications typically comprise a base oil, such as a mineral oil or synthetic oil, and one or more additives. Additives deliver, for example, reduced friction and wear, increased viscosity, improved viscosity index, and resistance to corrosion, oxidation, aging or contamination.

The ability of a lubricant to reduce friction is dependent on its viscosity. Generally, the least viscous fluid, which still forces two moving surfaces apart, is desired. Many lubricant applications require good lubricant properties over a broad temperature range, for example, when the engine is cold as well as when it has reached its operating temperature. Therefore, a lubricant's viscosity should change as little as possible with temperature, to provide constant lubricant properties over a broad temperature range.

The temperature-dependence of a lubricant's viscosity is measured by the viscosity index (VI). The higher the viscosity index, the smaller is the relative change in viscosity with temperature. The viscosity index is determined from the kinematic viscosity at 40°C (KV_{40}) and the kinematic viscosity at 100°C (KV_{100}), which is a good reflection of most engines' operating conditions. Additives which increase the viscosity index are referred to as viscosity index improvers (VIIs).

Polymers of alkyl (meth)acrylates, and especially polyalkyl(meth)acrylate based comb polymers, are known in the art to act as good viscosity index improvers in lubricant oils.

US patents 5,565,130 and 5,597,871, for example, disclose using comb polymers comprising polybutadiene-derived macromonomers as viscosity index improvers. Low temperature properties are not disclosed therein.

WO 2007/003238 A1 describes oil-soluble comb polymers based on polyolefin-based macromonomers, especially polybutadiene-based methacrylic esters, and C1-C10 alkyl

methacrylates. The comb polymers can be used as an additive for lubricant oils, in order to improve the viscosity index and shear stability. They show a particularly high viscosity index-improving action in lubricant oils. Low temperature properties are not disclosed therein.

The viscosity index, however, does not properly reflect the lubricant's properties at temperatures lower than 40°C, for instance at a low temperature range of -20°C to +20°C. A lubricant having good lubricant properties at the operating temperature of a machine or an engine, therefore, does not necessarily have equally good properties during the engine's cold-start phase. The cold-start properties of a lubricant are, however, an important factor contributing to an improved fuel efficiency of engines.

The low-temperature properties of lubricants can be measured by the R-factor, which is defined as the ratio of the kinematic viscosity at -20°C to the kinematic viscosity at +20°C. Since the kinematic viscosity at -20°C is generally higher than at +20°C, the R-factor is generally greater than 1. Thus, a narrow viscosity difference between -20°C and +20°C is reflected by a low R-factor (an R-factor close to 1).

The problem of providing lubricant compositions having good viscosity properties at low operating temperatures has not been sufficiently addressed in the prior art. Mostly, the prior art reports the VI measured between 40°C and 100°C, but gives no indication of the viscosity characteristics at, for example, -20°C to +20°C.

Therefore, the aim of the present invention is to provide a lubricant composition with good low temperature viscosity properties. In particular, the difference of the kinematic viscosity of the lubricant composition at -20°C and +20°C should be small. The present invention further aims at providing an additive for a lubricant composition for lowering the difference between the kinematic viscosity at -20°C and +20°C.

It has been found that the use of certain comb polymers as additives for lubricant compositions results in a surprisingly low R-factor that cannot be achieved by using conventional viscosity index improvers. It has also been found that lubricant compositions comprising a synthetic base oil and the special comb polymers exhibit surprisingly good low-temperature viscosity characteristics, in particular a surprisingly good R-factor.

The present invention is therefore directed to a lubricant composition, comprising:

(A) a synthetic base oil; and

(B) a comb polymer, comprising the following monomers:

(a) an ester of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene; and

(b) 0.2% by weight to 15% by weight of styrene, based on the total weight of the comb polymer,

wherein the lubricant composition is characterized by an R-factor of 8 or less, the R-factor being the ratio of the kinematic viscosity at -20°C to the kinematic viscosity at +20°C.

The lubricant composition is preferably defined by an R-factor of less than or equal to 8, wherein the R-factor is defined as the ratio of the kinematic viscosity of the lubricant composition at -20°C (KV_{-20}) to the kinematic viscosity at +20°C (KV_{+20}), KV_{-20}/KV_{+20}, the kinematic viscosities are measured according to ASTM D445.
Preferably, the lubricant composition has an R-factor of 1 to 8.

The composition is preferably formulated to yield a certain kinematic viscosity at 40°C according to ASTM D445. This can be achieved by adjusting the relative amounts of comb polymer, base oil and optional additives. Preferably, the composition has a kinematic viscosity at 40°C according to ASTM D445 of 10 to 120 mm^2/s, more preferably 40 to 100 mm^2/s, most preferably 70 to 80 mm^2/s.

In a preferred embodiment, the lubricant composition comprises:

(A) 20 to 90% by weight, preferably 30 to 80% by weight, most preferably 35 to 80% by weight of the synthetic base oil and

(B) 10 to 80% by weight, preferably 20 to 70% by weight, most preferably 20 to 65% by weight of the comb polymer,

based on the total weight of the lubricant composition.

Suitable synthetic base oils are selected from API Group IV oils. Particularly preferred are polyalphaolefins (PAOs).

The synthetic base oil is typically characterized by its kinematic viscosity, i.e. the kinematic viscosity of the pure base oil without any additives. Preferably, the synthetic base oil has a kinematic viscosity at 100°C according to ASTM D445 of 1 mm^2/s to 20 mm^2/s, more preferably 1 to 10 mm^2/s, most preferably 1 to 5 mm^2/s and especially preferred 2 to 3 mm^2/s.

In one embodiment, the synthetic base oil is a polyalphaolefin having a kinematic viscosity at 100°C according to ASTM D445 of 1 mm^2/s to 20 mm^2/s, more preferably 1 to 10 mm^2/s, most preferably 1 to 5 mm^2/s and especially preferred 2 to 3 mm^2/s.

A comb polymer in the context of this invention comprises a first polymer, which is also referred to as backbone or main chain, and a multitude of further polymers which are referred to as side chains and are bonded covalently to the backbone. In the present case, the backbone of the comb polymer is formed by the interlinked unsaturated groups of the mentioned (meth)acrylates. The ester groups of the (meth)acrylic esters, the phenyl radicals of the styrene monomers and the substituents of further free-radically polymerizable comonomers form the side chains of the comb polymer. The term "main chain" does not necessarily mean that the chain length of the main chain is greater than that of the side chains.

One important aspect of the invention is the amount of styrene in the comb polymer. In the context of the present invention, the amount of monomers, such as styrene, is given in percent by weight based on the total weight of the monomer mixture. Here, the term "total weight of the monomer mixture" refers to the total weight of the monomers, excluding any additives, such as polymerization initiators, polymerization promotors, chain transfer agents and diluents, which might be added to the monomer mixture to facilitate polymerization. Provided that all the different monomers present in the monomer mixture are equally well incorporated into the copolymer, the relative amounts of monomers in the monomer mixture correspond to the relative amounts of the corresponding monomer units in the copolymer.

In one embodiment, the comb polymer (B) comprises:

(a) at least 20% by weight of esters of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene,

(b) 0.2% by weight to 15% by weight of styrene, and

(c) optionally further comonomers,

based on the total weight of the comb polymer.

The hydroxylated hydrogenated polybutadiene for use in accordance with the invention has a number-average molar mass M_n of 4.000 to 6.000 g/mol, preferably 4.000 to 5.000 g/mol. Because of their high molar mass, the hydroxylated hydrogenated polybutadienes can also be referred to as macroalcohols in the context of this invention.

The number-average weight M_n is determined by size exclusion chromatography using commercially available polybutadiene standards. The determination is effected to DIN 55672-1 by gel permeation chromatography with THF as eluent.

Preferably, the hydroxylated hydrogenated polybutadiene has a hydrogenation level of at least 99%. An alternative measure of the hydrogenation level which can be determined on the copolymer of the invention is the iodine number. The iodine number refers to the number of grams of iodine which can be added onto 100 g of copolymer. Preferably, the copolymer of the invention has an iodine number of not more than 5 g of iodine per 100 g of copolymer. The iodine number is determined by the Wijs method according to DIN 53241-1:1995-05.

Preferred hydroxylated hydrogenated polybutadienes can be obtained according to GB 2270317.

Some hydroxylated hydrogenated polybutadienes are also commercially available. The commercially hydroxylated hydrogenated polybutadienes include, for example, Kraton Liquid® L-1203, a hydrogenated polybutadiene OH-functionalized to an extent of about 98% by weight (also called olefin copolymer OCP) having about 50% each of 1,2 repeat units and 1,4 repeat units, of M_n = 4200 g/mol, from Kraton Polymers GmbH (Eschborn, Germany). A further supplier of suitable alcohols based on hydrogenated polybutadiene is Cray Valley (Paris), a daughter company of Total (Paris), or the Sartomer Company (Exton, PA, USA).

Preference is given to monohydroxylated hydrogenated polybutadienes. More preferably, the hydroxylated hydrogenated polybutadiene is a hydroxyethyl- or hydroxypropyl-terminated hydrogenated polybutadiene. Particular preference is given to hydroxypropyl-terminated polybutadienes.

These monohydroxylated hydrogenated polybutadienes can be prepared by first converting butadiene monomers by anionic polymerization to polybutadiene. Subsequently, by reaction of the polybutadiene monomers with ethylene oxide or propylene oxide, a hydroxy-functionalized polybutadiene can be prepared. This hydroxylated polybutadiene can be hydrogenated in the presence of a suitable transition metal catalyst.

The esters of (meth)acrylic acid for use in accordance with the invention and a hydroxylated hydrogenated polybutadiene described are also referred to as macromonomers in the context of this invention because of their high molar mass.

The term "(meth)acrylic acid" refers to acrylic acid and methacrylic acid and to mixtures thereof; methacrylic acid being particularly preferred. The term "(meth)acrylate" refers to esters of acrylic acid and esters of methacrylic acid and to mixtures thereof; esters of methacrylic acid being particularly preferred.

The macromonomers for use in accordance with the invention can be prepared by transesterification of alkyl (meth)acrylates. Reaction of the alkyl (meth)acrylate with the hydroxylated hydrogenated polybutadiene forms the ester of the invention. Preference is given to using methyl (meth)acrylate or ethyl (meth)acrylate as reactant.

This transesterification is widely known. For example, it is possible for this purpose to use a heterogeneous catalyst system, such as lithium hydroxide/calcium oxide mixture (LiOH/CaO), pure lithium hydroxide (LiOH), lithium methoxide (LiOMe) or sodium methoxide (NaOMe) or a homogeneous catalyst system such as isopropyl titanate (Ti(OiPr)4) or dioctyltin oxide (Sn(OCt)2O). The reaction is an equilibrium reaction. Therefore, the low molecular weight alcohol released is typically removed, for example by distillation.

In addition, the macromonomers can be obtained by a direct esterification proceeding, for example, from (meth)acrylic acid or (meth)acrylic anhydride, preferably under acidic catalysis by p-toluenesulfonic acid or methanesulfonic acid, or from free methacrylic acid by the DCC method (dicyclohexylcarbodiimide).

Furthermore, the present hydroxylated hydrogenated polybutadiene can be converted to an ester by reaction with an acid chloride such as (meth)acryloyl chloride.

Preferably, in the above-detailed preparations of the esters of the invention, polymerization inhibitors are used, for example the 4-hydroxy-2,2,6,6-tetramethylpiperidinooxyl radical and/or hydroquinone monomethyl ether.

Some of the macromonomers for use in accordance with the invention are also commercially available, for example Kraton Liquid® L-1253 which is produced from Kraton Liquid® L-1203 and is a hydrogenated polybutadiene methacrylate-functionalized to an extent of about 96% by weight, having about 50% each of 1,2 repeat units and 1,4 repeat units, from Kraton Polymers GmbH (Eschborn, Germany). Kraton® L-1253 is likewise synthesized according to GB 2270317.

In addition to the macromonomer and styrene, the monomer mixture may also comprise further comonomers, for example other alkyl (meth)acrylates.

Particularly preferred are alkyl (meth)acrylates having 1 to 22 carbon atoms in the alkyl chain (also referred to as C_1 to C_{22} alkyl (meth)acrylates).

Suitable alkyl (meth)acrylates are, for example, methyl and ethyl acrylate, propyl methacrylate, butyl methacrylate (BMA) and acrylate (BA), isobutyl methacrylate (IBMA), hexyl and cyclohexyl methacrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate (EHA), 2-ethylhexyl methacrylate, octyl methacrylate, nonyl methacrylate, decyl methacrylate, isodecyl methacrylate (IDMA, based on branched (C10)alkyl isomer mixture), undecyl methacrylate, dodecyl methacrylate (also known as lauryl methacrylate), tridecyl methacrylate, tetradecyl methacrylate (also known as myristyl methacrylate), pentadecyl methacrylate, hexadecyl methacrylate (also known as cetyl methacrylate), heptadecyl

methacrylate, octadecyl methacrylate (also known as stearyl methacrylate), nonadecyl methacrylate, eicosyl methacrylate, behenyl methacrylate and combinations thereof.

The suitable C10-15 alkyl (meth)acrylates include, for example, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate and/or pentadecyl (meth)acrylate.

Particularly preferred C10-15 alkyl (meth)acrylates are (meth)acrylic esters of a linear C12-14 alcohol mixture (C12-14 alkyl (meth)acrylate).

In one embodiment, the comb polymer (B) comprises:

(a) 20% by weight to 50% by weight of esters of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene,

(b) 0.2% by weight to 15% by weight of styrene, and

(c) up to 70% by weight of alkyl (meth)acrylates having 1 to 22 carbon atoms in the alkyl chain,

based on the total weight of the comb polymer.

In one embodiment, the comb polymer comprises:

(a) 20% by weight to 35% by weight of esters of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene,

(b) 0.2% by weight to 15% by weight of styrene,

(c) 0.2% by weight to 20% by weight of alkyl (meth)acrylates having 12 to 15 carbon atoms in the alkyl chain, and

(d) 50% by weight to 70% by weight of alkyl (meth)acrylates having 1 to 4 carbon atoms in the alkyl chain,

based on the total weight of the comb polymer.

In one embodiment, the comb polymer (B) comprises:

(a) 25% by weight to 30%by weight of esters of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene,

(b) 0.2% by weight to 15% by weight of styrene,

(c) 0.2% by weight to 15% by weight of alkyl methacrylates having 12 to 14 carbon atoms in the alkyl chain,

(d) 50% by weight to 65% by weight of butylmethacrylate, and

(e) 0.1% by weight to 0.2% by weight of methylmethacrylate,

based on the total weight of the comb polymer.

The polyalkyl(meth)acrylate based comb polymer in accordance with the invention may preferably be obtained by radical polymerization. However, the comb polymer may also be obtained by polymer-analogous reactions and/or graft copolymerization.

In one embodiment, the comb polymer may be obtained by radical polymerization involving the steps of

a) providing a monomer mixture comprising the indicated monomers; and

b) initiating radical polymerization in the monomer mixture.

The polymerization reaction is preferably initiated by mixing the monomer mixture with a radical initiator. In some cases, it may be required to heat the reaction mixture to the reaction temperatures specified below to initiate the polymerization.

Radical initiators may be selected from any of the well-known free-radical-producing compounds such as peroxy, hydroperoxy and azo initiators, including, for example, acetyl peroxide, benzoyl peroxide, lauroyl peroxide, tert-butyl peroxyisobutyrate, caproyl peroxide, cumene hydroperoxide, 1, 1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, azobisisobutyronitrile and tert-butyl peroctoate (also known as tert-butylperoxy-2-ethylhexanoate). Preferable radical initiators are benzoyl peroxide, lauroyl peroxide, tert-butyl peroxyisobutyrate, azobisisobutyronitrile and tert-butyl peroctoate. Tert-butyl peroctoate is particularly preferred. The initiator concentration is typically between 0.025 and 1 wt-%, preferably from 0.05 to 0.75 wt-%, more preferably from 0.1 to 0.5 wt-% and most preferably from 0.2 to 0.4 wt-%, based on the total weight of the monomers.

The polymerization is preferably conducted at a temperature below the boiling point of the reaction mixtures. Preferably, the temperature is in the range of 60 to 150°C, more preferably 85 to 130°C, most preferably 90 to 110°C.

One or more polymerization promoters may also be added to the monomer mixture. Suitable promoters include, for example, quaternary ammonium salts such as benzyl(hydrogenated-tallow)-dimethylammonium chloride and amines. Preferably the promoters are soluble in hydrocarbons. When used, these promoters are present at levels from 1 to 50 wt-%, preferably from 5 to 25 wt-%, based on total weight of initiator.

Chain transfer agents may also be added to control the molecular weight of the copolymer. The preferred chain transfer agents are alkyl mercaptans such as lauryl mercaptan (also known as dodecyl mercaptan, DDM). The amount of chain transfer agent is preferably 5 wt-% or less, more preferably 2 wt-% or less, based on the total weight of monomers.

Diluents may also be added to the monomer mixture. Preferably, the first and second reaction mixture each comprise up to 60 wt-% diluent, more preferably 5 to 60 wt-%, most preferably 10 to 60 wt-%.

Among the diluents suitable for use in the process of the present invention for non-aqueous solution polymerizations are aromatic hydrocarbons (such as benzene, toluene, xylene and aromatic naphthas), chlorinated hydrocarbons (such as ethylene dichloride, chlorobenzene and dichlorobenzene), esters (such as ethyl propionate or butyl acetate), (C6-C20)aliphatic hydrocarbons (such as cyclohexane, heptane and octane), mineral oils (such as paraffinic and naphthenic oils) or synthetic base oils (such as poly([alpha]-olefin) oligomer (PAO) lubricating oils, for example, [alpha]-decene dimers, trimers and mixtures thereof).

The lubricant composition in accordance with the present invention may further comprise auxiliary additives selected from the group consisting of pour point depressants, antiwear agents, antioxidants, dispersants, detergents, friction modifiers, antifoam agents, extreme pressure additives, and corrosion inhibitors. The auxiliary additives are preferably added in an amount of 0.1 to 25 weight-%, based on the total weight of the lubricant composition.

Suitable pour-point depressants include ethylene-vinyl acetate copolymers, chlorinated paraffin-naphthalene condensates, chlorinated paraffin-phenol condensates,

polymethacrylates, polyalkylstyrenes, etc. Preferred are polymethacrylates having a mass-average molecular weight of from 5.000 to 50.000 g/mol.

The preferred antiwear and extreme pressure additives include sulfur-containing compounds such as zinc dithiophosphate, zinc di-C3-12-alkyldithiophosphates (ZnDTPs), zinc phosphate, zinc dithiocarbamate, molybdenum dithiocarbamate, molybdenum dithiophosphate, disulfides, sulfurized olefins, sulfurized oils and fats, sulfurized esters, thiocarbonates, thiocarbamates, polysulfides, etc.; phosphorus-containing compounds such as phosphites, phosphates, for example trialkyl phosphates, triaryl phosphates, e.g. tricresyl phosphate, amine-neutralized mono- and dialkyl phosphates, ethoxylated mono- and dialkyl phosphates,phosphonates, phosphines, amine salts or metal salts of those compounds, etc.; sulfur and phosphorus-containing anti-wear agents such as thiophosphites, thiophosphates, thiophosphonates, amine salts or metal salts of those compounds, etc..

The suitable antioxidants include, for example, phenol-based antioxidants and amine-based antioxidants.

Phenol-based antioxidants include, for example, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; 4,4' -methylenebis(2,6-di-tert-butylphenol); 4,4' -bis(2,6-di-t-butylphenol); 4,4' -b is(2-methyl-6-t-butylphenol); 2,2' -methylenebis(4-ethyl-6-t-butylphenol); 2,2' -methylenebis(4-methyl-6-t-butyl phenol); 4,4' -butyl idenebis(3-methyl-6-t-butylphenol); 4,4'-isopropylidenebis(2,6-di-t-butylphenol); 2,2'-methylenebis(4-methyl-6-nonylphenol); 2,2'-isobutylidenebis(4,6-dimethylphenol); 2,2'-methylenebis(4-methyl-6-cyclohexylphenol); 2,6-di-t-butyl-4-methylphenol; 2,6-di-t-butyl-4-ethyl-phenol; 2,4-dimethyl-6-t-butylphenol; 2,6-di-t-amyl-p-cresol; 2,6-di-t-butyi-4-(N,N'-dimethylaminomethylphenol); 4,4'thiobis(2-methyl-6-t-butylphenol); 4,4'-thiobis(3-methyl-6-t-butylphenol); 2,2'-thiobis(4-methyl-6-t-butylphenol); bis(3-methyl-4-hydroxy-5-t-butylbenzyl) sulfide; bis(3,5-di-t-butyl-4-hydroxybenzyl) sulfide; n-octyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate; n-octadecyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate; 2,2'-thio[diethyl-bis-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], etc. Of those, especially preferred are bis-phenol-based antioxidants and ester group containing phenol-based antioxidants.

The amine-based antioxidants include, for example, monoalkyldiphenylamines such as monooctyldiphenylamine, monononyldiphenylamine, etc.; dialkyldiphenylamines such as

4,4' -dibutyldiphenylamine, 4,4'-dipentyldiphe nylamine, 4,4'- dihexyldiphenylamine, 4,4'-diheptyldiphenylamine, 4,4'-dioctyldiphenylamine, 4,4'-dinonyldiphenylamine, etc.; polyalkyldiphenylamines such as tetrabutyldiphenylamine, tetrahexyldiphenylamine, tetraoctyldiphenylamine, tetranonyldiphenylamine, etc.; naphthylamines, concretely alpha-naphthylamine, phenyl-alpha-naphthylamine and further alkyl-substituted phenyl-alpha-naphthylamines such as butylphenyl-alpha-naphthylamine, pentylphenyl-alpha-naphthylamine, hexylphenyl-alpha-naphthylamine, heptylphenyl-alpha-naphthylamine, octylphenyl-alpha-naphthylamine, nonylphenyl-alpha-naphthylamine, etc. Of those, diphenylamines are preferred to naphthylamines, from the viewpoint of the antioxidation effect thereof.

Suitable antioxidants may further be selected from the group consisting of compounds containing sulfur and phosphorus, for example metal dithiophosphates, for example zinc dithiophosphates (ZnDTPs), "OOS triesters" = reaction products of dithiophosphoric acid with activated double bonds from olefins, cyclopentadiene, norbornadiene, α-pinene, polybutene, acrylic esters, maleic esters (ashless on combustion); organosulfur compounds, for example dialkyl sulfides, diaryl sulfides, polysulfides, modified thiols, thiophene derivatives, xanthates, thioglycols, thioaldehydes, sulfur-containing carboxylic acids; heterocyclic sulfur/nitrogen compounds, especially dialkyldimercaptothiadiazoles, 2-mercaptobenzimidazoles; zinc bis(dialkyldithiocarbamate) and methylene bis(dialkyldithiocarbamate); organophosphorus compounds, for example triaryl and trialkyl phosphites; organocopper compounds and overbased calcium- and magnesium-based phenoxides and salicylates.

Appropriate dispersants include poly(isobutylene) derivatives, for example poly(isobutylene)succinimides (PIBSIs), including borated PIBSIs; and ethylene-propylene oligomers having N/O functionalities.

The preferred detergents include metal-containing compounds, for example phenoxides; salicylates; thiophosphonates, especially thiopyrophosphonates, thiophosphonates and phosphonates; sulfonates and carbonates. As metal, these compounds may contain especially calcium, magnesium and barium. These compounds may preferably be used in neutral or overbased form.

Friction modifiers used may include mechanically active compounds, for example molybdenum disulfide, graphite (including fluorinated graphite), poly(trifluoroethylene), polyamide, polyimide; compounds that form adsorption layers, for example long-chain carboxylic acids, fatty acid esters, ethers, alcohols, amines, amides, imides; compounds which form layers through tribochemical reactions, for example saturated fatty acids, phosphoric acid and thiophosphoric esters, xanthogenates, sulfurized fatty acids; compounds that form polymer-like layers, for example ethoxylated dicarboxylic partial esters, dialkyl phthalates, methacrylates, unsaturated fatty acids, sulfurized olefins or organometallic compounds, for example molybdenum compounds (molybdenum dithiophosphates and molybdenum dithiocarbamates MoDTCs) and combinations thereof with ZnDTPs, copper-containing organic compounds.

Suitable antifoam agents are silicone oils, fluorosilicone oils, fluoroalkyl ethers, etc..

The above-detailed additives are described in detail, inter alia, in T. Mang, W. Dresel (eds.): "Lubricants and Lubrication", Wiley-VCH, Weinheim 2001; R. M. Mortier, S. T. Orszulik (eds.): "Chemistry and Technology of Lubricants".

The lubricant composition according to the invention can be useful for various applications including industrial gear oil, lubricant for wind turbine, compressor oil, hydraulic fluid, paper machine lubricant, engine or motor oil, transmission and/or drive-trains fluid, machine tools lubricant, metalworking fluids, and transformer oils to name a few.

In a further aspect, the invention also relates to the use of a comb polymer as described above as an additive for a base oil to produce a lubricant composition, characterized in that the lubricant composition preferably has an R-factor of less than or equal to 8, wherein the R-factor is defined as the ratio of the kinematic viscosity of the lubricant composition at -20°C to the kinematic viscosity at +20°C measured according to ASTM D445. Preferably, the lubricant composition has an R-factor of 1 to 8.

Preferably, the lubricant composition comprises a synthetic base oil. The base oil is preferably selected form the group consisting of polyalphaolefins, naphthenic base oils and mixtures thereof. More preferably, the lubricant composition comprises a

polyalphaolefin base oil having a kinematic viscosity at 100°C according to ASTM D445 of 1 mm^2/s to 20 mm^2/s, more preferably 1 to 10 mm^2/s, most preferably 1 to 5 mm^2/s and especially preferred 2 to 3 mm^2/s.

The lubricant composition preferably has a kinematic viscosity at 40°C according to ASTM D445 of 10 to 120 mm^2/s, more preferably 40 to 100 mm^2/s, most preferably 70 to 80 mm^2/s.

In a further aspect the invention relates to a method of producing a lubricant composition having an R-factor of less than or equal to 8, preferably 1 to 8, wherein the R-factor is defined as the ratio of the kinematic viscosity of the lubricant composition at -20°C to the kinematic viscosity at +20°C measured according to ASTM D445, the method comprising the step of adding a comb polymer according to the present invention to a synthetic base oil, the synthetic base oil being preferably a polyalphaolefin base oil having a kinematic viscosity at 100°C according to ASTM D445 of 1 mm^2/s to 20 mm^2/s, more preferably 1 to 10 mm^2/s, most preferably 1 to 5 mm^2/s and especially preferred 2 to 3 mm^2/s.

The method is preferably characterized by adding the comb polymer in an amount to get a lubricant composition with a kinematic viscosity at 40°C according to ASTM D445 of 10 to 120 mm^2/s, more preferably 40 to 100 mm^2/s, most preferably 70 to 80 mm^2/s.

Experimental Part

Synthesis of a hydroxylated hydrogenated polybutadiene

The macroalcohol prepared was a hydroxypropyl-terminated hydrogenated polybutadiene having a mean molar mass M_n = 4750 g/mol.

The macroalcohol was synthesized by an anionic polymerization of 1,3-butadiene with butyllithium at 20-45°C. On attainment of the desired degree of polymerization, the reaction was stopped by adding propylene oxide and lithium was removed by precipitation with methanol. Subsequently, the polymer was hydrogenated under a hydrogen atmosphere in the presence of a noble metal catalyst at up to 140°C and pressure 200 bar. After the hydrogenation had ended, the noble metal catalyst was

removed and organic solvent was drawn off under reduced pressure. Finally, the base oil NB 3020 was used for dilution to a polymer content of 70% by weight.

The vinyl content of the macroalcohol was 61%, the hydrogenation level > 99% and the OH functionality > 98%. These values were determined by H-NMR (nuclear resonance spectroscopy).

Synthesis of macromonomer (MM)

In a 2 L stirred apparatus equipped with saber stirrer, air inlet tube, thermocouple with controller, heating mantle, column having a random packing of 3 mm wire spirals, vapor divider, top thermometer, reflux condenser and substrate cooler, 1000 g of the above-described macroalcohol are dissolved in 450 g of methyl methacrylate (MMA) by stirring at 60°C. Added to the solution are 20 ppm of 2,2,6,6-tetramethylpiperidin-1-oxyl radical and 200 ppm of hydroquinone monomethyl ether. After heating to MMA reflux (bottom temperature about 110°C) while passing air through for stabilization, about 20 g of MMA are distilled off for azeotropic drying. After cooling to 95°C, 0.30 g of LiOCH3 is added and the mixture is heated back to reflux. After the reaction time of about 1 hour, the top temperature has fallen to ~64°C because of methanol formation. The methanol/MMA azeotrope formed is distilled off constantly until a constant top temperature of about 100°C is established again. At this temperature, the mixture is left to react for a further hour. For further workup, the bulk of MMA is drawn off under reduced pressure. Insoluble catalyst residues are removed by pressure filtration (Seitz T1000 depth filter). The content of NB 3020 "entrained" into the copolymer syntheses described further down was taken into account accordingly.

Synthesis of comb polymers

Comb polymers according to the invention were prepared according to the following free radical polymerization procedure.

In a glass beaker, a mixture of 100 g of all the monomers (e.g. as detailed in Table 1) is diluted in ester oil (e.g. diisononyl adipate) to reach approximately 60% w/w dilution at 90°C. Afterwards, 35% of this diluted mixture is charged into a continuously stirred glass reactor, followed by addition of 0.105 g of initiator *t*-butylperoxy 2-ethylhexanoate. The

rest of the monomer mixture is gradually added into the glass reactor at constant flow rate for 3 h, in parallel with the addition of another 0.195 g of initiator *t*-butylperoxy 2-ethylhexanoate, also being introduced at constant flow rate for 3 h. Reaction temperature is held constant at 90°C. After 3 hours, additional 2x0.2 g of initiator *t*-butylperoxy 2-ethylhexanoate is added to ensure the completion of the polymerization, 2 and 5 hours after the end of the monomer feeding, while the reaction is kept at 90°C. At the end of the reaction, additional dilution ester oil can be added.

Lauryl methacrylate is a mixture of linear C_{12} and C_{14} alkyl methacrylates with a ratio of C_{12} to C_{14} alkyl methacrylate of around 73/27.

The compositions of the monomer mixtures used to prepare exemplary copolymers according to the invention are given in the following Table 1. The amounts of monomers are given as weight-% based on the total weight of the comb polymer.

Table 1: Net compositions of the comb polymers prepared to support the present invention

comb polymer	**A** (inventive)	**B** (inventive)	**C** (CE)
macromonomer	30%	25%	42%
lauryl methacrylate (C_{12} to C_{14} methacrylate)	15%	0.2%	0.2%
methyl methacrylate	0.2%	0.2%	0.2%
n-butyl methacrylate	54.6%	63.55%	17.8%
styrene	0.2%	11.05%	39.8%
Total	100	100	100

CE = comparative example

Comb polymers **A** and **B** are inventive examples and have a styrene content claimed by the present invention. Comb polymer **C** is a comparative example and comprises a higher amount of styrene. It was prepared to show that a higher amount of styrene leads to a higher R-factor.

The following polyalkylmethacrylates are known viscosity index improvers and were used in comparative lubricant compositions. They were prepared to show that an R-factor within the claimed range of 1-8 can only be reached by using comb polymers which comprise a certain amount of an ester of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene.

Comparative copolymer **D** is a polyalkylmethacrylate prepared through similar aforementioned free radical polymerization procedure from 89.97% by weight of dodecyl pentadecyl methacrylate and 10.03% by weight of methyl methacrylate. Dodecyl pentadecyl methacrylate is a mixture of branched and linear C_{12} to C_{15} alkyl methacrylates with an average composition of 16 to 26% by weight of C_{12} alkyl methacrylate, 24 to 34% by weight of C_{13} alkyl methacrylate, 24 to 34% by weight of C_{14} alkyl methacrylate, and 16 to 26% by weight of C_{15} alkyl methacrylate, and approximately 80% linear alkyl methacrylates.

Comparative copolymer **E** is a polyalkylmethacrylate prepared through similar aforementioned free radical polymerization procedure from 99.80% by weight of C_{12} to C_{15} alkyl methacrylate (comprising 20% C_{12} alkyl methacrylate, 34% C_{13} alkyl methacrylate, 29% C_{14} alkyl methacrylate, and 17% C_{15} alkyl methacrylate, with approximately 40% linear alkyl methacrylates) and 0.20% by weight of methyl methacrylate.

Lubricant compositions were obtained by mixing a poly-alpha-olefin base oil (PAO2) having a kinematic viscosity at 100°C of 2 mm^2/s according to ASTM D445 and the indicated amount of copolymers as viscosity index improvers according to the following table targeting a KV_{40} of 76 mm^2/s.

Table 2: lubricant compositions comprising comb polymers and base oil

No	Base oil	Copolymer	Amount of styrene [% by weight]*)	Amount of copolymer [% by weight]**)	
1	PAO2	**A**	0.2	25.2	
2	PAO2	**B**	11.0	63.9	
3	PAO2	**C**	39.8	40.8	CE
4	PAO2	**D**	--	41.1	CE
5	PAO2	**E**	--	48.5	CE

*) based on the total weight of the comb polymer

**) based on the total weight of the lubricant composition

CE: comparative example

The lubricant compositions were tested by determining the kinematic viscosity at different temperatures, the viscosity index and the R-factor. The kinematic viscosity was determined according to ASTM D445, the viscosity index was determined according to ASTM D2270, and the R-factor was calculated as the ratio of the kinematic viscosity at -20°C to the kinematic viscosity at +20°C. The results are given in the following Table 3.

Table 3: viscosity data of lubricant compositions

No.	Kinematic viscosity (mm^2/s)							VI	R-factor	
	100°C	**40°C**	**20°C**	**10°C**	**0°C**	**-10°C**	**-20°C**			
1	24.36	75.76	140.2	191.8	264.1	381.1	635.7	345	4.53	
2	102.1	76.40	130.2	193.0	319.9	597.2	877.4	810	6.74	
3	27.01	76.59	140.8	215.1	362.7	674.4	1387	373	9.85	CE
4	17.55	76.08	165.0	264.3	450.8	825.2	1686	251	10.22	CE
5	14.83	76.39	180.2	304.5	550.5	1491	2375	205	13.18	CE

CE: comparative example

The data demonstrate that the lubricant compositions according to the invention (compositions 1 and 2, comprising the comb polymers A and B, respectively) have a high viscosity index as well as a low R-factor. The compositions according to the invention, therefore, guarantee a good viscosity characteristic at low operating temperature, defined as an R-factor lower than 8. In contrast, the comparative lubricant compositions (compositions 3, 4 and 5, comprising comb polymers with a higher amount of styrene or

conventional polyalkylmethacrylates D and E) exhibit a good viscosity index but do not perform as well at low operating temperatures. They show R-factors greater than 8. The data, therefore, show that the use of comb polymers according to the present invention has the surprising advantage over the use of conventional viscosity index improvers of improving the viscosity characteristics of a lubricant not only at normal operating temperatures but also at low operating temperatures.

When formulated to a given KV_{40} of 76 mm^2/s, the data of Table 3 show that with decreasing temperature the kinematic viscosity of the formulations is increasing.

By using the inventive polymers (Examples 1 and 2) the viscosity increase is much lower compared to the use of standard polymers (Examples 4 and 5) or a polymer with higher styrene content (Example 3).

When formulated to a given KV_{40} of 76 mm^2/s, the lubricant compositions comprising the comb polymers according to the present invention show a KV_{20} in the range of 130 to 140 and a KV_{-20} in the range of 640 to 870.

It is further shown that the definition of VI is not appropriate to extrapolate viscosities down to temperatures below 40°C, e.g. to -20°C.

Claims

1. A lubricant composition, comprising:

(A) 20 to 90% by weight of a synthetic base oil; and

(B) 10 to 80% by weight of a comb polymer, comprising the following monomers:

(a) 20 to 35% by weight of esters of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene; and

(b) 0.2% by weight to 15% by weight of styrene,

(c) 0.2 to 20% by weight of alkyl methacrylates having 12 to 15 carbon atoms in the alkyl chain,

(d) 50 to 70% by weight of alkyl (meth)acrylates having 1 to 4 carbon atoms in the alkyl chain,

based on the total weight of the comb polymer.

2. The lubricant composition according to claim 1, wherein the lubricant composition is characterized by a ratio of the kinematic viscosity of the lubricant composition at -20°C (KV_{-20}) to the kinematic viscosity at +20°C (KV_{+20}), KV_{-20}/KV_{+20}, of 8 or less, wherein the kinematic viscosities are measured according to ASTM D445.

3. The lubricant composition according to claim 1 or 2, wherein the synthetic base oil (A) is a polyalphaolefin having a kinematic viscosity at 100°C according to ASTM D445 of 1 to 20 mm^2/s.

4. The lubricant composition according to claim 1 or 2, wherein the synthetic base oil (A) is a polyalphaolefin having a kinematic viscosity at 100°C according to ASTM D445 of 1 to 10 mm^2/s.

5. The lubricant composition according to claim 1 or 2, wherein the synthetic base oil (A) is a polyalphaolefin having a kinematic viscosity at 100°C according to ASTM D445 of 1 to 5 mm^2/s.

6. The lubricant composition according to claim 1 or 2, wherein the synthetic base oil (A) is a polyalphaolefin having a kinematic viscosity at 100°C according to ASTM D445 of 2 to 3 mm^2/s.

7. The lubricant composition according to any one of the preceding claims, characterized in that it comprises 30 to 80% by weight of the synthetic base oil (A) and 20 to 70% by weight of the comb polymer (B), based on the total weight of the lubricant composition.

8. The lubricant composition according to any one of the preceding claims, wherein the hydroxylated hydrogenated polybutadiene of component (a) has a number-average molecular weight M_n to DIN 55672-1 of 4.000 to 5.000 g/mol.

9. The lubricant composition according to any one of the preceding claims, wherein the comb polymer (B) comprises:

(a) 25 to 30%by weight of esters of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene,
(b) 0.2 to 15% by weight of styrene,
(c) 0.2 to 15% by weight of alkyl methacrylates having 12 to 14 carbon atoms in the alkyl chain,
(d) 50 to 65% by weight of butylmethacrylate, and
(e) 0.1 to 0.2% by weight of methylmethacrylate,

based on the total weight of the comb polymer.

10. Use of a comb polymer, comprising:

(a) 20 to 35% by weight of esters of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene,
(b) 0.2 to 15% by weight of styrene,
(c) 0.2 to 20% by weight of alkyl methacrylates having 12 to 15 carbon atoms in the alkyl chain,
(d) 50 to 65% by weight of alkyl (meth)acrylates having 1 to 4 carbon atoms in the alkyl chain,

based on the total weight of the comb polymer,

as an additive for a base oil to produce a lubricant composition having an R-factor of less than or equal to 8, wherein the R-factor is defined as the ratio of the kinematic viscosity of the lubricant composition at -20°C to the kinematic viscosity at +20°C measured according to ASTM D445.

11. The use according to claim 10, wherein the base oil is a polyalphaolefin base oil having a kinematic viscosity at 100°C according to ASTM D445 of 1 mm^2/s to 20 mm^2/s.

12. The use according to claim 10, wherein the base oil is a polyalphaolefin base oil having a kinematic viscosity at 100°C according to ASTM D445 of 1 to 10 mm^2/s.

13. The use according to claim 10, wherein the base oil is a polyalphaolefin base oil having a kinematic viscosity at 100°C according to ASTM D445 of 1 to 5 mm^2/s.

14. The use according to claim 10, wherein the base oil is a polyalphaolefin base oil having a kinematic viscosity at 100°C according to ASTM D445 of 2 to 3 mm^2/s.

15. The use according to claims 10 to 14, characterized in that the lubricant composition has an R-factor of 1 to 8.

16. The use according to claims 10 to 15, characterized in that the comb polymer (B) comprises:

(a) 25 to 30%by weight of esters of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene,
(b) 0.2 to 15% by weight of styrene,
(c) 0.2 to 15% by weight of alkyl methacrylates having 12 to 14 carbon atoms in the alkyl chain,
(d) 50 to 65% by weight of butylmethacrylate, and
(e) 0.1 to 0.2% by weight of methylmethacrylate,

based on the total weight of the comb polymer.