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(54) MOTOR HAVING IMPROVED PROPERTIES

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(57) ABSTRACT

The present invention describes a motor designed for Fuel compatibility comprising a lubricant composition comprises at least one ester group containing polymer having a high polarity.

MOTOR HAVING IMPROVED PROPERTIES

[0001] The present application relates to a motor having improved properties. Furthermore the present invention describes a use of polymers to improve the emulsion stability of lubricants.

[0002] Fuels are nowadays generally obtained from fossil sources. However, these resources are limited, so that replacements are being sought. Therefore, interest is rising in renewable raw materials which can be used to produce fuels.

[0003] Alternate fuels for transportation, such as methanol, ethanol, etc. have been studied by the automotive industry for a number of years. While such fuels offer some advantages of reduced engine emissions, their use is accompanied by a number of deficiencies and limitations which must be addressed if they are to become viable alternatives to gasoline.

[0004] In view of the declining ecological quality and decreasing world crude oil reserves, the use of pure bio alcohols, such as ethanol (E100) or methanol (M100) has been an important target in many countries. However, many issues, ranging from different combustion characteristic to corrosion of seal materials, have been reported as hindrances to the use of bio alcohols as a replacement for fossil gasoline. Another major obstacle is the high amount of water formed by the combustion process or being present based on the production process of the alcohol in comparison to conventional gasoline.

[0005] The water formed during combustion, along with alcohol which bypasses the piston rings or is carried away by the blow-by gases, tends to accumulate in the oil.

[0006] The alcohol and water may accumulate in the lubricating oil resulting from the use of such alternate fuels increase corrosion and wear problems in engines using such alternate fuels, especially alcohol.

[0007] The problems mentioned above depend of the type of use of the passenger car. Using the car on very short range circles lead to very critical problems resulting in short time lubricant changes. Furthermore, the issues are more critical to motors having a high sophisticated emission control system and further technical approaches for fuel savings. The more sophisticated the motor the more sensitive the motor on lubricant decline, e.g. based on undue water content.

[0008] Lubricant decline, especially high water content and phase separation have detrimental effects on various properties of the motor. These are especially critical for motors having Flex Fuel compatibility. High water content usually may cause problems regarding cold start and cold run characteristics of the motor. In addition thereto, the life time and the fuel consumption of the motor are negatively influenced by a high water content of the lubricant.

[0009] There have been many attempts to date to improve cold start and cold run characteristics of the motors by engineering techniques and new facilities. However, these options are connected with disadvantages based on high costs and the fact that usually only the latest cars can benefit from such improvements. Therefore, further opportunities to improve the cold start and cold run characteristics, the life time and the fuel consumption of the motor would be helpful.

[0010] The use of ester group containing polymers is known in prior art, e.g. U.S. Pat. No. 4,290,925 described grafted polymethacrylates containing N-vinyl-2-pyrrolidone which are useful for preparing stable emulsions of olefin copolymers.

[0011] U.S. Pat. No. 4,057,623 described copolymers of alkyl methacrylates and N-vinyl-2-pyrrolidone which are useful for producing water-in-oil emulsions for cosmetic applications. U.S. Pat. No. 3,519,565 described copolymers of alkyl methacrylates and N-vinylthiopyrrolidone which are useful for reducing engine sludge and varnish.

[0012] In addition thereto GB2307916A discloses that multifunctional olefinic copolymer viscosity index improver with dispersant properties in combination with further additives can improve the emulsion stability of lubricants. However, no hints are mention with regard to ester group containing polymer having a high polarity. In addition thereto, no specific motor type has been disclosed.

[0013] In view of the prior art, it was thus an object of the present invention to provide a solution which is not limited to new motor designs and can be applied to existing flex-fuel motors. Especially the cold start and cold run characteristics of flex-fuel motors should be improved. Furthermore, the improvement of life time and fuel consumption is a further object of the present invention.

[0014] These improvements should be achieved without environmental drawbacks.

[0015] It was a further object of the invention to provide additives for lubricating oils which provide improved cold start and cold run characteristics of flex-fuel motors. In addition thereto the additive should improve the life time and the fuel consumption of flex-fuel motors.

[0016] Furthermore, the additives should be producible in a simple and inexpensive manner, and especially commercially available components should be used. In this context, they should be producible on the industrial scale without new plants or plants of complicated construction being required for this purpose.

[0017] It was a further aim of the present invention to provide an additive which brings about a multitude of desirable properties in the lubricant. This can minimize the number of different additives.

[0018] Furthermore, the additive should not exhibit any adverse effects on the fuel consumption or the environmental compatibility of the lubricant.

[0019] Moreover, the additive should improve the emulsion stability of lubricating oils comprising a high amount of water.

[0020] These objects and also further objects which are not stated explicitly but are immediately derivable or discernible from the connections discussed herein by way of introduction are achieved by a motor having all features of claim **1**. Appropriate modifications to the inventive motor are protected in the claims referring back to claim **1**. With regard to the use, claim **22** provides a solution to the underlying problem.

[0021] The present invention accordingly provides a motor designed for Flex Fuel compatibility comprising a lubricant composition, characterized in that the lubricant composition comprises at least one ester group containing polymer having a high polarity.

[0022] It is thus possible in an unforeseeable manner to provide a motor designed for Flex Fuel compatibility having an improved cold start and cold run characteristics. In addition thereto, the motor of the present invention shows an enhanced life time and lowered fuel consumption.

[0023] In addition thereto, the motor of the present invention enables extended oil change intervals. Thus the motor provides significant improvements in economic aspects based on lower amounts of motor oil based on a specific mileage.

[0024] Moreover, the solution presented by the present invention is not limited to new motor designs and can be applied to existing flex-fuel motors.

[0025] Furthermore, the motor of the present invention can have a very high compression without being detrimental effected regarding the cold start and cold run characteristics and life time and the fuel consumption of flex-fuel motors.

[0026] Furthermore, the additives used in order to obtain a lubricant being able to solve the problems mentioned above can be prepared in a simple and inexpensive manner, and it is possible to use commercially available components in particular. At the same time, production is possible on the industrial scale, without new plants or plants of complex construction being required for that purpose.

[0027] Furthermore, the polymers for use in accordance with the invention exhibit a particularly favorable profile of properties. For instance, the polymers can be configured so as to be surprisingly shear-stable, such that the lubricants have a very long service life. In addition, the additive for use in accordance with the invention may bring about a multitude of desirable properties in the lubricant. For example, it is possible to produce lubricants with outstanding low-temperature properties or viscosity properties, which comprise the present polymers comprising ester groups. This allows the number of different additives to be minimized. Furthermore, the present polymers comprising ester groups are compatible with many additives. This allows the lubricants to be adjusted to a wide variety of different requirements.

[0028] Furthermore, the additives for use do not exhibit any adverse effects on fuel consumption or the environmental compatibility of the lubricant.

[0029] Surprisingly, present polymers comprising ester groups improve the emulsion stability of lubricating oils comprising a high amount of water.

[0030] The present invention provides a new motor designed for Flex Fuel compatibility. These motors are usually part of flex-fuel vehicles.

[0031] A flexible-fuel vehicle (FFV) or dual-fuel vehicle (colloquially called a flex-fuel vehicle) is an alternative fuel vehicle with an internal combustion engine designed to run on more than one fuel, usually gasoline blended with either ethanol or methanol fuel, and both fuels are stored in the same common tank. Flex-fuel engines are capable of burning any proportion of the resulting blend in the combustion chamber as fuel injection and spark timing are adjusted automatically according to the actual blend detected by electronic sensors. Flex-fuel vehicles are distinguished from bi-fuel vehicles, where two fuels are stored in separate tanks and the engine runs on one fuel at a time, for example, compressed natural gas (CNG), liquefied petroleum gas (LPG), or hydrogen.

[0032] Though technology exists to allow ethanol FFVs to run on any mixture of gasoline and ethanol, from pure gasoline up to 100% ethanol (E100), North American and European flex-fuel vehicles are optimized to run on a maximum blend of 15% gasoline with 85% anhydrous ethanol (called E85 fuel). This limit in the ethanol content is set to reduce ethanol emissions at low temperatures and to avoid cold starting problems during cold weather, at temperatures lower than 11° C. (52° F.). The alcohol content is reduced during the winter in regions where temperatures fall below 0° C. (32° F.) to a winter blend of E70 in the U.S. or to E75 in Sweden from November until March. Brazilian flex fuel vehicles are optimized to run on any mix of E20-E25 gasoline and up to 100% hydrous ethanol fuel (E100). The Brazilian flex vehicles are built-in with a small gasoline reservoir for cold starting the engine when temperatures drop below 15° C. (59° F.).

[0033] Preferably, the motor of the present invention is designed to fuels comprising at least 5%, especially at least 10%, particularly 20%, more especially at least 50% and more preferably at least 80% by volume of alcohol, e.g. methanol and/or ethanol. Furthermore, the motor of the present invention is preferably designed to fuels comprising at least 5%, especially at least 10%, particularly 20%, more especially at least 50% and more preferably at least 80% by volume of gasoline.

[0034] Preferably, the motor comprises a compression of at least 10:1, more preferably at least 12:1.

[0035] According to a special aspect of the present invention, the motor may comprise a fuel injection pump.

[0036] Unforeseeable advantages can be achieved by a motor comprising a multi valve technique.

[0037] Furthermore, the motor of the present invention may comprise an exhaust gas recirculation and/or a secondary-air system.

[0038] Preferably, the motor comprises an engine management for optimization of the fuel injection and the spark timing.

[0039] Preferred motor of the present invention meet the requirements of exhaust emission standard Euro 5, more preferably EURO 6 as defined in Directive No. 715/2007/EC.

[0040] The motor of the present invention comprises a lubricant composition including at least one ester group containing polymer having a high polarity.

[0041] Polymers comprising ester groups are understood in the context of the present invention to mean polymers obtainable by polymerizing monomer compositions which comprise ethylenically unsaturated compounds having at least one ester group, which are referred to hereinafter as ester monomers. Accordingly, these polymers contain ester groups as part of the side chain. These polymers include especially polyalkyl (meth)acrylates (PAMA), polyalkyl fumarates and/or polyalkyl maleates.

[0042] Ester monomers are known per se. They include especially (meth)acrylates, maleates and fumarates, which may have different alcohol radicals. The expression "(meth)acrylates" encompasses methacrylates and acrylates, and mixtures of the two. These monomers are widely known.

[0043] The polymer comprising ester groups comprises preferably at least 40% by weight, more preferably at least 60% by weight, especially preferably at least 80% by weight and most preferably at least 90% by weight of repeat units derived from ester monomers.

[0044] Polymers usable in accordance with the invention have a high polarity. Consequently, the polymer may be a statistical copolymer comprising a high amount of dispersing repeat units being derived from a dispersing monomer. Preferably, the statistical copolymer comprises at least 7%, more preferably at least 9% by weight of dispersing repeat units being derived from a dispersing monomer. In addition thereto, the polymer may be a graft copolymer having an nonpolar polymer as graft base and an dispersing monomer as graft layer. Surprising improvements can be achieved with graft copolymers preferably comprising 0.5 to 10% by weight, especially 0.8 to 7% by weight, more preferably 1 to

5% by weight of dispersing repeat units being derived from at least one dispersing monomer, preferably a heterocyclic vinyl compound.

[0045] The term “repeat unit” is widely known in the technical field. The present polymers can preferably be obtained by means of free-radical polymerization of monomers. This opens up double bonds to form covalent bonds. Accordingly, the repeat unit arises from the monomers used.

[0046] Dispersing monomers are understood to mean especially monomers with functional groups, for which it can be assumed that polymers with these functional groups can keep particles, especially soot particles, in solution (cf. R. M. Mortier, S. T. Orszulik (eds.): “Chemistry and Technology of Lubricants”, Blackie Academic & Professional, London, 2nd ed. 1997). These include especially monomers which have boron-, phosphorus-, silicon-, sulfur-, oxygen- and nitrogen-containing groups, preference being given to oxygen- and nitrogen-functionalized monomers.

[0047] The nonpolar graft base may comprise a small proportion of dispersing repeat units, which is preferably less than 20% by weight, more preferably less than 10% by weight and most preferably less than 5% by weight, based on the weight of the nonpolar graft base. In a particularly appropriate configuration, the nonpolar graft base comprises essentially no dispersing repeat units.

[0048] The nonpolar graft base of the polymer comprising ester groups may have 5 to 100% by weight, especially 20 to 98% by weight, preferably 30 to 95 and most preferably 70 to 92% by weight of repeat units derived from ester monomers having 7 to 15 carbon atoms in the alcohol radical.

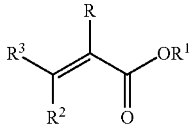
[0049] In a particular aspect, the nonpolar graft base of the polymer comprising ester groups may have 0 to 80% by weight, preferably 0.5 to 60% by weight, more preferably 2 to 50% by weight and most preferably 5 to 20% by weight of repeat units derived from ester monomers having 16 to 40 carbon atoms in the alcohol radical.

[0050] In addition, the nonpolar graft base of the polymer comprising ester groups may have 0 to 40% by weight, preferably 0.1 to 30% by weight and more preferably 0.5 to 20% by weight of repeat units derived from ester monomers having 1 to 6 carbon atoms in the alcohol radical.

[0051] The nonpolar graft base of the polymer comprising ester groups comprises preferably at least 40% by weight, more preferably at least 60% by weight, especially preferably at least 80% by weight and most preferably at least 90% by weight of repeat units derived from ester monomers.

[0052] Mixtures from which the graft base of the useful polymers comprising ester groups or the statistical polymers are obtainable may contain 0 to 40% by weight, especially 0.1 to 30% by weight and more preferably 0.5 to 20% by weight of one or more ethylenically unsaturated ester compounds of the formula (I)

(I)



in which R is hydrogen or methyl, R^1 is a linear or branched alkyl radical having 1 to 6 carbon atoms, R^2 and R^3 are each independently hydrogen or a group of the formula —COOR' in which R' is hydrogen or an alkyl group having 1 to 6 carbon atoms.

[0053] Examples of component (I) include

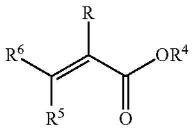
(meth)acrylates, fumarates and maleates which derive from saturated alcohols, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, iso-propyl (meth)acrylate, n-butyl (meth)acrylate, tert-butyl (meth)acrylate and pentyl (meth)acrylate, hexyl (meth)acrylate;

cycloalkyl (meth)acrylates such as cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate;

(meth)acrylates which derive from unsaturated alcohols, such as 2-propynyl (meth)acrylate, allyl (meth)acrylate and vinyl (meth)acrylate.

[0054] The compositions to be polymerized to prepare the graft base or the statistical polymers preferably contain 5 to 100% by weight, preferably 10 to 98% by weight and especially preferably 20 to 95% by weight of one or more ethylenically unsaturated ester compounds of the formula (II)

(II)



in which R is hydrogen or methyl, R^4 is a linear or branched alkyl radical having 7 to 15 carbon atoms, R^5 and R^6 are each independently hydrogen or a group of the formula —COOR" in which R" is hydrogen or an alkyl group having 7 to 15 carbon atoms.

[0055] Examples of component (II) include:

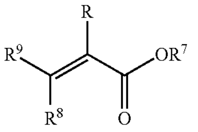
(meth)acrylates, fumarates and maleates which derive from saturated alcohols, such as 2-ethylhexyl (meth)acrylate, heptyl (meth)acrylate, 2-tert-butylheptyl (meth)acrylate, octyl (meth)acrylate, 3-isopropylheptyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate;

(meth)acrylates which derive from unsaturated alcohols, for example oleyl (meth)acrylate;

cycloalkyl (meth)acrylates, such as 3-vinylcyclohexyl (meth)acrylate, bornyl (meth)acrylate; and the corresponding fumarates and maleates.

[0056] In addition, preferred monomer compositions for preparing the graft base or the statistical polymers comprise 0 to 80% by weight, preferably 0.5 to 60% by weight, more preferably 2 to 50% by weight and most preferably 5 to 20% by weight of one or more ethylenically unsaturated ester compounds of the formula (III)

(III)



in which R is hydrogen or methyl, R^7 is a linear or branched alkyl radical having 16 to 40, preferably 16 to 30, carbon atoms, R^8 and R^9 are each independently hydrogen or a group of the formula —COOR''' in which R''' is hydrogen or an alkyl group having 16 to 40, preferably 16 to 30, carbon atoms.

[0057] Examples of component (III) include (meth)acrylates which derive from saturated alcohols, such as hexadecyl (meth)acrylate, 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate, 5-ethyloctadecyl (meth)acrylate, 3-isopropyloctadecyl (meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate, cetyleicosyl (meth)acrylate, stearyleicosyl (meth)acrylate, docosyl (meth)acrylate and/or eicosyltetratriacontyl (meth)acrylate;

cycloalkyl (meth)acrylates such as 2,4,5-tri-t-butyl-3-vinylcyclohexyl (meth)acrylate, 2,3,4,5-tetra-t-butylcyclohexyl (meth)acrylate;

and the corresponding fumarates and maleates.

[0058] The ester compounds with a long-chain alcohol radical, especially components (II) and (III), can be obtained, for example, by reacting (meth)acrylates, fumarates, maleates and/or the corresponding acids with long-chain fatty alcohols, which generally gives a mixture of esters, for example (meth)acrylates with different long-chain alcohol radicals. These fatty alcohols include Oxo Alcohol® 7911, Oxo Alcohol® 7900, Oxo Alcohol® 1100; Alfol® 610, Alfol® 810, Lial® 125 and Nafol® types (Sasol); Alphanol® 79 (ICI); Epal® 610 and Epal® 810 (Afton); Linevol® 79, Linevol® 911 and Neodol® 25E (Shell); Dehydad®, Hydrenol® and Lorol® types (Cognis); Acropol® 35 and Exxal® 10 (Exxon Chemicals); Kalcol® 2465 (Kao Chemicals).

[0059] Among the ethylenically unsaturated ester compounds, the (meth)acrylates are particularly preferred over the maleates and fumarates, i.e. R^2, R^3, R^5, R^6, R^8 and R^9 of the formulae (I), (II) and (III) are each hydrogen in particularly preferred embodiments.

[0060] The weight ratio of ester monomers of the formula (II) to the ester monomers of the formula (III) may be within a wide range. The ratio of ester compounds of the formula (II) which have 7 to 15 carbon atoms in the alcohol radical to the ester compounds of the formula (III) which have 16 to 40 carbon atoms in the alcohol radical is preferably in the range from 50:1 to 1:30, more preferably in the range from 10:1 to 1:3, especially preferably 5:1 to 1:1.

[0061] In addition, the monomer mixture for preparing the graft base or the statistical polymers may comprise ethylenically unsaturated monomers which can be copolymerized with the ethylenically unsaturated ester compounds of the formulae (I), (II) and/or (III).

[0062] The preferred comonomers include

vinyl halides, for example vinyl chloride, vinyl fluoride, vinylidene chloride and vinylidene fluoride;

styrene, substituted styrenes having an alkyl substituent in the side chain, for example α-methylstyrene and α-ethylstyrene, substituted styrenes having an alkyl substituent on the ring, such as vinyltoluene and p-methylstyrene, halogenated styrenes, for example monochlorostyrenes, dichlorostyrenes, tribromostyrenes and tetrabromostyrenes;

vinyl and isoprenyl ethers;

maleic acid and maleic acid derivatives different from those mentioned under (I), (II) and (III), for example maleic anhydride, methylmaleic anhydride, maleimide, methylmaleimide;

fumaric acid and fumaric acid derivatives different from those mentioned under (I), (II) and (III).

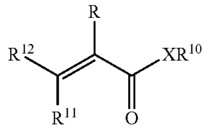
[0063] In addition, monomer mixtures for preparing the graft base may comprise dispersing monomers.

[0064] The proportion of comonomers is preferably 0 to 50% by weight, more preferably 0.1 to 40% by weight and most preferably 0.5 to 20% by weight, based on the weight of the monomer composition for preparing the graft base or the statistical polymers.

[0065] In addition to the graft base, a preferred polymer usable in accordance with the invention comprises at least one graft layer which comprises repeat units derived from dispersing monomers.

[0066] Dispersing monomers have been used for some time for functionalizing polymeric additives in lubricant oils, and are therefore known to those skilled in the art (cf. R. M. Mortier, S. T. Orszulik (eds.): "Chemistry and Technology of Lubricants", Blackie Academic & Professional, London, 2^{nd} ed. 1997). Appropriately, it is possible to use especially heterocyclic vinyl compounds and/or ethylenically unsaturated, polar ester compounds of the formula (IV)

(IV)



in which R is hydrogen or methyl, X is oxygen, sulfur or an amino group of the formula —NH— or —NR^a— in which R^a is an alkyl radical having 1 to 40 and preferably 1 to 4 carbon atoms, R^{10} is a radical which comprises 2 to 1000, especially 2 to 100 and preferably 2 to 20 carbon atoms and has at least one heteroatom, preferably at least two heteroatoms, R^{11} and R^{12} are each independently hydrogen or a group of the formula —COX'$R^{10'}$ in which X' is oxygen or an amino group of the formula —NH— or —$NR^{a'}$— in which $R^{a'}$ is an alkyl radical having 1 to 40 and preferably 1 to 4 carbon atoms, and $R^{10'}$ is a radical comprising 1 to 100, preferably 1 to 30 and more preferably 1 to 15 carbon atoms, as dispersing monomers.

[0067] The expression "radical comprising 2 to 1000 carbon" denotes radicals of organic compounds having 2 to 1000 carbon atoms. Similar definitions apply for corresponding terms. It encompasses aromatic and heteroaromatic groups, and alkyl, cycloalkyl, alkoxy, cycloalkoxy, alkenyl, alkanoyl, alkoxycarbonyl groups, and also heteroaliphatic groups. The groups mentioned may be branched or unbranched. In addition, these groups may have customary substituents. Substituents are, for example, linear and branched alkyl groups having 1 to 6 carbon atoms, for example methyl, ethyl, propyl, butyl, pentyl, 2-methylbutyl or hexyl; cycloalkyl groups, for example cyclopentyl and cyclohexyl; aromatic groups such as phenyl or naphthyl; amino groups, hydroxyl groups, ether groups, ester groups and halides.

[0068] According to the invention, aromatic groups denote radicals of mono- or polycyclic aromatic compounds having preferably 6 to 20 and especially 6 to 12 carbon atoms. Heteroaromatic groups denote aryl radicals in which at least one CH group has been replaced by N and/or at least two adjacent CH groups have been replaced by S, NH or O, heteroaromatic groups having 3 to 19 carbon atoms.

[0069] Aromatic or heteroaromatic groups preferred in accordance with the invention derive from benzene, naphthalene, biphenyl, diphenyl ether, diphenylmethane, diphenyldimethylmethane, bisphenone, diphenyl sulfone, thiophene, furan, pyrrole, triazole, oxazole, imidazole, isothiazole, isoxazole, pyrazole, 1,3,4-oxadiazole, 2,5-diphenyl-1,3,4-oxadiazole, 1,3,4-thiadiazole, 1,3,4-triazole, 2,5-diphenyl-1,3,4-triazole, 1,2,5-triphenyl-1,3,4-triazole, 1,2,4-oxadiazole, 1,2,4-thiadiazole, 1,2,4-triazole, 1,2,3-triazole, 1,2,3,4-tetrazole, benzo[b]thiophene, benzo[b]furan, indole, benzo[c]thiophene, benzo[c]furan, isoindole, benzoxazole, benzothiazole, benzimidazole, benzisoxazole, benzisothiazole, benzopyrazole, benzothiadiazole, benzotriazole, dibenzofuran, dibenzothiophene, carbazole, pyridine, bipyridine, pyrazine, pyrazole, pyrimidine, pyridazine, 1,3,5-triazine, 1,2,4-triazine, 1,2,4,5-triazine, tetrazine, quinoline, isoquinoline, quinoxaline, quinazoline, cinnoline, 1,8-naphthyridine, 1,5-naphthyridine, 1,6-naphthyridine, 1,7-naphthyridine, phthalazine, pyridopyrimidine, purine, pteridine or quinolizine, 4H-quinolizine, diphenyl ether, anthracene, benzopyrrole, benzoxathiadiazole, benzoxadiazole, benzo-pyridine, benzopyrazine, benzopyrazidine, benzopyrimidine, benzotriazine, indolizine, pyridopyridine, imidazopyrimidine, pyrazinopyrimidine, carbazole, aciridine, phenazine, benzoquinoline, phenoxazine, phenothiazine, acridizine, benzopteridine, phenanthroline and phenanthrene, each of which may also optionally be substituted.

[0070] The preferred alkyl groups include the methyl, ethyl, propyl, isopropyl, 1-butyl, 2-butyl, 2-methylpropyl, tert-butyl radical, pentyl, 2-methylbutyl, 1,1-dimethylpropyl, hexyl, heptyl, octyl, 1,1,3,3-tetramethylbutyl, nonyl, 1-decyl, 2-decyl, undecyl, dodecyl, pentadecyl and the eicosyl group.

[0071] The preferred cycloalkyl groups include the cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and the cyclooctyl group, each of which is optionally substituted with branched or unbranched alkyl groups.

[0072] The preferred alkanoyl groups include the formyl, acetyl, propionyl, 2-methylpropionyl, butyryl, valeroyl, pivaloyl, hexanoyl, decanoyl and the dodecanoyl group.

[0073] The preferred alkoxycarbonyl groups include the methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxy-carbonyl, tert-butoxycarbonyl, hexyloxycarbonyl, 2-methylhexyloxycarbonyl, decyloxycarbonyl or dodecyloxycarbonyl group.

[0074] The preferred alkoxy groups include alkoxy groups whose hydrocarbon radical is one of the aforementioned preferred alkyl groups.

[0075] The preferred cycloalkoxy groups include cycloalkoxy groups whose hydrocarbon radical is one of the aforementioned preferred cycloalkyl groups.

[0076] The preferred heteroatoms which are present in the R^{10} radical include oxygen, nitrogen, sulfur, boron, silicon and phosphorus, preference being given to oxygen and nitrogen.

[0077] The R^{10} radical comprises at least one, preferably at least two, preferentially at least three, heteroatoms.

[0078] The R^{10} radical in ester compounds of the formula (IV) preferably has at least 2 different heteroatoms. In this case, the R^{10} radical in at least one of the ester compounds of the formula (IV) may comprise at least one nitrogen atom and at least one oxygen atom.

[0079] Examples of ethylenically unsaturated, polar ester compounds of the formula (IV) include aminoalkyl (meth) acrylates, aminoalkyl (meth)acrylamides, hydroxyalkyl (meth)acrylates, heterocyclic (meth)acrylates and/or carbonyl-containing (meth)acrylates.

[0080] The hydroxyalkyl (meth)acrylates include

[0081] 2-hydroxypropyl (meth)acrylate,

[0082] 3,4-dihydroxybutyl (meth)acrylate,

[0083] 2-hydroxyethyl (meth)acrylate,

[0084] 3-hydroxypropyl (meth)acrylate,

[0085] 2,5-dimethyl-1,6-hexanediol (meth)acrylate and

[0086] 1,10-decanediol (meth)acrylate.

[0087] Appropriate carbonyl-containing (meth)acrylates include, for example,

[0088] 2-carboxyethyl (meth)acrylate,

[0089] carboxymethyl (meth)acrylate,

[0090] oxazolidinylethyl (meth)acrylate,

[0091] N-(methacryloyloxy)formamide,

[0092] acetonyl (meth)acrylate,

[0093] mono-2-(meth)acryloyloxyethyl succinate,

[0094] N-(meth)acryloylmorpholine,

[0095] N-(meth)acryloyl-2-pyrrolidinone,

[0096] N-(2-(meth)acryloyloxyethyl)-2-pyrrolidinone,

[0097] N-(3-(meth)acryloyloxypropyl)-2-pyrrolidinone,

[0098] N-(2-(meth)acryloyloxypentadecyl)-2-pyrrolidinone,

[0099] N-(3-(meth)acryloyloxyheptadecyl)-2-pyrrolidinone and

[0100] N-(2-(meth)acryloyloxyethyl)ethyleneurea.

[0101] 2-Acetoacetoxyethyl (meth)acrylate

[0102] The heterocyclic (meth)acrylates include

[0103] 2-(1-imidazolyl)ethyl (meth)acrylate,

[0104] 2-(4-morpholinyl)ethyl (meth)acrylate and

[0105] 1-(2-(meth)acryloyloxyethyl)-2-pyrrolidone.

[0106] Of particular interest are additionally aminoalkyl (meth)acrylates and aminoalkyl (meth)acrylatamides, for example

[0107] dimethylaminopropyl (meth)acrylate,

[0108] dimethylaminodiglykol (meth)acrylate,

[0109] dimethylaminoethyl (meth)acrylate,

[0110] dimethylaminopropyl (meth)acrylamide,

[0111] 3-diethylaminopentyl(meth)acrylate and

[0112] 3-dibutylaminohexadecyl (meth)acrylate.

[0113] In addition, it is possible to use phosphorus-, boron- and/or silicon-containing (meth)acrylates to prepare the polar segments D, such as

[0114] 2-(dimethylphosphato)propyl (meth)acrylate,

[0115] 2-(ethylenephosphito)propyl (meth)acrylate,

[0116] dimethylphosphinomethyl (meth)acrylate,

[0117] dimethylphosphonoethyl (meth)acrylate,

[0118] diethyl(meth)acryloyl phosphonate,

[0119] dipropyl(meth)acryloyl phosphate, 2-(dibutylphosphono)ethyl (meth)acrylate,

[0120] 2,3-butylene(meth)acryloylethyl borate,

[0121] methyldiethoxy(meth)acryloylethoxysilane,

[0122] diethylphosphatoethyl (meth)acrylate.

[0123] According to a very preferred embodiment heterocyclic vinyl compounds are used as dispersing monomers. Surprisingly, the heterocyclic vinyl compounds show improved properties in view of other dispersing monomers.

[0124] The preferred heterocyclic vinyl compounds include 2-vinylpyridine, 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3 dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, N-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane, vinylfuran, vinylthiophene, vinylthiolane, vinylthiazoles and hydrogenated vinylthiazoles, vinyloxazoles and hydrogenated vinyloxazoles, particular preference being given to using N-vinylimidazole and N-vinylpyrrolidone for functionalization.

[0125] The monomers detailed above can be used individually or as a mixture.

[0126] Of particular interest are especially polymers which comprise ester groups and are obtained using 2-hydroxypropyl methacrylate, 2-hydroxyethyl methacrylate, mono-2-methacryloyloxyethyl succinate, N-(2-methacryloyloxyethyl)ethyleneurea, 2-acetoacetoxyethyl methacrylate, 2-(4-morpholinyl)ethyl methacrylate, dimethylaminodiglycol methacrylate, dimethylaminoethyl methacrylate and/or dimethylaminopropylmethacrylamide.

[0127] Special improvements can be achieved with ester groups comprise polymers being obtained using N-vinyl-2-pyrrolidine and/or N-vinyl-2-pyrrolidone.

[0128] In addition to the dispersing monomers, a composition for preparing the graft layer may also comprise non-dispersing monomers which have been detailed above. These include especially ethylenically unsaturated ester compounds of the formulae (I), (II) and/or (III).

[0129] The proportion of dispersing repeat units, based on the weight of the polymers comprising ester groups, is preferably in the range from 0.5% by weight to 20% by weight, more preferably in the range from 1.5% by weight to 15% by weight and most preferably in the range from 2.5% by weight to 10% by weight. At the same time, these repeat units preferably form a segment-like structure within the polymer comprising ester groups, such that preferably at least 70% by weight, more preferably at least 80% by weight, based on the total weight of the dispersing repeat units, are part of a graft layer.

[0130] The present invention describes polymers which preferably have a high oil solubility. The term “oil-soluble” means that a mixture of a base oil and a polymer comprising ester groups is preparable without macroscopic phase formation, which has at least 0.1% by weight, preferably at least 0.5% by weight, of the polymers. The polymer may be present in dispersed and/or dissolved form in this mixture. The oil solubility depends especially on the proportion of the lipophilic side chains and on the base oil. This property is known to those skilled in the art and can be adjusted readily for the particular base oil via the proportion of lipophilic monomers.

[0131] Of particular interest, among others, are polymers which comprise ester groups and preferably have a weight-average molecular weight M_w in the range from 7500 to 1 000 000 g/mol, more preferably 10 000 to 600 000 g/mol and most preferably 15 000 to 80 000 g/mol.

[0132] The number-average molecular weight M_n may preferably be in the range from 5000 to 800 000 g/mol, more preferably 7500 to 500 000 g/mol and most preferably 10 000 to 80 000 g/mol.

[0133] According to a special embodiment of the present invention, the ester group containing polymer, preferably a polyalkyl(meth)acrylat may have a weight-average molecular weight M_w in the range from 2000 to 1 000 000 g/mol, especially from 20 000 to 800 000 g/mol, more preferably 40 000 to 500 000 g/mol and most preferably 60 000 to 250 000 g/mol.

[0134] According to a further aspect of the present invention, the ester group containing polymer, preferably a polyalkyl(meth)acrylat may have a number average molecular weight M_n in the range from 2 000 to 100 000 g/mol, especially from 4 000 to 60 000 g/mol and most preferably 5 000 to 30 000 g/mol.

[0135] Polymers having a high molecular weight are especially useful as viscosity index improvers. Polymers having a low molecular weight are especially useful as pour point depressants and flow improvers.

[0136] Additionally appropriate are polymers which comprise ester groups and whose polydispersity index M_w/M_n is in the range from 1 to 5, more preferably in the range from 1.05 to 4. The number-average and weight-average molecular weights can be determined by known processes, for example gel permeation chromatography (GPC).

[0137] According to a preferred embodiment of the present invention, the ester group containing polymer has a —CO—NR_2-peak in the range of 1689 to 1697 cm^{-1}, more preferably in the range of 1689 to 1692 cm^1 as measured by FTIR spectroscopy (25° C.)

[0138] The polymer comprising ester groups may have a variety of structures. Preferably, the polymer may especially be present as a graft copolymer.

[0139] The polymers comprising ester groups for use in accordance with the invention can be obtained in various ways. A preferred process consists in free-radical graft copolymerization which is known per se, wherein, for example, a nonpolar graft base is obtained in a first step, onto which dispersing monomers are grafted in a second step.

[0140] Therefore, according to a preferred embodiment, the ester group containing polymer preferably is a graft copolymer having an nonpolar alkyl (meth)acrylate polymer as graft base and an dispersing monomer as graft layer.

[0141] Customary free-radical polymerization, which is especially suitable for preparing graft copolymers, is detailed in K. Matyjaszewski, T. P. Davis, Handbook of Radical Polymerization, Wiley Interscience, Hoboken 2002. In general, a polymerization initiator and a chain transferer are used for that purpose.

[0142] The usable initiators include the azo initiators widely known in the technical field, such as AIBN and 1,1-azobiscyclohexanecarbonitrile, and also peroxy compounds such as methyl ethyl ketone peroxide, acetylacetone peroxide, dilauryl peroxide, tert-butyl per-2-ethylhexanoate, ketone peroxide, tert-butyl peroctoate, methyl isobutyl ketone peroxide, cyclohexanone peroxide, dibenzoyl peroxide, tert-butyl peroxybenzoate, tert-butyl peroxyisopropylcarbonate, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy-3,5,5-trimethylhexanoate, dicumyl peroxide, 1,1-bis (tert-butylperoxy)cyclohexane, 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, cumyl hydroperoxide, tert-butyl hydroperoxide, bis(4-tert-butylcyclohexyl) peroxydicarbonate, mixtures of two or more of the aforementioned compounds with one another, and mixtures of the aforementioned compounds with compounds which have not been mentioned but can likewise form free radicals. Suitable chain transferers are in particular oil-soluble mercaptans, for example n-dodecyl mercaptan or 2-mercaptoethanol, or else chain transferers from the class of the terpenes, for example terpinolene.

[0143] The polymerization may be carried out at standard pressure, reduced pressure or elevated pressure. The polymerization temperature too is uncritical. However, it is generally in the range of −20°-200° C., preferably 50°-150° C. and more preferably 80°-130° C.

[0144] The polymerization may be carried out with or without solvent. The term solvent is to be understood here in a broad sense. The solvent is selected according to the polarity of the monomers used, preference being given to using 100N oil, relatively light gas oil and/or aromatic hydrocarbons, for example toluene or xylene.

[0145] In addition to the ester group containing polymer the lubricant used in the motor of the present invention includes base oil. Preferred base oils include especially mineral oils, synthetic oils and natural oils.

[0146] Mineral oils are known per se and commercially available. They are generally obtained from mineral oil or crude oil by distillation and/or refining and optionally further purification and finishing processes, the term mineral oil including in particular the higher-boiling fractions of crude or mineral oil. In general, the boiling point of mineral oil is higher than 200° C., preferably higher than 300° C., at 5000 Pa. The production by low-temperature carbonization of shale oil, coking of bituminous coal, distillation of brown coal with exclusion of air, and also hydrogenation of bituminous or brown coal is likewise possible. Accordingly, mineral oils have, depending on their origin, different proportions of aromatic, cyclic, branched and linear hydrocarbons.

[0147] In general, a distinction is drawn between paraffin-base, naphthenic and aromatic fractions in crude oils or mineral oils, in which the term paraffin-base fraction represents longer-chain or highly branched isoalkanes, and naphthenic fraction represents cycloalkanes. In addition, mineral oils, depending on their origin and finishing, have different fractions of n-alkanes, isoalkanes having a low degree of branching, known as mono-methyl-branched paraffins, and compounds having heteroatoms, in particular O, N and/or S, to which a degree of polar properties are attributed. However, the assignment is difficult, since individual alkane molecules may have both long-chain branched groups and cycloalkane radicals, and aromatic parts. For the purposes of the present invention, the assignment can be effected to DIN 51 378, for example. Polar fractions can also be determined to ASTM D 2007.

[0148] The proportion of n-alkanes in preferred mineral oils is less than 3% by weight, the fraction of O-, N- and/or S-containing compounds less than 6% by weight. The fraction of the aromatics and of the mono-methyl-branched paraffins is generally in each case in the range from 0 to 40% by weight. In one interesting aspect, mineral oil comprises mainly naphthenic and paraffin-base alkanes which have generally more than 13, preferably more than 18 and most preferably more than 20 carbon atoms. The fraction of these compounds is generally 60% by weight, preferably 80% by weight, without any intention that this should impose a restriction. A preferred mineral oil contains 0.5 to 30% by weight of aromatic fractions, 15 to 40% by weight of naphthenic fractions, 35 to 80% by weight of paraffin-base fractions, up to 3% by weight of n-alkanes and 0.05 to 5% by weight of polar compounds, based in each case on the total weight of the mineral oil.

[0149] An analysis of particularly preferred mineral oils, which was effected by means of conventional processes such as urea separation and liquid chromatography on silica gel, shows, for example, the following constituents, the percentages relating to the total weight of the particular mineral oil used:

n-alkanes having approx. 18 to 31 carbon atoms:
0.7-1.0%,
slightly branched alkanes having 18 to 31 carbon atoms:
1.0-8.0%,
aromatics having 14 to 32 carbon atoms:
0.4-10.7%,
iso- and cycloalkanes having 20 to 32 carbon atoms:
60.7-82.4%,
polar compounds:
0.1-0.8%,
loss:
6.9-19.4%.

[0150] An improved class of mineral oils (reduced sulfur content, reduced nitrogen content, higher viscosity index, lower pour point) results from hydrogen treatment of the mineral oils (hydroisomerization, hydrocracking, hydrotreatment, hydrofinishing). In the presence of hydrogen, this essentially reduces aromatic components and builds up naphthenic components.

[0151] Valuable information with regard to the analysis of mineral oils and a list of mineral oils which have a different composition can be found, for example, 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", Blackie Academic & Professional, London, 2nd ed. 1997; or J. Bartz: "Additive für Schmierstoffe", Expert-Verlag, Renningen-Malmsheim 1994.

[0152] Synthetic oils include organic esters, for example diesters and polyesters, polyalkylene glycols, polyethers, synthetic hydrocarbons, especially polyolefins, among which preference is given to polyalphaolefins (PAOs), silicone oils and perfluoroalkyl ethers. In addition, it is possible to use synthetic base oils originating from gas to liquid (GTL), coal to liquid (CTL) or biomass to liquid (BTL) processes. They are usually somewhat more expensive than the mineral oils, but have advantages with regard to their performance.

[0153] Natural oils are animal or vegetable oils, for example neatsfoot oils or jojoba oils.

[0154] Base oils for lubricant oil formulations are divided into groups according to API (American Petroleum Institute). Mineral oils are divided into group I (non-hydrogen-treated) and, depending on the degree of saturation, sulfur content and viscosity index, into groups II and III (both hydrogen-treated). PAOs correspond to group IV. All other base oils are encompassed in group V.

[0155] These lubricant oils may also be used as mixtures and are in many cases commercially available.

[0156] The concentration of the polymers comprising ester groups in the lubricant oil composition is preferably in the range of 0.01 to 30% by weight, more preferably in the range of 0.1-20% by weight and most preferably in the range of 0.5-10% by weight, based on the total weight of the composition.

[0157] In addition to the polymers comprising ester groups for use in accordance with the invention, the lubricant oil compositions detailed here may also comprise further additives. These additives include VI improvers, pour point improvers and DI additives (dispersants, detergents, defoamers, corrosion inhibitors, antioxidants, antiwear and extreme pressure additives, friction modifiers).

[0158] The additionally usable VI improvers include especially polyalkyl (meth)acrylates having 1 to 30 carbon atoms in the alcohol group (PAMA; partly N/O-functional with advantageous additional properties as dispersants, antiwear additives and/or friction modifiers), which differ from the copolymers detailed in claim **1**, and poly(iso)butenes (PIB), fumarate-olefin copolymers, styrene-maleate copolymers, hydrogenated styrene-diene copolymers (HSD) and olefin copolymers (OCP).

[0159] The pour point improvers include especially polyalkyl (meth)acrylates (PAMA) having 1 to 30 carbon atoms in the alcohol group.

[0160] Compilations of VI improvers and pour point improvers for lubricant oils are also detailed 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”, Blackie Academic & Professional, London, 2nd ed. 1997; or J. Bartz: “Additive für Schmierstoffe”, Expert-Verlag, Renningen-Malmsheim 1994.

[0161] Appropriate dispersants include poly(isobutylene) derivatives, e.g. poly(isobutylene)succinimides (PIBSIs); ethylene-propylene oligomers with N/O functionalities.

[0162] The preferred detergents include metal-containing compounds, for example phenoxides; salicylates; thio-phosphonates, especially thiopyrophosphonates, thio-phosphonates and phosphonates; sulfonates and carbonates. As metals, these compounds may comprise especially calcium, magnesium and barium. These compounds may be used preferably in neutral or overbased form.

[0163] Of particular interest are additionally defoamers, which are in many cases divided into silicone-containing and silicone-free defoamers. The silicone-containing defoamers include linear poly(dimethylsiloxane) and cyclic poly(dimethylsiloxane). The silicone-free defoamers which may be used are in many cases polyethers, for example poly(ethylene glycol) or tributyl phosphate.

[0164] In a particular embodiment, the inventive lubricant oil compositions may comprise corrosion inhibitors. These are in many cases divided into antirust additives and metal passivators/deactivators. The antirust additives used may, inter alia, be sulfonates, for example petroleumsulfonates or (in many cases overbased) synthetic alkylbenzenesulfonates, e.g. dinonylnaphthenesulfonates; carboxylic acid derivatives, for example lanolin (wool fat), oxidized paraffins, zinc naphthenates, alkylated succinic acids, 4-nonylphenoxy-acetic acid, amides and imides (N-acylsarcosine, imidazoline derivatives); amine-neutralized mono- and dialkyl phosphates; morpholine, dicyclohexylamine or diethanolamine. The metal passivators/deactivators include benzotriazole, tolyltriazole, 2-mercaptobenzothiazole, dialkyl-2,5-dimercapto-1,3,4-thiadiazole; N,N'-disalicylideneethylenediamine, N,N'-disalicylidenepropylenediamine; zinc dialkyldithiophosphates and dialkyl dithiocarbamates.

[0165] A further preferred group of additives is that of antioxidants. The antioxidants include, for example, phenols, for example 2,6-di-tert-butylphenol (2,6-DTB), butylated hydroxytoluene (BHT), 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol); aromatic amines, especially alkylated diphenylamines, N-phenyl-1-naphthylamine (PNA), polymeric 2,2,4-trimethyldihydroquinone (TMQ); compounds containing sulfur and phosphorus, for example metal dithiophosphates, e.g. zinc dithiophosphates (ZnDTP), “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 and methylene bis(dialkyldithiocarbamate); organophosphorus compounds, for example triaryl and trialkyl phosphites; organocopper compounds and overbased calcium- and magnesium-based phenolates and salicylates.

[0166] The preferred antiwear (AW) and extreme pressure (EP) additives include phosphorus compounds, for example trialkyl phosphates, triaryl phosphates, e.g. tricresyl phosphate, amine-neutralized mono- and dialkyl phosphates, ethoxylated mono- and dialkyl phosphates, phosphites, phosphonates, phosphines; compounds containing sulfur and phosphorus, for example metal dithiophosphates, e.g. zinc C_{3-12}dialkyldithiophosphates (ZnDTPs), ammonium dialkyldithiophosphates, antimony dialkyldithiophosphates, molybdenum dialkyldithiophosphates, lead dialkyldithiophosphates, “OOS triesters”=reaction products of dithiophosphoric acid with activated double bonds from olefins, cyclopentadiene, norbornadiene, α-pinene, polybutene, acrylic esters, maleic esters, triphenylphosphorothionate (TPPT); compounds containing sulfur and nitrogen, for example zinc bis(amyl dithiocarbamate) or methylenebis(di-n-butyl dithiocarbamate); sulfur compounds containing elemental sulfur and H_2S-sulfurized hydrocarbons (diisobutylene, terpene); sulfurized glycerides and fatty acid esters; overbased sulfonates; chlorine compounds or solids such as graphite or molybdenum disulfide.

[0167] A further preferred group of additives is that of friction modifiers. The friction modifiers used may include mechanically active compounds, for example molybdenum disulfide, graphite (including fluorinated graphite), poly(trifluoroethylene), polyamide, polyimide; compounds which 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 which form polymer-like layers, for example ethoxylated dicarboxylic acid partial esters, dialkyl phthalates, methacrylates, unsaturated fatty acids, sulfurized olefins or organometallic compounds, for example molybdenum compounds (molybdenum dithiophosphates and molybdenum dithiocarbamates MoDTC) and their combinations with ZnDTPs, copper-containing organic compounds.

[0168] Some of the additives detailed above may fulfill multiple functions. ZnDTP, for example, is primarily an antiwear additive and extreme pressure additive, but also has the character of an antioxidant and corrosion inhibitor (here: metal passivator/deactivator).

[0169] The additives detailed above are described in more detail, inter alia, in T. Mang, W. Dresel (eds.): “Lubricants and Lubrication”, Wiley-VCH, Weinheim 2001; J. Bartz: “Additive für Schmierstoffe”, Expert-Verlag, Renningen-Malmsheim 1994; R. M. Mortier, S. T. Orszulik (eds.): “Chemistry and Technology of Lubricants”, Blackie Academic & Professional, London, 2^{nd} ed. 1997.

[0170] Preferred lubricant oil compositions have a viscosity, measured at 40° C. to ASTM D 445, in the range of 10 to 120 mm^2/s, more preferably in the range of 20 to 100 mm^2/s. The kinematic viscosity KV_{100} measured at 100° C. is preferably at least 5.0 mm^2/s, more preferably at least 5.2 mm^2/s and most preferably at least 5.4 mm^2/s.

[0171] In a particular aspect of the present invention, preferred lubricant oil compositions have a viscosity index determined to ASTM D 2270 in the range of 100 to 400, more preferably in the range of 125 to 325 and most preferably in the range of 150 to 250.

[0172] Furthermore, lubricant compositions for the use in the motor of the present invention may preferably comprise a High Temperature High Shear (HTHS) viscosity of at least 2.4 mPas, more preferably at least 2.6 mPas as measured at 150° C. according to ASTM D4683. According to a further aspect of the present invention the lubricant may preferably comprise a high temperature high shear of at most 10 mPas, especially at most 7 mPas more preferably at most 5 mPas as measured at 100° C. according to ASTM D4683. The difference between the High Temperature High Shear (HTHS) viscosities as measure at 100° C. and 150° C. $HTHS_{100}$-$HTHS_{150}$ preferably comprises at most 4 mPas, especially at most 3.3 mPas and more preferably at most 2.5 mPas. The ratio of the High Temperature High Shear (HTHS) viscosity measured at 100° C. ($HTHS_{100}$) to the High Temperature High Shear (HTHS) viscosity measured at 150° C. ($HTHS_{150}$-$HTHS_{100}$/$HTHS_{150}$ preferably comprises at most at most 2.0 mPas, especially at most 1.9 mPas. High Temperature High Shear (HTHS) viscosity can be determined according to D4683.

[0173] In addition thereto, the lubricant useful as component of the present motor may comprises a high shear stability index (SSI). According to a useful embodiment of the present invention, the shear stability index (SSI) as measured according to ASTM D2603 Ref. B (12.5 minutes sonic treatment) could preferably amount to 35 or less, more preferably to 20 or less. Preferably, lubricants comprising a shear stability index (SSI) as measured according to DIN 51381 (30 cycles Bosch-pump) of at most 5, especially at most 2 and more preferably at most 1 could be used.

[0174] The lubricant useful for the present invention can preferably be designed to meet the requirements of the SAE classifications as specified in SAE J300. E.g. the requirements of the viscosity grades 0W, 5W, 10W, 15W, 20W, 25W, 20, 30, 40, 50, and 60 (single-grade) and 0W-40, 10W-30, 10W-60, 15W-40, 20W-20 and 20W-50 (multi-grade) could be adjusted.

[0175] Preferably, the lubricant composition meets the gasoline engine oil quality specifications ILSAC's GF-5, especially the emulsion retention bench test stating that a mixture of formulated oil (80%), E85 fuel (10%), and water (10%) must form a stable emulsion for at least 24 hours after mixing at 0 and 25° C.

[0176] Consequently, the lubricant of the present invention may contain at least about 1%, especially at least 5%, particularly at least 10% by volume of water. Astonishingly, such high amounts of water do not impart unduly high lowering of the motor characteristics such as life time, cold run performance and fuel consumption.

[0177] Surprisingly, the present invention provides a lubricant forming highly stable emulsions with water. Therefore, a specific aspect of the present invention is the use of polymers having a high polarity as emulsion stabilizer in lubricants.

[0178] The invention will be illustrated in detail hereinafter with reference to examples and comparative examples, without any intention that this should impose a restriction. Unless otherwise specified, the percentages are weight percent.

PREPARATION EXAMPLES

List of Abbreviations

[0179] MMA=methyl methacrylate
N1214MA=methacrylic acid ester of NAFOL1214
L125MA=methacrylic acid ester of LIAL125
A1618MA=methacrylic acid ester of ALFOL 1620
DMAEMA=dimethylaminoethyl methacrylate
NVP=N-vinyl-2-pyrrolidone
nDDM=n-dodecylmercapton
tBPO=t-butylperoctoate
tBPB=t-butylperbenzoate

Comparative Example 1

[0180] 107.5 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 100° C. A mixture of 500 grams of a L125MA, 8.5 grams of nDDM and 2 grams of tBPO was added to the round bottom flask via an addition funnel over the course of two hours. The temperature of the reaction mixture was maintained at 100° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 100° C. for an additional 2 hours. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Comparative Example 2

[0181] 107.5 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 100° C. A mixture of 375 grams of N1214MA, 125 grams of MMA, 7.5 grams of nDDM and 2 grams of tBPO was added to the round bottom flask via an addition funnel over the course of two hours. The temperature of the reaction mixture was maintained at 100° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 100° C. for an additional 2 hours. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Comparative Example 3

[0182] 111 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 100° C. A mixture of 385 grams of N1214MA, 100 grams of MMA, 15 grams of DMAEMA, 4.0 grams of nDDM and 2 grams of tBPO was added to the round bottom flask via an addition funnel over the course of two hours. The temperature of the reaction mixture was maintained at 100° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 100° C. for an additional 2 hours. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Comparative Example 4

[0183] 112.5 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 100° C. A mixture of 225 grams of N1214MA, 275 grams of A1618MA, 5.0 grams of nDDM and 2 grams of tBPO was added to the round bottom flask via an addition funnel over the course of two hours. The temperature of the reaction mixture was maintained at 100° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 100° C. for an additional 2 hours. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Comparative Example 5

[0184] 325 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 110° C. A mixture of 415 grams of N1214MA, 70 grams of MMA, 15 grams of NVP and 5.0 grams of tBPO was added to the round bottom flask via an addition funnel over the course of two hours. The temperature of the reaction mixture was maintained at 110° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 110° C. for an additional 2 hours. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Example 1

[0185] 325 grams of mineral oil were charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 100° C. A mixture of 485 grams of N1214MA and 3.75 grams of tBPO was added to the round bottom flask via an addition funnel over the course of three hours. The temperature of the reaction mixture was maintained at 100° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 100° C. for an additional 2 hours. The temperature was raised to 130° C. and 15 grams of NVP was added to the reaction mixture with 2 grams of tBPB. The reaction mixture was held for an additional hour at 130° C. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Example 2

[0186] 325 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 110° C. A mixture of 415 grams of N1214MA, 70 grams of MMA and 5.0 grams of tBPO was added to the round bottom flask via an addition funnel over the course of three hours. The temperature of the reaction mixture was maintained at 110° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 110° C. for an additional 2 hours. The temperature was raised to 130° C. and 15 grams of NVP was added to the reaction mixture with 2 grams of tBPB. The reaction mixture was held for an additional hour at 130° C. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Example 3

[0187] 325 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 110° C. A mixture of 210 grams of N1214MA, 275 grams of A1618MA and 7.5 grams of tBPO was added to the round bottom flask via an addition funnel over the course of three hours. The temperature of the reaction mixture was maintained at 110° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 110° C. for an additional 2 hours. The temperature was raised to 130° C. and 15 grams of NVP was added to the reaction mixture with 2 grams of tBPB. The reaction mixture was held for an additional hour at 130° C. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Example 4

[0188] 325 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 110° C. A mixture of 320 grams of N1214MA, 160 grams of L125MA, 5 grams of MMA and 7.5 grams of tBPO was added to the round bottom flask via an addition funnel over the course of three hours. The temperature of the reaction mixture was maintained at 110° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 110° C. for an additional 2 hours. The temperature was raised to 130° C. and 25 grams of NVP was added to the reaction mixture with grams of tBPB. The reaction mixture was held for an additional hour at 130° C. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Example 5

[0189] 325 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 110° C. A mixture of 475 grams of N1214MA and 7.5 grams of tBPO was added to the round bottom flask via an addition funnel over the course of three hours. The temperature of the reaction mixture was maintained at 110° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 110° C. for an additional 2 hours. The temperature was raised to 130° C. and 25 grams of NVP was added to the reaction mixture with 2 grams of tBPB. The reaction mixture was held for an additional hour at 130° C. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Example 6

[0190] 325 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and were heated under an atmosphere of nitrogen to 110° C. A mixture of 450 grams of a N1214MA and 7.5 grams of tBPO was added to the round bottom flask via an addition funnel over the course of three hours. The temperature of the reaction mixture was maintained at 110° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 110° C. for an additional 2 hours. The temperature was raised to 130° C. and 50 grams of NVP was added to the reaction mixture with 2 grams of tBPB. The reaction mixture was held for an additional hour at 130° C. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Example 7

[0191] 325 grams of mineral oil was charged to a four-neck round glass bottom flask equipped with glass stirrer, condenser and thermocouple and heated under an atmosphere of nitrogen to 110° C. A mixture of 425 grams of N1214MA, 25 grams of MMA, 50 grams of NVP and 5.0 grams of tBPO was added to the round bottom flask via an addition funnel over the course of two hours. The temperature of the reaction mixture was maintained at 110° C. throughout the course of the addition. Following the complete of addition the mixture, the reaction mixture was held at 110° C. for an additional 2 hours. Additional mineral oil was added to achieve the desired concentration of polymer in oil.

Use Examples

Emulsion Stability

[0192] 1.0 grams of the experimental additive was mixed with 99.0 grams of an API Group I oil mixture having a kinematic viscosity of 5.4 cSt at 100° C. 80 mL of this blend of additive and oil was transferred to a 100 mL graduated cylinder to which 10 mL of an ethanol/heptane (85/15 v/v) solution and 10 mL of water was added. This mixture was rapidly stirred for 5 minutes and allowed to stand at room temperature for 24 hours. A passing test was defined as the lack of a water layer after the end of the 24 hour period.

FTIR Spectroscopy

[0193] The additives were placed between silver chloride plates and sandwiched into a Teflon cell holder. Using a Thermo Nicolet Avatar 370 FT-IR, the additives were scanned 32 times at a resolution of 4 cm^{-1}. A background scan was taken followed by the sample scan. The peak location of the disubstituted amine, —CO—NR_2—, is observed as a shoulder peak to the strong carbonyl, C═O, stretching peak.

TABLE 1

Additive compositions

		Comparative Examples Comparative Example Number				
		1	2	3	4	5
Amount of monomer	MMA	—	25	20	—	14
	N1214MA	—	75	77	45	83
	L125MA	100	—	—	—	—
	A1618MA	—	—	—	55	—
	DMAEMA	—	—	3	—	—
	NVP	—	—	—	—	3
% polymer		88	70	70	65	65
Mw, g/mol		25,000	40,000	100,000	75,000	90,000
FTIR Analysis, cm^{-1}		n.o.	n.o.	n.o.	n.o.	1696
Emulsion Stability		Fail	Fail	Fail	Fail	Fail

TABLE 2

Additive compositions

		Examples				
Example Number		1	2	3	4	5
Amount of monomer	MMA	—	14	—	1	—
	N1214MA	97	83	42	64	88
	L125MA	—	—	—	32	—
	A1618MA	—	—	55	—	6
	DMAEMA	—	—	—	—	—
	NVP	3	3	3	3	5
% polymer		55	57	57	58	57
Mw, g/mol		220,000	150,000	120,000	115,000	155,000
FTIR Analysis, cm^{-1}		1691	1691	1691	1691	1690
Emulsion Stability		Pass	Pass	Pass	Pass	Pass

		Examples	
Example Number		6	7
Amount of monomer	MMA	—	5
	N1214MA	90	85
	L125MA		
	A1618MA	—	—
	DMAEMA	—	—
	NVP	10	10
% polymer		57	65
Mw, g/mol		300,000	54,000
FTIR Analysis, cm^{-1}		1696	1695
Emulsion Stability		Pass	Pass

[0194] The results in Tables 1 and 2 demonstrate that lubricant compositions containing copolymers as described by the invention are capable of improving the emulsion retention of a lubricant oil formulation.

[0195] In addition thereto, the properties of the present polymers have been tested using modified emulsion stability test.

[0196] The results in Table 3 were obtained when the concentration of example additive was varied.

TABLE 3

Additional results from modified emulsion stability test*

Example	Amount of Additive	Emulsion Stability
6	0.15	Pass
9	0.15	Pass

[0197] The results in Table 4 were obtained when example additives were mixed with SAE 5W-30 engine oil.

TABLE 4

Additional results from modified emulsion stability test*

Example	Amount of Additive	Emulsion Stability
8	0.15	Pass
9	0.15	Pass

1: A motor, comprising a lubricant composition,

wherein the motor is suitable for a flexible-fuel vehicle or a dual-fuel vehicle and the lubricant composition comprises at least one ester group containing polymer having a high polarity.

2: The motor according to claim **1**, comprising a compression rate of at least 10:1.

3: The motor according to claim **1**, comprising a fuel injection pump.

4: The motor according to claim **1**, comprising a multi valve.

5: The motor according to claim **1**,

wherein the motor meets a requirement of exhaust emission standard Euro 5.

6: The motor according to claim **1**, comprising an exhaust gas recirculation.

7: The motor according to claim **1**, comprising a secondary-air system.

8: The motor according to claim **1**,

wherein the at least one ester group containing polymer is a statistical copolymer comprising at least 7% by weight of dispersing repeat units derived from a dispersing monomer.

9: The motor according to claim **8**,

wherein the at least one ester group containing polymer is a statistical copolymer comprising at least 7% by weight of dispersing repeat units derived from at least one heterocyclic vinyl compound.

10: The motor according to claim **1**,

wherein the at least one ester group containing polymer is a graft copolymer having an nonpolar polymer as a graft base and a dispersing monomer as a graft layer.

11: The motor according to claim **10**,

wherein the at least one ester group containing polymer comprises at least one heterocyclic vinyl compound as the graft layer.

12: The motor according to claim **11**

wherein the at least one ester group containing polymer is the graft copolymer comprising from 0.5 to 10% by weight of dispersing repeat units derived from the at least one heterocyclic vinyl compound.

13: The motor according to claim **12**,

wherein the at least one ester group containing polymer is the graft copolymer comprising from 1 to 5% by weight of dispersing repeat units derived from the at least one heterocyclic vinyl compound.

14: The motor according to claim **1**,

wherein the at least one ester group containing polymer has a —CO—NR_2— peak of 1689 to 1692 cm^{-1} as measured by FTIR spectroscopy.

15: The motor according to claim **1**,

wherein the at least one ester group containing polymer is selected from the group consisting of a polyalkyl (meth) acrylate (PAMA), a polyalkyl fumerate, a polyalkyl maleate, and a combination thereof.

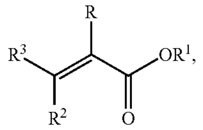
16: The motor according to claim **1**,

wherein the at least one ester group containing polymer has a weight-average molecular weight of from 10 000 to 600 000 g/mol.

17: The motor according to claim **1**,

wherein the at least one ester group containing polymer is a graft copolymer comprising a graft base obtained by a process comprising polymerizing a monomer composition comprising:

a) from 0 to 40% by weight, based on a weight of the monomer composition for preparing a nonpolar segment, of an ethylenically unsaturated ester compound of formula (I):



(I)

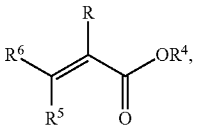
wherein

R is hydrogen or methyl,

R^1 is a linear or branched alkyl radical having 1 to 6 carbon atoms, and

R^2 and R^3 are each independently hydrogen or a group of formula —COOR' in which R' is hydrogen or an alkyl group having 1 to 6 carbon atoms,

b) from 5 to 100% by weight, based on the weight of the monomer composition for preparing the nonpolar segment, of an ethylenically unsaturated ester compound of formula (II):



(II)

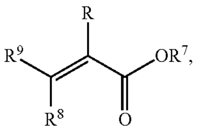
wherein

R is hydrogen or methyl,

R^4 is a linear or branched alkyl radical having 7 to 15 carbon atoms, and

R^5 and R^6 are each independently hydrogen or a group of the formula —COOR' in which R'' is hydrogen or an alkyl group having 7 to 15 carbon atoms,

c) from 0 to 80% by weight, based on the weight of the monomer composition for preparing the nonpolar segment, of an ethylenically unsaturated ester compound of formula (III):


(III)

wherein

R is hydrogen or methyl,

R^7 is a linear or branched alkyl radical having 16 to 30 carbon atoms, and

R^8 and R^9 are each independently hydrogen or a group of formula —COOR''' in which R''' is hydrogen or an alkyl group having 16 to 30 carbon atoms, and

d) from 0 to 50% by weight, based on the weight of the monomer composition for preparing the hydrophobic segments, of a comonomer.

18: The motor according to claim **1**,

wherein the at least one ester group containing polymer comprises at least one heterocyclic vinyl compound selected from the group consisting of 2-vinylpyridine, 3-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, N-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, 2-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane, vinylfuran, vinylthiophene, vinylthiolane, a vinylthiazole and a hydrogenated vinylthiazole, a vinyloxazole, a hydrogenated vinyloxazole, and a combination thereof.

19: The motor according to claim **1**,

wherein the lubricant composition comprises at least one additional additive which is not a polymer comprising an ester group having a high polarity.

20: The motor as claimed in claim **19**,

wherein the at least one additive is a viscosity index improver, a pour point improver, a dispersant, a detergent, a defoamer, a corrosion inhibitor, an antioxidant, an antiwear additive, an extreme pressure additive, a friction modifier, or a combination thereof.

21: The motor as claimed in claim **20**,

wherein the antiwear additive, the extreme pressure additive, or both is selected from the group consisting of a phosphorous compound, a compound comprising sulfur and phosphorous, a compound comprising sulfur and nitrogen, a sulfur compound comprising elemental sulfur and ¾S-sulfurized hydrocarbon, a sulfurized glyceride and a fatty acid ester, an overbased sulfonate, a chlorine compound, graphite, molybdenum disulfide, and a combination thereof.

22: A process for producing an emulsion stabilizer in a lubricant, comprising:

contacting the lubricant with a polymer comprising an ester group having a high polarity.

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