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(54) **TRANSMISSION OIL FORMULATION FOR REDUCING FUEL CONSUMPTION**

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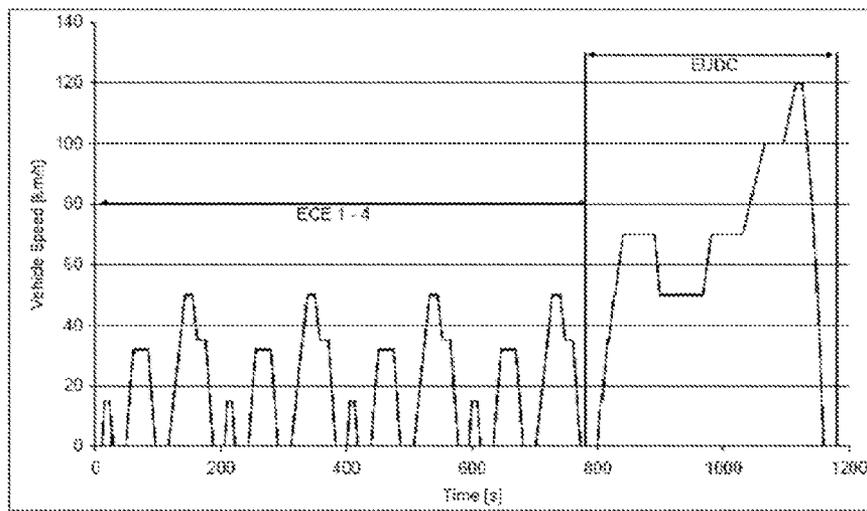
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(57) **ABSTRACT**

The present invention relates to a transmission oil formulation comprising a base oil and a copolymer obtained by free-radical polymerization from a monomer composition. The invention also relates to the use of the transmission oil formulation as transmission oil for reducing the fuel consumption of motor vehicles.

Figure 1

2.3 New European Driving Cycle (NEDC)



TRANSMISSION OIL FORMULATION FOR REDUCING FUEL CONSUMPTION

[0001] The present invention relates to a transmission oil formulation having advantageous viscosity properties, by means of which it is possible to lower the fuel consumption of motor vehicles.

[0002] The reduction of fuel consumption of motor vehicles is becoming ever more important for various reasons. As well as many improvements to the construction of the motor vehicles themselves, efforts are also being made to minimize churning losses caused by the lubricants, for example by motor and transmission oils.

[0003] In order to achieve this aim, the fresh oil viscosity of the lubricant is typically lowered. For automatic transmission oils, this is the reason why the DEXRON-VI specification from General Motors, for example, requires that the kinematic viscosity of fresh oil at 100° C. be not more than 6.4 mm²/s.

[0004] However, there are limits to lowering of the fresh oil viscosity, since a reduction in the viscosity also leads to a reduction in the lubricant film thickness. An insufficient lubricant film thickness leads to increased wear and a shorter lifetime of the machine parts to be lubricated. In the worst case, the lubricant film thickness is so low that the surface roughness of the materials is greater than the lubricant film thickness. Under these conditions, the machine parts come into point contact, which leads to pressure and load spikes in underlying material layers and ultimately to material fatigue.

[0005] Prolonged mechanical stress typically leads to a reduction in the viscosity of the lubricant, since the mechanical stress, for example, reduces the size of polymeric constituents of the lubricant. This effect is also referred to as permanent shear loss. Since permanent shear loss leads to lasting reduction in lubricant film thickness, lubricants are required to not go below a particular minimum viscosity even after a long period of stress. A recognized method for characterizing the permanent shear loss of a lubricant is the tapered roller bearing test to CEC-L-45-A-99. For automatic transmission oils, for example, the DEXRON-VI specification specifies a kinematic minimum viscosity at 100° C. of 5.5 mm²/s after a 20 h tapered roller bearing test.

[0006] In order to lower fuel consumption while complying with the minimum viscosity, it is customary to increase the viscosity index of the lubricant. The viscosity index (VI) describes the temperature dependence of the viscosity of a lubricant. Lubricants having a low viscosity index exhibit a greater temperature dependence of the change in viscosity than those having a high viscosity index. An increase in the viscosity index at constant viscosity at a particular temperature means that the viscosity is less at lower temperatures than for a comparable lubricant with a lower viscosity index. Reduced viscosity at lower temperatures, in turn, reduces churning losses and hence fuel consumption. However, this advantage is restricted to the warm-up phase of a motor vehicle.

[0007] There is therefore an interest in providing a lubricant through which fuel consumption can be reduced at higher operating temperatures as well.

[0008] Lubricant film thickness is not determined exclusively by the viscosity of the lubricant, but is a function of viscosity and the relative sliding or rolling speed of the machine parts moving relative to one another. At the same viscosity, the lubricant film thickness rises with speed. At high speed, a relatively low viscosity of lubricant would

accordingly be sufficient to assure an adequate lubricant film thickness. A low viscosity would be advantageous at this operating point, since the reduced fluid friction would result in less energy being consumed, which leads to a fuel saving.

[0009] At high speeds, the shear forces that occur typically result automatically in a reduction in the viscosity of the lubricant. This so-called shear loss may be permanent, as occurs, for example, in the event of lasting mechanical stress on lubricants. However, shear loss may also be temporary, such that the original viscosity is re-established in the event that the speed is reduced and the associated shear forces are lower. Temporary shear loss as a result of shear forces is also referred to as shear dilution.

[0010] An ideal lubricant would accordingly have maximum shear dilution in order to reduce fuel consumption at high sliding or rolling speed. At the same time, an ideal lubricant would have only a low permanent shear loss in order to maximize the lifetime of the machine parts.

[0011] Lubricant properties are typically improved by addition of additives to lubricant oils.

[0012] For example, U.S. Pat. No. 5,565,130 and U.S. Pat. No. 5,597,871 disclose using comb polymers based, for example, on polybutadiene as viscosity index improvers. However, no satisfactory improvement in fuel consumption is disclosed therein.

[0013] WO 2007/003238 A1 describes oil-soluble comb polymers based on polyolefin-based macromonomers, especially polybutadiene-based methacrylic esters, and C1 to 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. However, no improvement in coefficient of traction and fuel consumption is disclosed.

[0014] WO 2009/007147 A1 discloses the use of comb polymers based on polyolefin-based macromonomers, especially polybutadiene-based methacrylic esters, and C1 to C10 alkyl methacrylates for improving the fuel consumption of motor vehicles. However, the comb polymers are disclosed only as additives for motor oil.

[0015] WO 2010/102903 A1 discloses the use of comb polymers as antifatigue additives for transmission, motor and hydraulic oils. However, no reduction in fuel consumption is described.

[0016] DE 10 2009 001 447 A1 describes the use of comb polymers for improving the load-bearing capacity of hydraulic oils having a high viscosity index. A high viscosity index and associated higher viscosities of the formulation at operating temperatures of about 80° C., for a given ISO grade, enable the reduction of fuel consumption in hydraulic systems. Of particular significance in this context is the improvement of the volumetric efficiency of the hydraulic systems. This is favorably influenced by higher lubricant viscosities, since leakage flows in the hydraulic pump are minimized as a result. However, improvement in the volumetric efficiency is accompanied by reduced mechanical efficiency. In the case of transmission oils, however, mechanical efficiency is crucial, which is the reason why low viscosities and, in particular, low coefficients of traction of the lubricant oil are required in the transmission oil sector. Therefore, the development of energy-efficient hydraulic oils does not permit any conclusions about the development of transmission oils.

[0017] WO 2012/025901 A1 discloses the use of comb polymers in lubricants in combination with particular friction

modifiers. There is no disclosure of combinations of comb polymers and base oils specifically matched to the demands of transmission oils.

[0018] Since the properties of the lubricants disclosed in the prior art are still unsatisfactory in relation to use as a transmission oil and in respect of the reduction in fuel consumption, it is the aim of the present invention to provide a transmission oil formulation having a kinematic minimum viscosity at 100° C. of 5.5 mm²/s to ASTM D445 after a 20 h tapered roller bearing test CEC-L-45-A-99, and simultaneously high shear dilution. In addition, the kinematic fresh oil viscosity at 100° C. should be not more than 6.4 mm²/s to ASTM D445 and preferably about 6.0 mm²/s. The transmission oil formulation should also have a high viscosity index, preferably a viscosity index of greater than 180 to ASTM D2270, more preferably greater than 190.

[0019] In addition, the transmission oil formulation should have a low coefficient of traction. The coefficient of traction is the force required to move a load, divided by the load. The numerical value of the coefficient expresses how easy it is to shear a lubricant film. Transmission oils ideally have a low coefficient of traction because, when the coefficient of traction is low, less energy is consumed because of lubricant shearing.

[0020] This object is achieved by a transmission oil formulation comprising

(i) a base oil having a kinematic viscosity at 100° C. of at least 1.5 mm²/s to ASTM D445 and an aromatics content of less than 15% by weight to ASTM D 2007; and

(ii) a copolymer obtained by free-radical polymerization from a monomer composition, said monomer composition comprising the following monomers:

(A) 30% to 50% by weight of an ester of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene, where the hydroxylated hydrogenated polybutadiene has a number-average molar mass M_n to DIN 55672-1 of 4000 to 6000 g/mol;

(B1) 0.2% to 50% by weight of methyl(meth)acrylate;

(B2) 0.2% to 50% by weight of butyl(meth)acrylate;

(B3) 0.2% to 5% by weight of C5-C30 alkyl(meth)acrylates;

(C) 10% to 50% by weight of styrene monomers having 8 to 17 carbon atoms; and

(D) 0% to 5% by weight of further free-radically polymerizable comonomers,

where the sum total of the proportions by weight of monomers (B1), (B2) and (B3) is at least 10% by weight.

[0021] The specified proportions by weight of components (A) to (D) are based on the total weight of the monomer composition.

[0022] In a preferred embodiment, the proportions of components (A) to (D) add up to 100% by weight.

[0023] More preferably, the sum total of the proportions by weight of monomers (B1) to (B3) is at least 15% by weight, most preferably 15% to 45% by weight.

[0024] The transmission oil formulation of the invention meets the prerequisite mentioned in terms of fresh oil viscosity, minimum viscosity by the tapered roller bearing test and viscosity index. In addition, the transmission oil formulation of the invention has an advantageous temporary shear loss as a result of shear forces.

[0025] It has also been found that, surprisingly, the inventive combination of a base oil having a low aromatics content with the copolymer described leads to a reduction in the coefficient of traction of the transmission oil formulation.

[0026] The use of the transmission oil formulation of the invention additionally leads to a decrease in fuel consumption in a motor vehicle rolling test bed test, this effect being observed not just during the cold start phase but also after the transmission oil formulation has heated up.

[0027] The copolymer for use in accordance with the invention as component (ii) of the transmission oil formulation can be obtained via free-radical polymerization of the monomers mentioned. It is preferable here for the double bonds of the ethylenically unsaturated groups and vinyl groups of the monomers mentioned to be opened with formation of covalent bonds between the monomers. The copolymer that forms is a comb polymer.

[0028] 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 monomers mentioned. The ester groups of the (meth)acrylic esters, the phenyl radicals of the styrene monomers and the substituents of the further free-radically polymerizable comonomers form the side chains of the comb polymer.

[0029] The styrene monomers having 8 to 17 carbon atoms for use in accordance with the invention are styrene and substituted styrene. Examples of styrene monomers having 8 to 17 carbon atoms are 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. Particular preference is given to unsubstituted styrene.

[0030] Preferably, the monomer composition comprises 10%-45% by weight of styrene monomers having 8 to 17 carbon atoms.

[0031] The term “(meth)acrylic acid” refers to acrylic acid, methacrylic acid and mixtures of acrylic acid and methacrylic acid. The term “(meth)acrylate” refers to esters of acrylic acid, esters of methacrylic acid or mixtures of esters of acrylic acid and methacrylic acid.

[0032] Preferably, the monomer composition comprises, as monomer (B1), 0.2% to 45% by weight of methyl methacrylate. Likewise preferably, the monomer composition comprises, as monomer (B2), 0.2% to 45% by weight of butyl methacrylate and/or butyl acrylate, more preferably n-butyl methacrylate and/or n-butyl acrylate.

[0033] The C5 to C30 alkyl(meth)acrylates for use in accordance with the invention are esters of (meth)acrylic acid and alcohols having 5 to 30 carbon atoms. The term “C5 to C30 alkyl(meth)acrylates” encompasses individual (meth)acrylic esters with an alcohol of a particular length, and likewise mixtures of (meth)acrylic esters with alcohols of different lengths.

[0034] The suitable C5 to C30 alkyl(meth)acrylates include, for example, pentyl(meth)acrylate, hexyl(meth)acrylate, 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, 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 eicosyltetracontyl(meth)acrylate.

[0035] Particularly preferred C5 to C30 alkyl(meth)acrylates are methacrylic esters of a linear C12 to C14 alcohol mixture (C12 to C14 alkyl methacrylate).

[0036] The hydroxylated hydrogenated polybutadiene for use in accordance with the invention has a number-average molar mass M_n of 4000 to 6000 g/mol, preferably 4000 to 5000 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.

[0037] The number-average molar mass 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.

[0038] 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.

[0039] Preferred hydroxylated hydrogenated polybutadienes can be obtained according to GB 2270317.

[0040] 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).

[0041] 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.

[0042] 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.

[0043] 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.

[0044] 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.

[0045] 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.

[0046] 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).

[0047] Furthermore, the present hydroxylated hydrogenated polybutadiene can be converted to an ester by reaction with an acid chloride such as (meth)acryloyl chloride.

[0048] 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-tetramethylpiperidinoxyl radical and/or hydroquinone monomethyl ether.

[0049] 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.

[0050] The monomer composition of the invention may comprise, as monomer (D), up to 5% by weight of further free-radically polymerizable comonomers. Preferably, the monomer composition comprises, as component (D), 0.2% to 5% by weight of further free-radically polymerizable comonomers.

[0051] Monomer (D) does not include the compounds already described as monomers (A) to (C).

[0052] The further comonomers which are suitable as comonomers for preparation of copolymers by free-radical polymerization are known to those skilled in the art. Suitable monomers are described, for example, in WO 2010/102903 or in Mortier, Roy M., Malcolm F. Fox, and Stefan T. Orszulik, "Chemistry and technology of lubricants" (Springer Science+ Business Media, 2010).

[0053] In a preferred embodiment, the further free-radically polymerizable comonomers are selected from the group consisting of maleic anhydride, (di)alkyl fumarates, (di)alkyl maleates, aminoalkyl(meth)acrylates, aminoalkyl(meth)acrylamides, hydroxyalkyl(meth)acrylates, carbonyl-containing (meth)acrylates, heterocyclic(meth)acrylates, heterocyclic vinyl compounds and mixtures thereof. In this context, the use of aminoalkyl(meth)acrylamides in particular is advantageous.

[0054] If maleic anhydride is used as monomer, it can be reacted with primary or secondary amines after polymeriza-

tion. Such processes are described, for example, in WO 2007/070845 and DE 10 2007 031 247. Particular preference is given to primary amines. Suitable amines for this purpose are, for example, N,N-dimethylaminopropylamine, N-morpholinopropylamine and N-phenyl-1,4-phenylenediamine.

[0055] The notation “(di)alkyl fumarate” or “(di)alkyl maleate” means that it is possible to use monoesters, diesters and mixtures of esters of fumaric acid or of maleic acid.

[0056] Suitable (di)alkyl fumarates include monomethyl fumarate, dimethyl fumarate, monoethyl fumarate, diethyl fumarate, methyl ethyl fumarate, monobutyl fumarate, dibutyl fumarate, dipentyl fumarate and dihexyl fumarate. Preferred (di)alkyl fumarates comprise 1 to 10, preferably 1 to 8 and more preferably 1 to 4 carbon atoms in each of the alcohol groups. The alcohol groups here may be linear or branched.

[0057] Suitable (di)alkyl maleates include monomethyl maleate, dimethyl maleate, monoethyl maleate, diethyl maleate, methyl ethyl maleate, monobutyl maleate, dibutyl maleate. Preferred (di)alkyl maleates comprise 1 to 10, preferably 1 to 8 and more preferably 1 to 4 carbon atoms in each of the alcohol groups. The alcohol groups here may be linear or branched.

[0058] Suitable aminoalkyl(meth)acrylates are, for example, N,N-dimethylaminoethyl(meth)acrylate, N,N-dimethylaminopropyl(meth)acrylate, N,N-diethylaminopentyl(meth)acrylate and N,N-dibutylaminohexadecyl(meth)acrylate.

[0059] An example of a suitable aminoalkyl(meth)acrylamide is N,N-dimethylaminopropylmethacrylamide.

[0060] Suitable hydroxyalkyl(meth)acrylates include 2-hydroxypropyl(meth)acrylate, 3,4-dihydroxybutyl(meth)acrylate, 2-hydroxyethyl(meth)acrylate, 3-hydroxypropyl(meth)acrylate, 2,5-dimethyl-1,6-hexanediol(meth)acrylate and 1,10-decanediol(meth)acrylate.

[0061] Suitable carbonyl-containing (meth)acrylates are, for example, 2-carboxyethyl(meth)acrylate, carboxymethyl(meth)acrylate, oxazolidinylethyl(meth)acrylate, N-(methacryloyloxy)formamide, acetyl(meth)acrylate, mono-2-(meth)acryloyloxyethyl succinate, N-(meth)acryloylmorpholine, N-(meth)acryloyl-2-pyrrolidinone, N-(2-(meth)acryloyloxyethyl)-2-pyrrolidinone, N-(3-(meth)acryloyloxypropyl)-2-pyrrolidinone, N-(2-(meth)acryloyloxy-pentadecyl)-2-pyrrolidinone, N-(3-(meth)acryloyloxy-heptadecyl)-2-pyrrolidinone, N-(2-(meth)acryloyloxyethyl)ethyleneurea and 2-acetoacetoxyethyl(meth)acrylate.

[0062] Suitable heterocyclic(meth)acrylates include 2-(1-imidazolyl)ethyl(meth)acrylate, 2-(4-morpholinyl)ethyl(meth)acrylate, 1-(2-methacryloyloxyethyl)-2-pyrrolidinone, N-methacryloylmorpholine, N-methacryloyl-2-pyrrolidinone, N-(2-methacryloyloxyethyl)-2-pyrrolidinone and N-(3-methacryloyloxypropyl)-2-pyrrolidinone.

[0063] Suitable heterocyclic vinyl compounds are, for example, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine, 3-ethyl-4-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, vinylpyrimidine, vinylpiperidine, 9-vinylcarbazole, 3-vinylcarbazole, 4-vinylcarbazole, 1-vinylimidazole, 2-methyl-1-vinylimidazole, N-vinylpyrrolidone, N-vinylpyrrolidine, 3-vinylpyrrolidine, N-vinylcaprolactam, N-vinylbutyrolactam, vinyloxolane, vinylfuran, vinyloxazoles and hydrogenated vinyloxazoles.

[0064] The copolymer for use in accordance with the invention can be characterized on the basis of its molar branching level (“f-branch”). The molar branching level refers to the percentage in mol % of macromonomers (component (A))

used, based on the total molar amount of all the monomers in the monomer composition. The molar amount of the macromonomers used is calculated on the basis of the number-average molar mass M_n of the macromonomers. The calculation of the branching level is described in detail in WO 2007/003238 A1, especially on pages 13 and 14, to which reference is made here explicitly.

[0065] The copolymer for use in accordance with the invention preferably has a molar branching level of 1.0 to 3.1 mol %, more preferably 1.2 to 2.8 mol % and most preferably 1.4 to 1.8 mol %.

[0066] The copolymer for use in accordance with the invention can be prepared by free-radical polymerization and by related methods of controlled free-radical polymerization, for example ATRP (=atom transfer radical polymerization) or RAFT (=reversible addition fragmentation chain transfer).

[0067] Standard free-radical polymerization is detailed, inter alia, in Ullmann’s Encyclopedia of Industrial Chemistry, Sixth Edition. In general, a polymerization initiator and optionally a chain transfer agent are used for this purpose.

[0068] The usable initiators include 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-ethylhexanoyloxy)-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 unspecified compounds which can likewise form free radicals. Suitable chain transfer agents are especially oil-soluble mercaptans, for example n-dodecyl mercaptan or 2-mercaptoethanol, or else chain transfer agents from the class of the terpenes, for example terpinolene.

[0069] The ATRP method is known per se. It is assumed that this is a “living” free-radical polymerization, but no restriction is intended by the description of the mechanism. In these processes, a transition metal compound is reacted with a compound having a transferable atom group. This involves transfer of the transferable atom group to the transition metal compound, as a result of which the metal is oxidized. This reaction forms a free radical which adds onto ethylenic groups. However, the transfer of the atom group to the transition metal compound is reversible, and so the atom group is transferred back to the growing polymer chain, which results in formation of a controlled polymerization system. It is accordingly possible to control the formation of the polymer, the molecular weight and the molecular weight distribution.

[0070] This reaction regime is described, for example, by J.-S. Wang, et al., J. Am. Chem. Soc., vol. 117, p. 5614-5615 (1995), by Matyjaszewski, Macromolecules, vol. 28, p. 7901-7910 (1995). In addition, patent applications WO 96/30421, WO 97/47661, WO 97/18247, WO 98/40415 and WO 99/10387 disclose variants of the above-elucidated ATRP. In addition, the polymers of the invention can also be obtained via RAFT methods, for example. This method is described in detail, for example, in WO 98/01478 and WO 2004/083169.

[0071] The polymerization can be conducted under standard pressure, reduced pressure or elevated pressure. The polymerization temperature is also uncritical. In general, however, it is in the range from -20 to 200°C ., preferably 50 to 150°C . and more preferably 80 to 130°C .

[0072] The polymerization can be conducted with or without solvent. The term "solvent" should be understood here in a broad sense. The solvent is selected according to the polarity of the monomers used, it being possible with preference to use 100N oil, comparatively light gas oil and/or aromatic hydrocarbons, for example toluene or xylene.

[0073] As well as an above-detailed free-radical copolymerization of the monomers described, the inventive copolymers can also be obtained by polymer-analogous reactions.

[0074] In this case, a polymer is first prepared from low molecular weight monomers in a known manner, and is then converted. In this case, the backbone of the copolymer may be synthesized from a reactive monomer such as maleic anhydride, methacrylic acid or else glycidyl methacrylate and other unreactive short-chain backbone monomers. In this case, the above-detailed initiator systems such as t-butyl perbenzoate or t-butyl per-2-ethylhexanoate and chain transfer agents such as n-dodecyl mercaptan may be used.

[0075] In a further step, it is possible, for example in an alcoholysis or aminolysis, to generate the side chains, which are also referred to as arms. In this case, it is possible to use the above-detailed hydroxylated hydrogenated polybutadienes.

[0076] The reaction of the backbone polymer formed at first with macroalcohols corresponds essentially to the reactions of the macroalcohols with low molecular weight compounds detailed above in connection with the synthesis of the macromonomers.

[0077] Thus, the macroalcohols can be joined to the present maleic anhydride or methacrylic acid functionalities in the backbone polymer with catalysis, for example, by p-toluenesulfonic acid or methanesulfonic acid. By addition of low molecular weight alcohols and/or amines such as n-butanol or N-(3-aminopropyl)morpholine, this polymer-analogous reaction is conducted to complete conversions, especially in the case of maleic anhydride backbones.

[0078] In the case of glycidyl functionalities in the backbone, an addition of the macroalcohol can be conducted, so as to form comb polymers.

[0079] In addition, the macroalcohols can be reacted with a backbone containing short-chain ester functionalities by a polymer-analogous alcoholysis in order to generate comb polymers.

[0080] As well as the reaction of the backbone polymer with macromolecular compounds, it is possible to react suitably functionalized polymers, which have been obtained by conversion of low molecular weight monomers, with further low molecular weight polymers to form comb polymers. In this case, the backbone polymer prepared at first has several functionalities which serve as initiators of multiple graft polymerizations.

[0081] Thus, it is possible to initiate a multiple cationic polymerization of isobutene, which leads to comb polymers having polyolefin side arms. Suitable methods for graft copolymerizations of this kind include the above-detailed ATRP and/or RAFT methods, in order to obtain comb polymers having a defined architecture.

[0082] The transmission oil formulation of the invention comprises a base oil as component (i). This base oil has a

kinematic viscosity at 100°C . of at least $1.5\text{ mm}^2/\text{s}$ to ASTM D445 and an aromatics content of less than 15% by weight to ASTM D 2007.

[0083] The kinematic viscosity at 100°C . preferably $2\text{ mm}^2/\text{s}$, more preferably $3\text{ mm}^2/\text{s}$, to ASTM D445.

[0084] The aromatics content of the base oil refers to the proportion in % by weight, based on the weight of oil, of compounds having at least one aromatic structural element, and is determined to ASTM D 2007 by gel absorption chromatography. Preferably, the aromatics content to ASTM D 2007 is less than 10% by weight, preferably less than 5% by weight.

[0085] In a preferred embodiment, the base oil is additionally characterized by a small proportion of aromatic carbon atoms of not more than 2%, preferably not more than 0.5%, more preferably not more than 0.1%.

[0086] The proportion of aromatic carbon atoms is determined in the context of the present invention by infrared spectroscopy by the method of G. Brandes. This method was described in detail by G. Brandes in "Die Strukturgruppen von Erdölfractionen I. Mitteilung: Die Strukturgruppenanalyse mit Hilfe der Ultrarotspektroskopie", Brennstoff-Chemie 37 (17/18), 263 (1956). In this method, the amount of aromatic carbon atoms C_A is determined on the basis of the absorption band at 1610 cm^{-1} , and the amount of paraffinic carbon atoms C_P on the basis of the band at 720 cm^{-1} . For calibration, several oils having different aromatics and paraffin contents are analyzed, and C_A and C_P are determined by the Brandes method. The amount of naphthenic carbon atoms C_N is found from the difference from 100%, since no characteristic absorption can be assigned to naphthenes.

[0087] It has been found here, surprisingly, that particularly the combination of the copolymer for use in accordance with the invention with a base oil having a low proportion of aromatic carbon atoms or a low aromatics content leads to a reduction in the coefficient of traction.

[0088] A base oil is typically defined as an oil having a boiling point between 260 and 566°C . (500 and 1050 F), consisting of hydrocarbons having 18 to 40 carbon atoms. The base oil for use in accordance with the invention may be a mineral oil, a synthetic oil or a natural oil. It is likewise possible to use mixtures of various base oils. These oils are common knowledge.

[0089] Mineral oils are known per se and are commercially available. They are generally obtained from mineral oil or crude oil by distillation and/or refining and optionally further cleaning and finishing processes, the term "mineral oil" especially including the higher-boiling components of crude oil or mineral oil. In general, the boiling point of mineral oil is higher than 200°C ., preferably higher than 300°C ., at 5000 Pa . Production by low-temperature carbonization of shale oil, coking of hard coal, distillation of brown coal with exclusion of air, and hydrogenation of hard coal or brown coal is likewise possible. Accordingly, mineral oils, depending on their origin, have different proportions of aromatic, cyclic, branched and linear hydrocarbons.

[0090] A reduction in the aromatics content of mineral oils can be achieved by hydrogen treatment of the mineral oils. In this case, aromatic components are reduced in by hydrogenation and naphthenic components are built up.

[0091] Synthetic oils include organic esters, for example diesters and polyesters, polyalkylene glycols, polyethers, synthetic hydrocarbons, especially polyolefins, among which polyalphaolefins (PAO) are preferred, silicone oils and per-

fluoroalkyl 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 costly than the mineral oils, but have advantages in terms of their performance.

[0092] Natural oils are animal or vegetable oils, for example neatsfoot oils or jojoba oils.

[0093] Base oils for lubricant oil formulations are divided into groups according to the American Petroleum Institute (API) as a function of saturation level, sulfur content and viscosity index (API 1509, Annex E—API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils, September 2011). Mineral oils are subdivided into group I (non-hydrogen-treated) and, depending on the saturation level, 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. More preferably, the base oil for use in accordance with the invention is a group III oil as defined by the American Petroleum Institute, since the combination of the copolymer of the invention with a group III oil leads to an exceptional reduction in the coefficient of traction of the transmission oil formulation. A group III oil has a viscosity index to ASTM D2270 of at least 120, a proportion of saturated compounds to ASTM D 2007 of at least 90%, an aromatics content to ASTM D 2007 of less than 10% by weight and a sulfur content to one of the standards ASTM D1552, D2622, D3120, D4294 and D4927 of not more than 0.03% (API 1509, Annex E—API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils, September 2011). Group III oils for use in accordance with the invention additionally have the abovementioned kinematic viscosity.

[0094] The transmission oil formulation of the invention comprises preferably 60% to 99.9% by weight of base oil (component (i)) based on the total weight of the transmission oil formulation, preferably 60% to 90% by weight, more preferably 70% to 80% by weight, based on the total weight of the transmission oil formulation.

[0095] The concentration of the copolymer (component (ii)) in the transmission oil formulation is preferably in the range from 0.1% to 40% by weight, based on the total weight of the transmission oil formulation, more preferably in the range of 0.2%-20% by weight and most preferably in the range of 0.5%-10% by weight, based on the total weight of the transmission oil formulation.

[0096] In a particular embodiment, the proportions of components (i) and (ii) add up to 100% by weight.

[0097] The transmission oil formulation of the invention may also comprise, as component (iii), a second polymer selected from the group of the hydrogenated polybutadienes, hydroxylated hydrogenated polybutadienes or (meth)acrylic esters thereof, polyalkyl(meth)acrylates and mixtures thereof. Preferably, the transmission oil formulation comprises 0% to 3% by weight of component (iii) based on the total weight of the transmission oil formulation, preferably 0.005% to 2% by weight, based on the total weight of the transmission oil formulation.

[0098] The hydrogenated polybutadienes and the hydroxylated hydrogenated polybutadienes or the methacrylic esters thereof preferably have a number-average molar mass M_n of 4000 to 6000 g/mol. The hydroxylated hydrogenated polybutadienes may, for example, be the hydroxylated hydrogenated polybutadienes described, especially hydroxyethyl- or hydroxypropyl-terminated hydrogenated polybutadiene or

(meth)acrylic esters thereof. The polyalkyl(meth)acrylates may, for example, be polymerization products of the (meth)acrylic esters described.

[0099] If the transmission oil formulation contains component (iii), the proportions by weight of components (i), (ii) and (iii) may add up to 100% by weight.

[0100] The transmission oil formulation of the invention may also contain, as component (iv), further additives selected from the group consisting of dispersants, defoamers, detergents, antioxidants, antiwear additives, extreme pressure additives, friction modifiers, anticorrosion additives, dyes and mixtures thereof.

[0101] Preferably, the total concentration of additives is up to 20% by weight, more preferably 0.05% to 15% by weight, more preferably 5% to 15% by weight, based on the total weight of the transmission oil formulation. Dispersants (including borated dispersants) are preferably used in a concentration of 0% to 5% by weight, detergents in a concentration of 0.05% to 3% by weight, anticorrosion additives in a concentration of 0.05% to 2% by weight, friction modifiers in a concentration of 0.05% to 5% by weight, antiwear and extreme pressure additives each in a concentration of 0.1% to 3% by weight, antioxidants in a concentration of 0.5% to 1.5% by weight, defoamers in a concentration of 10 to 2500 ppm and dyes in a concentration of 0.01% to 1% by weight. The concentration is based in each case on the total weight of the transmission oil formulation.

[0102] According to the composition, the proportions by weight of components (i), (ii), (iii) and (iv) or (i), (ii) and (iv) may add up to 100% by weight.

[0103] Appropriate dispersants include poly(isobutylene) derivatives, for example poly(isobutylene)succinimides (PIBSIs), including borated PIBSIs; ethylene-propylene oligomers having N/O functionalities.

[0104] 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.

[0105] The suitable 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, 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-mercaptopbenzimidazoles; 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.

[0106] The preferred antiwear and extreme pressure 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 having sulfur and phosphorus, for example metal dithiophosphates, e.g. zinc di-C₃₋₁₂-alkyldithiophosphates (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, triphenyl phosphorothionate (TPPT); compounds having sulfur and nitrogen, for example zinc bis(amyldithiocarbamate) or methylenebis(di-n-butyl dithiocarbamate); sulfur compounds with elemental sulfur and H₂S sulfurized hydrocarbons (diisobutylene, terpene); sulfurized glycerides and fatty acid esters; overbased sulfonates; chlorine compounds or solids, such as graphite or molybdenum disulfide.

[0107] 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.

[0108] Some of the compounds listed 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).

[0109] 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".

[0110] The present invention also relates to the use of the above-described transmission oil formulation as transmission oil for reducing the fuel consumption of motor vehicles.

[0111] It is possible to use this transmission oil formulation in manual, automated manual, double clutch or DSG, automatic and continuous variable (CVC) transmissions. Particular preference is given to using the transmission oil formulation as transmission oil for automatic transmissions. In addition, the transmission oil formulation described can be used in transfer cases and axles or differentials.

DESCRIPTION OF ILLUSTRATIONS

[0112] FIG. 1 shows the speed profile of the New European Driving Cycle (NEDC) for determination of the fuel consumption of motor vehicles.

EXAMPLES

[0113] In the examples which follow, the following abbreviations are used:

MM1	methacrylic ester of a hydroxypropyl-terminated hydrogenated polybutadiene having $M_n = 4750$ g/mol
AMA1	methacrylic ester of a synthetic iso-C11-C15 alcohol mixture, iso content about 60%
AMA2	methacrylic ester of a synthetic C10-C15 alcohol mixture, iso content about 15%
AMA3	methacrylic ester of a linear C12-C14 alcohol mixture
AMA4	mixture of a methacrylic ester of a synthetic C10-C15 alcohol mixture, iso content about 15%, with a methacrylic ester of a linear C16-C18 alcohol mixture
BMA	n-butyl methacrylate
MMA	methyl methacrylate
Sty	styrene
BA	n-butyl acrylate
t-DDM	tert-dodecyl mercaptan
DMAPMAm	N,N-dimethylaminomethacrylamide
BDtBPB	2,2-bis(tert-butylperoxy)butane
n-DDM	dodecyl mercaptan
tBPO	tert-butyl peroctoate

Synthesis of a Hydroxylated Hydrogenated Polybutadiene

[0114] The macroalcohol prepared was a hydroxypropyl-terminated hydrogenated polybutadiene having mean molar mass $M_n = 4750$ g/mol.

[0115] 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 Nexbase 3020 (base oil of API group II, kinematic viscosity to ASTM D 445 at 100° C. of 2.1 to 2.3 mm²/S) was used for dilution to a polymer content of 70% by weight.

[0116] 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 MM1

[0117] 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 Nexbase 3020 "entrained" into the copolymer syntheses described further down was taken into account accordingly.

Synthesis of Copolymers

Copolymer 1

[0118] In a beaker, the following reaction mixture was made up: 87.9 g of 70% macromonomer solution in oil, 3.9 g of AMA3, 27.3 g of BMA, 51.9 g of Sty, 0.3 g of MMA, 5.1 g of DMAPMam, 65.0 g of Shell Risella 907 (light naphthenic/paraffinic base oil) and 8.6 g of Nexbase 3020. A 500 mL 4-neck round-bottom flask with saber stirrer, nitrogen blanketing, thermometer, regulated oil bath and reflux condenser was initially charged with 75 g of the reaction mixture and heated to 120° C. while stirring. During the heating phase, nitrogen was passed through the reaction flask for inertization. On attainment of 120° C., 0.09 g of BDtBPB was added to the reaction flask; at the same time, the feed consisting of the rest of the reaction mixture and 0.21 g of BDtBPB was started. The feed time was 3 hours; the reaction temperature was kept constant at 120° C. 2 and 5 hours after feeding had ended, another 0.30 g each time of BDtBPB was added, and the contents of the flask were diluted the next day by addition of 102.9 g of Nexbase 3020. A clear, highly viscous solution was obtained.

Copolymer 2

[0119] As copolymer 1, but with the following reaction mixture: 90.0 g of 70% macromonomer solution in oil, 0.3 g of AMA3, 19.2 g of BMA, 59.7 g of Sty, 0.3 g of MMA, 7.5 g of BA, 65.0 g of Shell Risella 907 (light naphthenic/paraffinic base oil) and 8.0 g of Nexbase 3020.

Copolymer 3

[0120] As copolymer 1, but with the following reaction mixture: 82.5 g of 70% macromonomer solution in oil, 7.4 g of AMA3, 63.0 g of BMA, 16.5 g of Sty, 0.3 g of MMA, 5.1 g of DMAPMam, 65.0 g of Shell Risella 907 (light naphthenic/paraffinic base oil) and 10.3 g of Nexbase 3020.

Copolymer 4

[0121] A 500 mL 4-neck round-bottom flask with saber stirrer, nitrogen blanketing, thermometer, regulated oil bath and reflux condenser was initially charged with 90.0 g of 70% macromonomer solution in oil, 0.3 g of AMA3, 0.3 g of BMA, 26.7 g of Sty, 59.7 g of MMA and 73 g of o-xylene, and heated to 120° C. while stirring. During the heating phase, nitrogen was passed through the reaction flask for inertization. On attainment of 120° C., 0.30 g of BDtBPB was added to the reaction flask; the reaction temperature was kept constant at 120° C. 2 and 5 hours after the first BDtBPB addition, another 0.30 g each time of BDtBPB was added, and the contents of the flask were diluted the next day by addition of 110.9 g of Nexbase 3020 and Shell Risella 907. The o-xylene was subsequently drawn off by applying reduced pressure. A highly viscous solution with whitish turbidity was obtained.

Copolymer 5

[0122] As copolymer 1, but with the following reaction mixture: 90.0 g of 70% macromonomer solution in oil, 0.3 g of AMA3, 26.7 g of BMA, 59.7 g of Sty, 0.3 g of MMA, 65.0 g of Shell Risella 907 (light naphthenic/paraffinic base oil) and 8.0 g of Nexbase 3020.

Copolymer 6 (Comparative Polymer)

[0123] In a beaker, the following reaction mixture was made up: 126.4 g of AMA2, 129.4 g of AMA1, 1.5 g of AMA4, 29.8 g of MMA, 5.1 g of DMAPMam and 4.1 g of n-DDM. A 500 mL 4-neck round-bottom flask with saber stirrer, nitrogen blanketing, thermometer, regulated oil bath and reflux condenser was initially charged with 108 g of 100N oil and 12 g of the reaction mixture, and heated to 100° C. while stirring. During the heating phase, nitrogen was passed through the reaction flask for inertization. On attainment of 100° C., 0.13 g of tBPO was added to the reaction flask; at the same time, the feed consisting of the rest of the reaction mixture and 0.70 g of tBPO was started. The feed time was 3.5 hours; the reaction temperature was kept constant at 100° C. 2 hours after the feed had ended, another 0.58 g of tBPO was added and the mixture was stirred at 100° C. overnight. A clear, viscous solution was obtained.

Copolymer 7 (Comparative Polymer)

[0124] A 500 mL 4-neck round-bottom flask with saber stirrer, nitrogen blanketing, thermometer, regulated oil bath and reflux condenser was initially charged with 241.1 g of AMA, 33.8 g of MMA, 114.6 g of 150N oil, 4.1 g of n-DDM and 3.0 g of t-DDM. The mixture was heated to 110° C. while stirring. During the heating phase, nitrogen was passed through the reaction flask for inertization. On attainment of 110° C., a mixture of 0.69 g of tBPO and 2.06 g of 150N oil was metered in by means of a syringe pump within 3 hours. 1 hour after the feed had ended, another 0.55 g of tBPO was added and the mixture was left to continue to react at 110° C. overnight. A clear, viscous solution was obtained.

Copolymer 8 (Comparative Polymer)

[0125] A 500 mL 4-neck round-bottom flask with saber stirrer, nitrogen blanketing, thermometer, regulated oil bath and reflux condenser was initially charged with 34.3 g of 70% macromonomer solution, 7.5 g of AMA3, 100.5 g of BMA, 18.0 g of Sty, 65.0 g of Shell Risella 907 (light naphthenic/paraffinic base oil) and 24.7 g of 100N oil. The mixture was heated to 120° C. while stirring. During the heating phase, nitrogen was passed through the reaction flask for inertization. On attainment of 120° C., 0.3 g of BDtBPB was added. 3 and 5 hours after the first BDtBPB addition, another 0.3 g each time of BDtBPB was added and the mixture was left to continue to react at 120° C. overnight. The next day, the contents of the flask were diluted by addition of 125 g of 150N oil. A clear, viscous solution was obtained.

Copolymer 9 (Comparative Polymer)

[0126] As copolymer 8, except that the initial charge was 25.7 g of 70% macromonomer solution, 7.5 g of AMA3, 106.5 g of BMA, 18.0 g of Sty, 65.0 g of Shell Risella 907 (light naphthenic/paraffinic base oil) and 27.3 g of 100N oil.

Copolymer 10 (Comparative Polymer)

[0127] As copolymer 8, except that the initial charge was 25.7 g of 70% macromonomer solution, 7.5 g of AMA3, 124.5 g of BMA, 65.0 g of Shell Risella 907 (light naphthenic/paraffinic base oil) and 27.3 g of 100N oil.

[0128] Table 1 shows an overview of the monomer compositions for the copolymer syntheses. Copolymers 1, 2, 4 and 5 are copolymers of the invention.

TABLE 1

	Copolymer									
	1	2	3	4	5	6	7	8	9	10
	Inv.	Inv.	Inv.	Inv.	Inv.	Comp.	Comp.	Comp.	Comp.	Comp.
MM1	41.0	42.0	38.5	42.0	42.0			16.0	12.0	12.0
AMA1						44.4	87.7			
AMA2						43.4				
AMA3	2.6	0.2	4.9	0.2	0.2			5.0	5.0	5.0
AMA4						0.5				
BMA	18.2	12.8	42.0	0.2	17.8			67.0	71.0	83.0
BA		5.0								
Sty	34.6	39.8	11.0	17.8	39.8			12.0	12.0	
MMA	0.2	0.2	0.2	39.8	0.2	9.9	12.3			
DMAPMAm	3.4		3.4			1.8				
f-branch	1.62	1.59	1.69	1.43	1.6	0.00	0.00	0.47	0.33	0.35

[0129] The calculations of the molar branching level (“f-branch”) are based on a macromonomer conversion of 94%, meaning that all the copolymers still contain residual macromonomer and are thus a polymer mixture of copolymer and hydroxypropyl-terminated hydrogenated polybutadiene. These polymers are not separated. The transmission oil formulations formulated from these copolymer additives thus still contain a polymer mixture.

Transmission Oil Formulations

[0130] The abovementioned copolymers were used to produce transmission oil formulations (Table 2). Transmission oil formulations E1 to E5 are formulations of the invention. Formulation CE6 is a comparative formulation known from the prior art.

[0131] The base oil used was Nexbase 3030 (available from Neste Oil N.V., Belgium). Nexbase 3030 is an API group III base oil having a proportion of aromatic carbon atoms (% CA) below the detection limit of the IR method (<0.1%).

[0132] The pour point depressant used is a copolymer of C12 to C18 methacrylates from Evonik Oil Additives. The DI package is a DEXRON VI-compatible DI package without viscosity improver.

[0133] The base oil viscosity of the formulations E1 to E5 and CE6 was 3.8 mm²/s at 100° C.

TABLE 2

	Transmission oil formulation					
	E1	E2	E3	E4	E5	CE 6
Copolymer 1	5.2					
Copolymer 2		5.4				
Copolymer 3			5.4			
Copolymer 4				10.7		
Copolymer 5					5.7	
Copolymer 6						8.5
DI package	15.0	15.0	15.0	15.0	15.0	15.0
Pour point depressant	0.3	0.3	0.3	0.3	0.3	0.3
Nexbase 3030	79.5	79.3	79.3	74.0	79.0	76.2

[0134] Also produced were comparative oil formulations according to Table 3 based on a 150 N formulation oil. The base oil viscosity of these formulations was 5.4 mm²/s at 100° C. These formulations were used to examine the lack of stability of copolymers 6 to 10 (see below).

TABLE 3

Composition of comparative oil formulations. The proportions by weight of the individual formulation components are reported in % by weight based on the total weight of the comparative oil formulation.					
Comparative oil formulation	CE1	CE2	CE3	CE4	CE5
Copolymer 6	24.6				
Copolymer 7		29.5			
Copolymer 8			15.0		
Copolymer 9				15.0	
Copolymer 10					15.0
DI package	0.6	0.6	0.6	0.6	0.6
150N formulation oil	74.8	69.9	84.4	84.4	84.4

Viscometric Evaluation of the Transmission Oil Formulations

[0135] The viscometric evaluation of the transmission oil formulations was made by determining the kinematic viscosity at 40° C. (KV40) and 100° C. (KV100) to ASTM D445, the viscosity index (VI) to ASTM D2270 and the dynamic viscosity at high temperature and high shear at 80° C. (HTHS 80° C.) and 100° C. (HTHS 100° C.) to ASTM 4683.

[0136] The dynamic viscosity (DV) at 100° C. under low shear was calculated from the product of density and kinematic viscosity at 100° C. (KV100).

[0137] In addition, the shear stability was determined on the basis of the kinematic viscosity at 100° C. after a 20-hour tapered roller bearing test CEC-L-45-A-99 (KV100 after TRB20h).

[0138] The viscosity values before and after shear were used to calculate the permanent shear stability index (PSSI) as follows:

$$PSSI = \frac{(KV100_{before\ shear} - KV100_{after\ shear})}{(KV100_{before\ shear} - \text{base oil viscosity})} * 100$$

[0139] The PSSI indicates the percentage loss of viscosity which has been introduced into the formulation via the polymer only. The PSSI is accordingly a characteristic feature of a polymer and is therefore very substantially independent of the amount added or of other formulation components (oil and other additives). This becomes clear from the comparison of the PSSI values of formulations CE1 and CE6, which contain the same polymer but different base oils and additives (see table 4 and table 5).

[0140] The temporary shear stability index (TSSI) was calculated from the dynamic viscosity under high shear and low shear as follows:

$$TSSI = \frac{(DV100_{low\ shear} - DV100_{high\ shear})}{(DV100_{low\ shear} - DV_{base\ oil})} * 100$$

[0141] The DV100 of the base oil of the transmission oil formulations (Nexbase 3030) was 2.45 mPas.

[0142] According to the DEXRON-VI specification, a transmission oil formulation must have a KV100 of not more than 6.4 mm²/s and a KV100 after shear of at least 5.5 mm²/s. It can be inferred from these requirements and a base oil viscosity of 3.8 mm²/s (Nexbase 3030) that a suitable transmission oil formulation must have a PSSI of not more than 34.

[0143] Of the comparative examples listed in table 4, only formulations CE1 and CE2 and hence copolymers 6 and 7 meet this requirement. The PSSI of formulations CE3 to CE5, containing copolymers 8 to 10, in contrast, is too high. The copolymers used in formulations CE3 to CE5 are thus not of adequate shear stability to serve as additives in transmission oil formulations.

[0144] This shows that the exact monomer composition of the inventive copolymers is crucial for the suitability thereof as a transmission oil additive.

[0145] Since the polymer in CE1 (copolymer 6), with comparable shear stability, achieves a much higher viscosity index than the polymer in CE2 (copolymer 7), further viscometric characterizations were restricted to copolymer 6.

TABLE 4

Viscometric evaluation of comparative oil formulations CE1 to CE5.					
Comparative oil formulation	CE1	CE2	CE3	CE4	CE5
KV40 (mm ² /s)	92.47	95.62	44.02	41.97	43.13
KV100 (mm ² /s)	14.22	13.97	14.12	13.95	15.97
vi.	159	149	336	347	385
KV100 after TRB20h (mm ² /s)	12.85	12.87	10.63	not determinable	10.50
PSSI	15.6	12.9	40.1	insoluble constituents	51.8

[0146] The measured data for the transmission oil formulations E1 to E5 and CE6 are summarized in Table 5. All these transmission oil formulations have the fresh oil viscosity KV100 required by the DEXRON-VI specification of not more than 6.4 mm²/s.

[0147] However, it is found that the comparative formulation CE6 has a much lower viscosity index than the inventive formulations E1 to E5. In addition, comparative formulation CE6 has a lower temporary shear loss than the formulations of the invention. This is shown by the higher TSSI values of formulations E1 to E6.

[0148] The temporary shear loss can additionally be calculated using the difference between the viscosity at 100° C. and high shear (HTHS 100° C.) and the dynamic viscosity at 100° C. and low shear. This difference is much higher for formulations E1 to E4 than for formulation CE6.

TABLE 5

Viscometric evaluation of transmission oil formulations E1 to E5 and CE6:						
	Transmission oil formulation					
	E1	E2	E3	E4	E5	CE6
KV40 (mm ² /s)	24.30	24.36	21.60	25.85	24.68	28.43
KV100 (mm ² /s)	6.02	6.02	6.12	6.02	6.02	6.03
VI	211	211	260	192	210	166

TABLE 5-continued

Viscometric evaluation of transmission oil formulations E1 to E5 and CE6:						
	Transmission oil formulation					
	E1	E2	E3	E4	E5	CE6
KV100 after TRB20h (mm ² /s)	5.63	5.6	5.429	5.67	5.70	5.71
PSSI	17.6	18.9	29.8	15.8	14.6	14.3
TSSI	15.5	12.7	28.0	17.3	13.0	1.1
PSSI/TSSI	1.1	1.5	1.1	0.9	1.1	13.0
HTHS 80° C. (mPas)	6.61	6.62	5.92	6.61	6.63	7.18
HTHS 100° C. (mPas)	4.43	4.49	4.17	4.39	4.49	4.78
Dynamic viscosity at 100° C. (low shear) (mPas)	4.79	4.79	4.84	4.80	4.79	4.81
Density 100° C. (g/cm ³)	0.7962	0.7952	0.7952	0.7968	0.7965	0.7969

Determination of the Coefficient of Traction of Transmission Oil Formulations

[0149] Traction measurements were conducted on a mini-traction machine (MTM 2). The measurement parameters and test specimens which follow were used for the measurements. For each measurement, a new set of test specimens was utilized.

Test rig	MTM 2 from PCS Instruments
Disk	Steel, AISI 52100, diameter = 46 mm RMS = 25-30 nm, Rockwell C hardness = 63 Modulus of elasticity = 207 GPa
Ball	Steel, AISI 52100, diameter = 19.05 mm RMS = 10-13 nm, Rockwell C hardness = 58-65 Modulus of elasticity = 207 GPa
Speed	2000 mm/s
Temperature	100° C.
Load	30-75N
Sliding/rolling ratio	50%

[0150] First of all, the traction behavior of transmission oil formulations based on aromatics-containing base oils was examined. In terms of their composition, these formulations correspond to hydraulic oils as described, for example, in DE 10 2009 001 447 A1. For this purpose, copolymer 5 or copolymer 7 was dissolved in a 100N oil of API group I (KV100=3.8 mm²/s; %-CA=2.1 by IR method, aromatics content 17%), and the coefficient of traction at 100° C. was measured as described above. The results are summarized in Table 6.

TABLE 6

Coefficient of traction of transmission oil formulations based on aromatics-containing formulation oil. The proportions by weight of the individual formulation components are reported in % by weight based on the total weight of the transmission oil formulation.		
Transmission oil formulation	E6	CE8
Copolymer 5	9.4	18.6
Copolymer 7		81.4
100N formulation oil	90.6	40.86
KV40° C. (mm ² /s)	30.31	7.50
KV100° C. (mm ² /s)	7.51	231
VI	231	152
Coefficient of traction	0.033	0.034

[0151] The deviation of the coefficients of traction of formulations E6 and CE8 is within the measurement error, and should not be regarded as significant. It can therefore be

concluded from the analysis that there is no significant difference in the traction behavior of the copolymers of the invention and of a known comparative polymer in aromatics-containing oils.

[0152] In addition, the traction behavior of transmission oil formulations based on base oils having a low aromatics content was examined. For this purpose, the coefficient of traction of formulations E1 to E5 and CE6 was determined. The results are shown in table 7.

TABLE 7

Coefficient of traction of transmission oil formulations based on formulation oil with low aromatics content. The percentage reduction in the coefficient of traction was calculated on the basis of the difference from CE6.		
Transmission oil formulation	Coefficient of traction	Reduction in coefficient of traction in %
E1	0.020	33.3
E2	0.024	20.0
E4	0.023	23.3
E5	0.021	30.0
E3	0.018	40.0
CE6	0.030	0.0

[0153] Surprisingly, the transmission oil formulations of the invention have a much lower coefficient of traction than the comparative formulation CE6. This demonstrates a synergistic effect with respect to the coefficient of traction, which is achieved by the inventive combination of a copolymer of the invention with a base oil having a low aromatics content, but not by the combination of a comparative copolymer with a base oil having a low aromatics content. This synergistic effect is an important prerequisite for formulation of fuel-saving transmission oils.

[0154] Especially compared with the transmission oil formulations based on aromatics-containing formulation oil in which the copolymers of the invention do not lead to any improvement over the comparative polymers, it was surprising that the coefficient of traction in a base oil having a low aromatics content can be distinctly reduced by a copolymer of the invention.

Measurement of Fuel Consumption

[0155] Fuel consumption measurements were conducted on a certified rolling test bed (ISP Salzbergen). The motor vehicle used for this purpose was a Hyundai ix35 (gasoline

engine, max. power 120 kW at 6200 rpm; maximum torque 194 Nm at 4600 rpm) with a six-speed step-change automatic transmission system. The motor vehicle was conditioned appropriately before each test. Before and after the candidate oils, a reference oil was run (factory-fill oil), in order to rule out unwanted drift of the measurement results. Each test oil (including the reference oil) was analyzed four times on successive days. Reported results are the mean value from four individual measurements in each case. Before the analysis of a new test oil, the automatic transmission system and torque converter were flushed five times with the new test oil to be analyzed, in order to avoid any carry-over effects. The consumption of fuel was calculated from the respective CO₂ emissions. For all tests, appropriate reference fuel (RF-02-08 E5, CEC E45) was used. The data for the test system used are summarized in the following tables:

2.1 Testing Facility—Chassis Dynamometer

[0156]

Supplier	MAHA-AIP GmbH & Co. KG
Type designation	ECDM 48L -4x4
Accuracy on vehicle load simulation (coast-down)	within 0.5%
Accuracy on vehicle speed control	+/- 0.08 km/h

2.2 Testing Facility—Gas Sampling and Analyzer System

[0157]

System	Horiba MEXA-7400HLE, Horiba CVS-7400S
CO/CO ₂ Analyser	MEXA AIA-721A/MEXA AIA-722
NO _x Analyser	MEXA CLA-750LE
HC Analyser	MEXA FLA-726LE
Accuracy on gas measurement	within 1% of measuring scale

[0158] The results of the fuel analysis are presented as follows: Fuel consumption in L/100 km for the ECE (European City Cycle) 1+2 (cold start) driving cycles, fuel consumption in L/100 km for the ECE 3+4 driving cycles (moderate oil temperature), fuel consumption in L/100 km for the EUDC (Ex-Urban Driving Cycle, “warm” operating range—oil temperature at the end of the test ~65° C.), and the NEDC (New European Driving Cycle) averaged from all the cycles, likewise in L/100 km. The speed profile of the NEDC is shown in FIG. 1.

[0159] Fuel consumption measurements were conducted with transmission oil formulations E1, E4 and CE6. The results are shown in table 8.

TABLE 8

Fuel consumption of transmission oil formulations E1, E4 and CE6 in liters per 100 km as a function of analysis cycle.						
Analysis cycle	Reference 1	E1	E4	CE6	Reference 2	% variation reference
ECE 1 + 2		12.73	12.83	12.87		
ECE 3 + 4		10.21	10.19	10.29		

TABLE 8-continued

Fuel consumption of transmission oil formulations E1, E4 and CE6 in liters per 100 km as a function of analysis cycle.						
Analysis cycle	Reference 1	E1	E4	CE6	Reference 2	% variation reference
EUDC		6.82	6.78	6.88		
NEDC	8.57	8.53	8.52	8.62	8.54	0.35

[0160] It is found that a lower fuel consumption is achieved with the transmission oil formulations of the invention than with the comparative formulation CE6. The percentage fuel saving of the transmission oil formulations of the invention compared to the comparative transmission oil formulation CE6 is shown in table 9. What is noticeable here is that the fuel saving is observed not just in the cold start phase (ECE 1+2). Instead, it becomes clear that a distinct advantage is still observed for the formulations of the invention even in the cycles in which the transmission oil has warmed up distinctly as a result of operation (EUDC in particular).

[0161] This effect cannot be explained by an increased viscosity index alone, since lubricants E1, E4 and CE6 are each set to the same KV100, and the viscosities of lubricants therefore increasingly match one another at higher operating temperature.

TABLE 9

Percentage fuel saving of the transmission oil formulations of the invention compared to the comparative transmission oil formulation CE6 as a function of analysis cycle.		
Transmission oil formulation	E1	E4
ECE 1+2	1.09	0.31
ECE 3+4	0.78	0.97
EUDC	0.87	1.45
NEDC	1.04	1.16

1: A transmission oil formulation comprising

- (i) a base oil having a kinematic viscosity at 100° C. of at least 1.5 mm²/s to ASTM D445 and an aromatics content of less than 15% by weight to ASTM D 2007; and
- (ii) a copolymer obtained by free-radical polymerization from a monomer composition, said monomer composition comprising the following monomers:
 - (A) 30% to 50% by weight of an ester of (meth)acrylic acid and a hydroxylated hydrogenated polybutadiene, where the hydroxylated hydrogenated polybutadiene has a number-average molar mass M_n to DIN 55672-1 of 4000 to 6000 g/mol;
 - (B1) 0.2% to 50% by weight of methyl(meth)acrylate;
 - (B2) 0.2% to 50% by weight of butyl(meth)acrylate;
 - (B3) 0.2% to 5% by weight of C5-C30 alkyl(meth)acrylates;
 - (C) 10% to 50% by weight of styrene monomers having 8 to 17 carbon atoms; and
 - (D) 0% to 5% by weight of further free-radically polymerizable comonomers,

where the sum total of the proportions by weight of monomers (B1), (B2) and (B3) is at least 10% by weight.

2: The transmission oil formulation as claimed in claim 1, characterized in that the monomer composition comprises as monomer (B1) 0.2% to 45% by weight of methyl methacrylate;

as monomer (B2) 0.2% to 45% by weight of n-butyl methacrylate and/or n-butyl acrylate; and

as monomer (B3) 0.2% to 5% by weight of C12-C14 alkyl(meth)acrylates.

3: The transmission oil formulation as claimed in claim 1, characterized in that the hydroxylated hydrogenated polybutadiene is a hydroxyethyl- or hydroxypropyl-terminated hydrogenated polybutadiene.

4: The transmission oil formulation as claimed in claim 1, characterized in that the copolymer has an iodine number to DIN 53241-1:1995-05 of up to 5 g of iodine per 100 g of copolymer.

5: The transmission oil formulation as claimed in claim 1, characterized in that the further free-radically polymerizable comonomers are selected from the group consisting of maleic anhydride, (di)alkyl fumarates, (di)alkyl maleates, aminoalkyl(meth)acrylates, aminoalkyl(meth)acrylamides, hydroxyalkyl(meth)acrylates, carbonyl-containing (meth)acrylates, heterocyclic(meth)acrylates, heterocyclic vinyl compounds and mixtures thereof.

6: The transmission oil formulation as claimed in claim 1, characterized in that the copolymer has a molar branching level of 1.0 to 3.1 mol %.

7: The transmission oil formulation as claimed in claim 1, characterized in that the base oil has a proportion of aromatic carbon atoms of not more than 2%.

8: The transmission oil formulation as claimed in claim 1, characterized in that the base oil is a group III oil as defined by the American Petroleum Institute.

9: The transmission oil formulation as claimed in claim 1, characterized in that the transmission oil formulation com-

prises 60% to 99.9% by weight of component (i) based on the total weight of the transmission oil formulation.

10: The transmission oil formulation as claimed in claim 1, characterized in that the transmission oil formulation comprises 0.1% to 40% by weight of component (ii) based on the total weight of the transmission oil formulation.

11: The transmission oil formulation as claimed in claim 1, characterized in that the transmission oil formulation additionally comprises, as component (iii), a second polymer selected from the group of the hydrogenated polybutadienes, hydroxylated hydrogenated polybutadienes or (meth)acrylic esters thereof, polyalkyl(meth)acrylates and mixtures thereof.

12: The transmission oil formulation as claimed in claim 11, characterized in that the transmission oil formulation comprises 0% to 3% by weight of component (iii) based on the total weight of the transmission oil formulation.

13: The transmission oil formulation as claimed in claim 1, characterized in that the transmission oil formulation additionally comprises, as component (iv), further additives selected from the group consisting of dispersants, defoamers, detergents, antioxidants, antiwear additives, extreme pressure additives, friction modifiers, anticorrosion additives, dyes and mixtures thereof.

14: The use of a transmission oil formulation as claimed in claim 1 as transmission oil for reducing the fuel consumption of motor vehicles.

15: The use as claimed in claim 14, characterized in that the transmission oil formulation is used as transmission oil for automatic transmission systems.

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