

Description

This invention relates to lubricating oil compositions containing lubeoil viscosity index improvers (VII) and to oil concentrates containing such VII additives.

A variety of polymeric materials are available to improve the viscosity index of lubricating oils intended for use in internal combustion engines. Such materials include hydrogenated styrene/isoprene diblock copolymers, olefin copolymers, and hydrogenated star (radial) copolymers having a divinylbenzene-derived nucleus and polyolefin arms. Continuing development of engines places increasing demands on the performance characteristics of lubricating oils, leading to continual efforts to achieve property benefits additional to the basic VII effect. One such property is the viscoelastic behaviour, and Applicants have now discovered that this property can be beneficially modified by the introductions of carboxyl groups onto the polymeric chains.

Accordingly, the present invention provides a lubricating oil composition which comprises a major proportion of a lubricating oil and, as viscosity index improver, a hydrogenated block copolymer or olefin copolymer functionalised by the presence of carboxyl groups attached to the polymer chain via a sulphonamide linkage (-SO₂NH-). Such functionalised polymers suitably bear the carboxyl functional substituent in the structure RSO₂NH-, and are conveniently prepared by reacting the hydrogenated block copolymer or the olefin copolymer with a sulphonyl azide of formula RSO₂N₃ (I), wherein R represents a carboxyl-containing organic group, in particular a carboxy-aromatic group such as a carboxyphenyl group.

The organic radical R in the general formula I may contain substituents other than carboxyl groups, examples of such substituents being halogen atoms, i.e. fluorine, chlorine, bromine or iodine atoms; cyano groups; hydroxyl groups; dialkylamino groups; nitro groups or benzoyl groups. Aromatic groups represented by R may carry, for example, an alkyl or a cycloalkyl group, and alkyl groups represented by R may carry, for example, an aromatic or a cycloalkyl group. It is not excluded that R represents a heterocyclic group, for example a thienyl, a furyl or a pyridyl group, or a group obtained by hydrogenation of one of these groups. Specific examples of groups R are 3-carboxy-4 hydroxyphenyl, 3-carboxy-4 chlorophenyl, 4-(carboxymethoxy)phenyl, 3,4-dicarboxyphenyl, 5-carboxynaphthyl, 2-neopentyl-5-carboxyphenyl and 2-ethyl-5-carboxyphenyl groups.

The process according to the present invention is preferably carried out by heating an admixture of the selectively hydrogenated block copolymer or the olefin copolymer and an azide of the general formula I to a temperature in the range of from 100°C to 300°C and particularly from 150°C to 250°C. The azide of the general formula I may be admixed with the block copolymer in any suitable manner, for example in a powder mixer, or in a melt, in a conventional rubber mill, or in an internal mixer, or in an extruder.

In addition to the azide, other ingredients can also be incorporated, for example stabilizers. If desired, the process according to the present invention may be carried out in the presence of a radical scavenger to prevent any degradation of aliphatic carbon-carbon bonds in the block copolymer. Examples of radical scavengers are sterically hindered phenols such as "Ixonox 220", a trade mark for 4,4'-methylene-bis-2,6-di-tert-butylphenol and "Ixonox 330", a trade mark for 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene.

The hydrogenated block copolymers modified for incorporation in the lubeoil compositions of this invention are products which are themselves known as VI improvers. Such copolymers may thus be diblock copolymers of the formula A-B wherein A is a monoalkenylaromatic polymer block, preferably polystyrene, having an average molecular weight between 5,000 and 50,000, and B is an olefin polymer block derived from mono- α olefins or conjugated dienes, having an average molecular weight between 10,000 and 1,000,000, wherein hydrogenation has reduced at least 80% of the aliphatic unsaturation but less than 20% of the aromatic unsaturation. Such hydrogenated diblock copolymers are commercially available, for example "Shellvis 50" ("Shellvis" is a trade mark), and are described in UK Patent 1336746. As detailed therein, the conjugated diene is preferably butadiene, isoprene or a mixture thereof. If the block copolymers contain α -mono-olefin polymer blocks as block B, preferred monoolefins are ethylene, propylene, and butylene, or mixtures thereof.

The blocks A and B may be homopolymer or copolymer blocks and, in the latter case, the imperative monomers should predominate. A typical polymer of this type prior to hydrogenation has the structure polystyrene/random styrene-butadiene rubber (SBR).

The block copolymers are hydrogenated to reduce their olefinic unsaturation by at least 50% and preferably at least 80% of the original olefinic double bonds, but preferably less than 10% of the aromatic unsaturation. Hydrogenation is preferably carried out in solution utilizing either homogeneous or heterogeneous catalysts. If both aromatic and olefinic double bonds are to be reduced then relatively stringent hydrogenation conditions may be employed. Preferably, however, the more readily saturated olefinic double bonds are first reduced at relatively mild hydrogenation conditions after which temperature and pressure may be increased so as to effectively cause reduction of aromatic unsaturation, if this is desired. Catalysts, such as cobalt or nickel salts or alkoxides reduced with aluminium alkyl compounds are preferred. Suitable catalysts include nickel acetate, nickel octoate, or nickel acetyl acetonate reduced with aluminium alkyl compounds, such as aluminium triethyl

or aluminium tri-isobutyl.

The block copolymers can be used in lubrils in proportion of, e.g., 0.75 - 10, preferably 1 - 4.5, %w. Other additives, such as detergents, may additionally be used.

Alternatively the block copolymer may be replaced by an olefin copolymer e.g. prepared from ethylene and propylene. More conveniently purely alternating ethylene-propylene copolymers can be prepared by anionic polymerisation of polyisoprene according to processes described for diblocks above or star polymers below, followed by deactivation of the catalyst and hydrogenation again according to the processes described herein for diblocks and stars. This olefin copolymer is to be considered as an ideal model for olefin copolymers marketed as VI improvers.

Alternatively, the block copolymer may be a hydrogenated star (radial) copolymer such as those comprising a poly(polyalkenyl coupling agent) nucleus (usually divinyl benzene) bearing at least four polymeric arms derived from conjugated dienes and/or monoalkenyl arenes, usually isoprene or butadiene optionally copolymerised with styrene, wherein hydrogenation has reduced at least 50% of the aliphatic unsaturation but less than 20% of the aromatic unsaturation. Such hydrogenated star polymers are commercially available, e.g. "Shellvis" 200 and 250, and are described in UK Patent 1575507. As detailed therein, the hydrogenated star polymers can be prepared by the reaction steps of

- (a) polymerizing one or more conjugated dienes and, optionally, one or more monoalkenyl aromatic compounds, in solution, in the presence of an anionic initiator to form a living polymer,
- (b) reacting the living polymer with at least 0.5 mole per mole of living polymer of a polyalkenyl coupling agent, having at least two non-conjugated alkenyl groups and no halogen atoms to form a star-shaped polymer, and
- (c) hydrogenating the star-shaped polymer to form a hydrogenated star-shaped polymer.

The living polymers produced in reaction step (a) of the present process are the precursors of the hydrogenated polymer chains which extend outwardly from the poly(poly-alkenyl coupling agent) nucleus.

As is well known, living polymers may be prepared by anionic solution polymerization of conjugated dienes and, optionally, monoalkenyl aromatic compounds in the presence of an alkali metal or an alkali-metal hydrocarbon, e.g. sodium naphthalene, as anionic initiator. The preferred initiator is lithium or a monolithium hydrocarbon. Suitable lithium hydrocarbons include unsaturated compounds such as allyl lithium, methallyl lithium; aromatic compounds such as phenyllithium, the tolyllithiums, the xylyllithiums and the naphthyllithiums and in particular the alkyl lithiums such as methylolithium, ethyllithium, propyllithium, butyllithium amyllithium, hexyllithium, 2-ethylolithium and n-hexadecyl-lithium.

Secondary-butyllithium is the preferred initiator. The initiators may be added to the polymerization mixture in two or more stages optionally together with additional monomer. The living polymers are olefinically and, optionally, aromatically unsaturated.

The living polymers obtained by reaction step (a), which are linear unsaturated living polymers, are prepared from one or more conjugated dienes, e.g. C₄ to C₁₂ conjugated dienes and, optionally, one or more monoalkenyl aromatic compounds.

Specific examples of suitable conjugated dienes include butadiene(1,3-butadiene); isoprene; 1,3-pentadiene (piperylene); 2,3-dimethyl-1,3-butadiene; 3-butyl-1,3-octadiene, 1-phenyl-1,3-butadiene; 1,3-hexadiene; and 4-ethyl-1,3-hexadiene with butadiene and/or isoprene being preferred. Apart from the one or more conjugated dienes the living polymers may also be partly derived from one or more monoalkenyl aromatic compounds. Preferred monoalkenyl aromatic compounds are the monovinyl aromatic compounds such as styrene, monovinyl naphthalene as well as the alkylated derivatives thereof such as o-, m- and p-methylstyrene, alpha-methylstyrene and tertiary-butylstyrene. Styrene is the preferred monoalkenyl aromatic compound. The living polymers may also be partly derived from small amounts of other monomers such as monovinylpyridines, alkyl esters of acrylic and methacrylic acids (e.g. methyl methacrylate, dodecylmethacrylate, octadecylmethacrylate), vinyl chloride, vinylidene chloride, monovinyl esters of carboxylic acids (e.g. vinyl acetate and vinyl stearate). Preferably the living polymers are derived entirely from hydrocarbon monomers. If a monoalkenyl aromatic compound is used in the preparation of the living polymers it is preferred that the amount thereof is below 50 %w, based on the weight of diene used.

The living polymers may be living homopolymers, living copolymers, living terpolymers, living tetrapolymers, etc. The living homopolymers may be represented by the formula A-M, wherein M is a carbanionic group, e.g. lithium, and A is polybutadiene or polyisoprene. Living polymers of isoprene are the preferred living homopolymers. The living copolymers may be represented by the formula A-B-M, wherein A-B is a block, random or tapered copolymer such as poly(butadiene/isoprene), poly(butadiene/styrene) or poly(isoprene/styrene). Such formulae, without further restriction, do not place a restriction on the arrangement on the monomers within the living polymers. For example living poly(isoprene/styrene) copolymers may be living polyisoprene-polystyrene block copolymers, living polystyrene-polyisoprene block copolymers, living poly(isoprene/styrene)

random copolymers, living poly(isoprene/styrene) tapered copolymers or living poly (isoprene/styrene/isoprene) block copolymers. As an example of a living terpolymer may be mentioned living poly(butadiene/styrene/isoprene)-terpolymers.

As stated above, the living copolymers may be living block copolymers, living random copolymers or living tapered copolymers. The living block copolymers may be prepared by the step-wise polymerization of the monomers e.g. by polymerizing isoprene to form living polyisoprene followed by the addition of the other monomer, e.g. styrene, to form a living block copolymer having the formula poly-isoprene-polystyrene-M, or styrene may be polymerized first to form living polystyrene followed by addition of isoprene to form a living block copolymer having the formula poly-styrene-polyisoprene-M.

The living random copolymers may be prepared by adding gradually the most reactive monomer to the polymerization reaction mixture, comprising either the less reactive monomer or a mixture of the monomers, in order that the molar ratio of the monomers present in the polymerization mixture is kept at a controlled level; it is also possible to achieve this by adding gradually a mixture of the monomers to be copolymerized to the polymerization mixture. Living random copolymers may also be prepared by carrying out the polymerization in the presence of a so-called randomizer. Randomizers are polar compounds which do not deactivate the catalyst and bring about a tendency to random copolymerization. Suitable randomizers are tertiary amines, such as trimethylamine, triethylamine, dimethylethylamine, tri-n-propyl-amine, tri-n-butylamine, dimethylaniline, pyridine, quinoline, N-ethylpiperidine, N-methylmorpholine; thioethers, such as dimethyl sulphide, diethyl sulphide, di-n-propyl sulphide, di-n-butyl sulphide, methyl ethyl sulphide; and in particular ethers, such as dimethyl ether, methyl ethyl ether, diethyl ether, di-n-propyl ether, di-n-butyl ether, di-octyl ether, di-benzyl ether, di-phenyl ether, anisole, 1,2-dimethyl-oxyethane, o-dimethoxy benzene, and cyclic ethers such as tetrahydrofuran.

Living tapered copolymers are prepared by polymerizing a mixture of monomers and result from the difference in reactivity between the monomers. For example, if monomer A is more reactive than monomer B then the composition of the copolymer gradually changes from that of nearly pure poly-A to that of nearly pure poly-B. Therefore in each living copolymer molecule three regions can be discerned, which gradually pass into each other, and which have no sharp boundaries. One of the outer regions consists nearly completely of units derived from monomer A and contains only of small amounts of units derived from monomer B, in the middle region the relative amount of units derived from monomer B greatly increases and the relative amount of units derived from monomer A decreases, while the other outer region consists nearly completely of units derived from monomer B and contains only small units derived from monomer A. Living tapered copolymers of butadiene and isoprene are preferred living tapered polymers.

Since the living polymers produced in reaction step (a) of the above process are the precursors of the hydrogenated polymer chains which extend outwardly from the poly(poly-alkenyl coupling agent) nucleus, it can be seen that the preferred hydrogenated polymer chains are hydrogenated polybutadiene chains, hydrogenated polyisoprene chains, hydrogenated poly(butadiene/isoprene) chains, hydrogenated poly(butadiene/styrene) chains and hydrogenated poly(isoprene/styrene) chains.

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

The temperature at which the polymerization is carried out may vary between wide limits such as from (-)50°C to 150°C, preferably from 20 to 80°C. The reaction is suitably carried out in an inert atmosphere such as nitrogen and may be carried out under pressure e.g. a pressure of from 0.5 to 10 bars (50,000 to 1,000,000 Pa).

The concentration of the initiator used to prepared the living polymer may also vary between wide limits and is determined by the desired molecular weight of the living polymer.

The molecular weight of the living polymers prepared in reaction step (a) may vary between wide limits. Suitable number average molecular weights are from 5,000 to 150,000 with a number average molecular weights of from 15,000 to 100,000 being preferred. Consequently the number average molecular weight of the hydrogenated polymer chains of the final star-shaped polymer may also vary between these limits.

The living polymers produced in reaction step (a) are then reacted, in reaction step (b), with polyalkenyl coupling agent. Polyalkenyl coupling agents capable of forming star-shaped polymers are well known to those skilled in the art. They are compounds having at least two alkenyl groups, usually attached to the same or different electron-withdrawing groups e.g. an aromatic nucleus. Such compounds have the property that at least two of the alkenyl groups are capable of independent reaction with different living polymers and in this respect are different from conventional conjugated diene polymerizable monomers such as butadiene, isoprene etc. Pure or technical grade polyalkenyl coupling agents may be used. Such compounds may be aliphatic, aromatic

or heterocyclic. Examples of aliphatic compounds include the polyvinyl and polyallyl acetylenes, phosphates and phosphites as well as the dimethacrylates, e.g. ethylene dimethacrylate. Examples of suitable heterocyclic compounds include divinyl pyridine and divinyl thiophene. The preferred coupling agents are the polyalkenyl aromatic compounds and the most preferred are the polyvinyl aromatic compounds. Examples of such compounds include those aromatic compounds, e.g. benzene, toluene, xylene, anthracene, naphthalene and durene which are substituted by at least two alkenyl groups preferably directly attached thereto. Examples include the polyvinyl benzenes e.g. divinyl, trivinyl and tetravinyl benzenes; divinyl, trivinyl and tetravinyl ortho-, meta- and para-xylenes, divinyl naphthalene, divinyl ethyl benzene, divinyl biphenyl, diisobutenyl benzene, diisopropenyl benzene and diisopropenyl biphenyl. The preferred aromatic compounds are represented by the formula $A(CH=CH_2)_x$ wherein A is an optionally substituted aromatic nucleus and x is an integer of at least 2. Divinyl benzene, in particular meta-divinyl benzene, is the most preferred aromatic compound. Pure or technical grade divinylbenzene (containing various amounts of other monomers e.g. styrene and ethyl styrene) may be used. The coupling agents may be used in admixture with small amounts of added monomers which increase the size of the nucleus, e.g. styrene or alkylated styrene. In this case, the nucleus may be described as a poly(dialkenyl coupling agent/monoalkenyl aromatic compound) nucleus e.g. a poly(divinylbenzene/monoalkenyl aromatic compound) nucleus. From the above it will be clear that the term divinylbenzene when used to describe the nucleus means either purified or technical grade divinyl benzene.

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

The amount of polyalkenyl coupling agent added may vary between wide limits but at least 0.5 mole is used per mole of unsaturated living polymer. Amounts of from 1 to 15 moles, preferably from 1.5 to 5 moles are preferred. The amount, which may be added in two or more stages, is usually such so as to convert at least 80 or 85 %w of the living polymers into star-shaped polymers.

The reaction step (b) may be carried out in the same solvent as for reaction step (a). A list of suitable solvents is given above. The reaction step (b) temperature may also vary between wide limits e.g. from 0° to 150°C, preferably from 20°C to 120°C. The reaction may also take place in an inert atmosphere e.g. nitrogen and under pressure e.g. a pressure of from 0.5 to 10 bars (50,000 to 1,000,000 Pa).

The star-shaped polymers prepared in reaction step (b) are characterized by having a dense centre or nucleus of cross-linked poly(polyalkenyl coupling agent) and a number of arms of substantially linear unsaturated polymers extending outwardly therefrom. The number of arms may vary considerably but is usually between 4 and 25, e.g. from 7 to 15. Star-shaped homopolymers may be represented by the formula $A-x-(A)_n$ and star-shaped copolymers may be represented by the formula $A-B-x-(B-A)_n$ wherein n is an integer, usually between 3 and 24 and x is the poly(polyalkenyl coupling agent) nucleus.

From the above it can be seen that x is preferably a poly(polyvinyl aromatic coupling agent) nucleus and more preferably a poly(divinylbenzene) nucleus. As stated above it is believed that the nuclei are cross-linked.

Such star-shaped polymers, which are still "living" may then be deactivated or "killed", in known manner, by the addition of a compound which reacts with the carbanionic end group. As examples of suitable deactivators may be mentioned compounds with one or more active hydrogen atoms such as water, alcohols (e.g. methanol, ethanol, isopropanol, 2-ethylhexanol) or carboxylic acids (e.g. acetic acid), compounds with one active halogen atom, e.g. a chlorine atom (e.g. benzyl chloride, chloromethane), compounds with one ester group and carbon dioxide. If not deactivated in this way, the living star-shaped polymers will be killed by the hydrogenation step (c).

However, before being killed the living star-shaped polymers may be reacted with further amounts of monomers such as the same or different dienes and/or monoalkenyl aromatic compounds of the types discussed above. The effect of this additional step, apart from increasing the number of polymer chains, is to produce a further living star-shaped polymer having at least two different types of polymer chains. For example a living star-shaped polymer derived from living polyisoprene may be reacted with further isoprene monomer to produce a further living star-shaped polymer having polyisoprene chains of different number average molecular weights. Alternatively, the living star-shaped polyisoprene homopolymer may be reacted with styrene monomer to produce a further living star-shaped copolymer having both polyisoprene and polystyrene homopolymer chains. Thus it can be seen that by different polymer chains is meant chains of different molecular weights and/or chains of different structures. These further polymerizations may take place under substantially the same conditions as described for reaction step (a) of the process. The additional chains may be homopolymer, copolymer chains etc., as described above.

The molecular weights of the star-shaped polymer to be hydrogenated in reaction step (c) may vary between wide limits. Suitable molecular weights are from 25,000 to 1,000,000 with molecular weights of from 100,000 to 750,000 being preferred and molecular weights of from 250,000 to 650,000 being particularly pre-

ferred. Suitably the molecular weights are expressed as peak molecular weights, determined by GPC on polystyrene scale.

In step (c), the star-shaped polymers may be hydrogenated by any suitable technique. Suitably at least 50%, preferably at least 70%, more preferably at least 90%, most preferably at least 95% of the olefinic unsaturation is hydrogenated. If the star-shaped polymer is partly derived from a monoalkenyl aromatic compound, then the amount of aromatic unsaturation which is hydrogenated, if any, will depend on the hydrogenation conditions used. However, preferably less than 10%, more preferably less than 5% of such aromatic unsaturation is hydrogenated. If the poly(polyalkenyl coupling agent) nucleus is a poly(polyalkenyl aromatic coupling agent) nucleus, the aromatic unsaturation of the nucleus may or may not be hydrogenated again depending on the hydrogenation conditions used. The molecular weights of the hydrogenated star-shaped polymers correspond to those of the unhydrogenated star-shaped polymers.

The hydrogenation can be carried out in any desired way. A hydrogenation catalyst may be used e.g. a copper or molybdenum compound. Compounds containing noble metals or noble-metal compounds can be used as hydrogenation catalysts. Preference is given to catalyst containing a non-noble metal or a compound thereof of Group VIII of the Periodic Table i.e. iron, cobalt and in particular nickel. As examples may be mentioned Raney nickel and nickel on kieselguhr. Special preference is given to hydrogenation catalysts which are obtained by causing metal hydrocarbyl compounds to react with organic compounds of any one of Group VIII metals iron, cobalt or nickel, the latter compounds containing at least one organic compound which is attached to the metal atom by means of an oxygen atom, for instance as described in U.K. patent specification 1,030,306. Preference is given to hydrogenation catalysts obtained by causing an aluminium trialkyl (e.g. aluminium triethyl or aluminium trisobutyl) to react with a nickel salt of an organic acid (e.g. nickel diisopropyl salicylate, nickel naphthenate, nickel 2-ethyl hexanoate, nickel di-tert-butyl benzoate, nickel salts of saturated monocarboxylic acids obtained by reaction of olefins having from 4 to 20 carbon atoms in the molecule with carbon monoxide and water in the presence of acid catalysts) or with nickel eolates or phenolates (e.g. nickel acetylacetonate, the nickel salt of butylacetophenone).

The hydrogenation of the star-shaped polymer is very suitably conducted in solution in a solvent which is inert during the hydrogenation reaction. Saturated hydrocarbons and mixtures of saturated hydrocarbons are very suitable and it is of advantage to carry out the hydrogenation in the same solvent in which the polymerization has been effected.

The hydrogenated star-shaped polymer may be recovered in solid form from the solvent in which it is hydrogenated by any convenient technique such as by evaporation of the solvent. Alternatively an oil, e.g. a lubricating oil, may be added to the solution and the solvent stripped off from the mixture so formed to produce concentrates.

The functionalised hydrogenated block copolymers may be added to a variety of oils to produce compositions according to the present invention. Examples of oils include fuel oils, e.g. middle distillate fuels, lubricating oils, such as synthetic lubricating oils e.g. an ester oil, but preferably mineral lubricating oils; crude oils and industrial oils. The concentration of the hydrogenated star-shaped polymers in such oils may vary between wide limits with amounts of between 0.15 and 10%, especially from 0.1 to 5%, preferably from 0.5 to 2.5 %w, being usual. The amounts are based on the weight of the composition. It is often convenient to prepare a concentrate of the functionalised copolymer, e.g. in a luboil, which may then be blended with a lubricating oil to form the desired final composition. Such concentrates suitably contain at least 10% w, preferably 10-25% w, of functionalised polymer.

Insofar as the oil is a lubricating oil it may also comprise other additives such as anticorrosion additives, and/or antioxidants and/or a detergent and/or an extreme-pressure additive and/or one or more additional VI improvers and/or pour-point depressants.

When prepared by reaction with the sulphonyl azide of formula I above, the functionalised hydrogenated star polymer see below products may be defined as being star polymers bearing on the radial arms functional groups of the formula $\text{RSO}_2\text{NH}-$, wherein R represents a carboxyl-containing organic group, in particular a carboxy-aromatic group such as a carboxyphenyl group, and the star polymer is as described above.

The invention is further illustrated in the following Examples.

Examples 1 - 26

Preparation of modified polymers

Two polymer types were modified by introduction of carboxyl groups, namely "Shellvis" 50 ("Shellvis" is a trade mark) - a polystyrene-ethylene/propylene diblock copolymer of mol. wt. 90,000 - (SV 50), a hydrogenated polyisoprene - an ethylene/propylene polymer of mol. wt. 90,000 (EP), and "Shellvis" 200 - a star-shaped

polymer comprising hydrogenated polyisoprene arms having mol. wt. 35,000 coupled with divinylbenzene, according to the procedure of UK Patent 1575507 (SV 200). Samples of these products were heated at 200-215°C in a Brabender mixer with varying amounts of 3-azidosulphonylbenzoic acid (ASB) in the presence of "IonoX" 330 (trade mark) antioxidant (1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene). Details of the reactant quantities and the carboxyl content of the product are set out in Table I, the final products having been purified by dissolution in tetrahydrofuran, filtration, precipitation of the carboxylated polymer by addition to ethanol, and, in some instances (as noted), converted into the sodium salt by neutralisation with sodium hydroxide.

TABLE I

Example	Substrate	ASB-intake mol/mol	Neutralisation by NaOH	TBN mmol/g	TBN after 2nd purification ^{a)} (mmol/g)	Na mmol/g	S mmol/g	N mmol/g	Number of carboxylate groups/ polymer chain ^{b)} mol/mol	Efficiency of ASB-reaction ^{c)} (%)
1 ^{d)}	SV50	0	0							
2 ^{e)}	SV50	0	0	0.002			0.002	0.001		
3	SV50	1.7	0.019	0.017			0.014	0.016	1.2	73
4	SV50	2.3	0.025				0.021		1.9	84
5	SV50	4.8	0.053	0.081	0.079 ^{h)}			0.038	3.4 ^{k)}	72 ^{k)}
6	SV50	5.6	0.063				0.055		5.0	88
7	SV50	9.5	0.105				0.083		7.5	79
8	SV50	10.1	0.112	0.093			0.082	0.066	7.4	73
9	SV50	17.8	0.198	0.513	0.213	0.470	0.157	0.109	14.1	79
10	SV50	18.1	0.201				0.138		12.4	68
11	SV50	37.0	0.411				0.212		19.1	52
12	SV50	38.3	0.426	0.852	0.377	0.772	0.192	0.193	17.3	45
13	SV50	59.9	0.666	0.592		0.772	0.258		23.2	39
14	SV50	62.4	0.693				0.260		23.4 ^{h)}	37
15 ^{e)}	EP	0	0				0.002			

TABLE I (Continued)

Example	Substrate	ASB-intake mol/mol	Neutralisation by NaOH	TBN mmol/g	TBN after 2 nd purification ^{a)} (mmol/g)	Na mmol/g	S mmol/g	N mmol/g	Number of carboxylate groups/ polymer chain mol/mol	Efficiency of ASB-reaction (%)
16	EP	1.4	0.016	N			0.009		0.8	54
17	EP	4.9	0.055	N			0.028		2.5	50
18	EP	9.6	0.106	N			0.040		3.6	38
19	EP	17.9	0.199	N			0.062		5.6	31
20	EP	35.4	0.393	N			0.082		7.4	21
21	EP	58.8	0.654	N			0.100		9.0	15
22	SV 200		0.023	N			0.022	0.017	0.8 ^{l)}	94
23	SV 200		0.055	N			0.050	0.050	1.8 ^{l)}	92
24	SV 200		0.109	N			0.053 ^{m)}	0.046 ^{m)}	1.9 ^{l)m)}	49 ^{m)}
25	SV 200		0.197	N			0.031 ^{m)}	0.029 ^{m)}	1.1 ^{l)m)}	16 ^{m)}
26	SV 200		0.396	N			0.104	0.090	3.6 ^{l)}	26

a) 2nd purification to remove excess NaOH: dissolve in THF, add equal amount of toluene, filter, wash with toluene/THF 1/1 and evaporate solvent of filtrate

b) calculated from S-analyses, using Mn of 90,000 for the calculation of the number of carboxylate groups per polymer chain

5

10

15

20

25

30

35

40

45

50

55

- d) subjected to reaction conditions without Ionox 330
- e) subjected to reaction conditions in the presence of Ionox 330
- f) TAN = 0.001 mmol/g
- g) TAN = 0.001 mmol/g
- h) too high, considering turbidity of filtrate
- k) calc from N-analyses
- l) for SV 200: number of carboxylate groups per arm, based on S-analysis and $\text{arm-M}_n = 35,000$
- m) in homogeneous sample

Example 27Determination of Rheological Properties

The modified polymers prepared as described in Examples 1 - 21 were added to a preblended mixture of ashless dispersant, ZDTP, dispersant "SAP 001" (overbased calcium alkylsalicylate) and luboil "HVI-60", to give 1.0% w polymer, 2.0% w SAP 001 and 7.7% w of ashless dispersant and ZDTP, in each case based on the final blend.

All oils were clear, bright amber with no deposits except that prepared from Example 9 which was cloudy amber.

Kinematic viscosities at 100°C were measured with an Ubbelohde viscometer. High-temperature, high-shear viscosities were determined at 150°C and 10^8 s^{-1} using a Ravenfield tapered-plug viscometer. Elastic properties were measured at 40°C and at shear rates in the range 10^5 s^{-1} to 10^6 s^{-1} with a Lodge Stressmeter. This instrument determines the first normal stress difference, P_N , as a function of shear stress, σ . The constants A and B in the relation

$$\log P_N = A + B \log \sigma \quad (1)$$

were determined by regression analysis. P_N at a shear rate of 10^6 s^{-1} was calculated by replacing in Equation (1) by the product of 10^6 and η (this relation follows from the definition of viscosity = $\sigma/\text{shear rate}$). The first normal stress difference was assumed to be independent of temperature in the range 40°C to 150°C. At the time the elastic measurements were made the stressmeter could be operated only up to 60°C. Although measurements made on a variety of (non-ionic) VI improver chemistries showed that first normal stress difference is independent of temperature in the range 20°C to 60°C, the assumption of temperature independence up to 150°C is questionable, particularly with micelle forming VI improvers. The Stressmeter can now be operated up to 140°C and future evaluations of ionomers will be carried out at this temperature.

Two further elastic properties (compliance, J, and relaxation time, τ) were calculated at 150°C and 10^6 s^{-1} from P_N and using the following relations:

$$J = P_N/2^2 \quad (2)$$

$$\tau = \eta J \quad (3)$$

The minimum value, $(h_m)_{\min}$, of the minimum oil film thickness was estimated using the following model (see SAE Paper 860376) developed from an analysis of experimental $(h_m)_{\min}$ in the front main bearing of the 3.8 l Buick V-6 gasoline engine:

$$(h_m)_{\min} = 0.035 + 0.52\eta + 1.16 \quad (4)$$

where η and τ are at 150°C and 10^6 s^{-1} . The units of $(h_m)_{\min}$ are μm when η is in $\text{mPa}\cdot\text{s}$ and τ in μs .

The results of these evaluations are given in Table 2.

TABLE 2

Polymer Type	Example	$V_K(100^\circ\text{C})$ mm^2/s	η at 150°C 10^6s^{-1} MPa.s	Normal Stress at 10^6s^{-1} KPa	Compliance J 10^{-4}Pa^{-1}	Relax. Time $\eta \times J$ μs	Calc. $(h_m)_{\min}$ τ μm
"Shellvis" 50	SV50 ref.	14.0	2.94	1.65	0.95	0.28	1.83
	3	11.7	2.95	3.71	2.13	0.63	2.24
	6	12.5	2.75	3.22	2.13	0.59	2.09
	5	12.3	2.76	4.66	3.06	0.84	2.39
	7	13.0	2.66	3.79	2.68	0.71	2.18
	8	13.1	2.68	4.83	3.36	0.90	2.41
	10	13.3	2.63	4.04	2.56	0.67	2.12
	9	13.9	2.64	3.54	2.90	0.77	2.24

TABLE 2 (Continued)

Polymer Type	Example	$V_k(100^\circ\text{C})$ mm^2/s	η at 150°C 10^6s^{-1} $\text{mPa}\cdot\text{s}$	Normal Stress at 10^6s^{-1} kPa	Compliance J 10^{-4}Pa^{-1}	Relax. Time $\eta \times J$ μs	Calc. $(h_m)_{\text{min}}$ τ μm
"Shellvis" 50	11	14.1	2.58	1.05	0.79	0.20	1.55
	12	14.5	2.54	4.45	3.45	0.88	2.32
Hydrogenated Isoprene	15	9.41	2.92	4.12	2.41	0.70	2.30
	16	9.84	3.02	4.55	2.49	0.75	2.41
	17	10.67	3.11	5.91	3.06	0.95	2.68
	18	11.00	3.08	7.31	3.85	1.19	2.94
	19	12.85	3.05	9.26	4.98	1.52	3.31

TABLE 2 (Continued)

Polymer Type	Example	$V_K(100^\circ\text{C})$ mm^2/s	η at 150°C 10^6s^{-1} mPa.s	Normal Stress at 10^6s^{-1} KPa	Compliance J 10^{-4}Pa^{-1}	Relax. Time $\eta \times J$ μs	Calc. (h_m) γ μm
Hydrogenated Isoprene	20	12.79	2.93	8.50	4.95	1.45	3.17
	21	12.37	2.74	7.19	4.79	1.31	2.91
"Shellvis" 200	22	15.10	3.71	4.71	1.71	0.63	2.63
	23	13.80	3.37	4.27	1.88	0.63	2.45
	24	13.50	3.03	3.22	1.75	0.53	2.16
	25	14.90	2.90	3.04	1.81	0.52	2.08
	26	13.50	2.80	3.09	1.97	0.55	2.06



Claims

5 Claims for the following Contracting States: BE, DE, FR, GB, IT, NL

1. Lubricating oil composition comprising a major proportion of a mineral lubricating oil and, as viscosity index improver, a hydrogenated block copolymer or olefin copolymer functionalised by the presence of carboxyl groups attached to the polymer chain by a sulphonamido linkage.

10 2. Composition as claimed in claim 1 wherein the carboxyl functional substituent has the structure $\text{RSO}_2\text{NH-}$, wherein R represents a carboxyl-containing organic group.

3. Composition as claimed in claim 2 wherein R represents a carboxyphenyl group.

4. Composition as claimed in claim 2 or 3 wherein the hydrogenated block copolymer or olefin copolymer is functionalised by reaction with a sulphonyl azide of formula RSO_2N_3 , R being as defined in Claim 2 or 3.

15 5. Composition as claimed in claim 4 wherein the functionalisation reaction between the hydrogenated block copolymer or olefin copolymer and the sulphonyl azide is effected by heating the reactants together at a temperature in the range of from 100°C to 300°C , optionally in the presence of a radical scavenger.

6. Composition as claimed in any one of the preceding claims wherein the hydrogenated block copolymer or olefin copolymer which is functionalised is (a) a diblock copolymer of the formula A-B wherein A is a mono-alkenylaromatic polymer block having a molecular weight between 5,000 and 50,000, and B is an olefin polymer block derived from mono- α olefins or conjugated dienes having an average molecular weight between 10,000 and 1,000,000, wherein hydrogenation has reduced at least 50% of the aliphatic unsaturation but less than 20% of the aromatic unsaturation; (b) a hydrogenated polyalkadiene of molecular weight between 10,000 and 1,000,000 wherein hydrogenation has reduced at least 80% of the aliphatic unsaturation but less than 20% of the aromatic unsaturation; (c) a hydrogenated star polymer comprising a poly(polyalkenyl coupling agent) nucleus bearing at least 4 arms derived from conjugated dienes and/or monoalkenylarenes, wherein hydrogenation has reduced at least 80% of the aliphatic unsaturation but less than 20% of the aromatic unsaturation.

20 7. Composition as claimed in claim 6 wherein in (a) block A is polystyrene and block B is derived from ethylene, propylene, butylene, isoprene, butadiene, or mixtures thereof, in (b) olefin copolymer is polybutadiene or polyisoprene, and in (c) the star nucleus is derived from divinylbenzene and the polymeric arms are derived from isoprene or butadiene, optionally copolymerised with styrene.

30 8. An oil concentrate comprising a lubricating oil and between 10 and 30% w of a carboxyl functionalised block copolymer or olefin copolymer as defined in any one of claims 1-7.

35 Claims for the following Contracting State : ES

1. Lubricating oil composition comprising a major proportion of a mineral lubricating oil and, as viscosity index improver, a hydrogenated block copolymer or olefin copolymer functionalised by the presence of carboxyl groups attached to the polymer chain by a sulphonamido linkage.

40 2. Composition as claimed in claim 1 wherein the carboxyl functional substituent has the structure $\text{RSO}_2\text{NH-}$, wherein R represents a carboxyl-containing organic group.

3. Composition as claimed in claim 2 wherein R represents a carboxyphenyl group.

4. Composition as claimed in claim 2 or 3 wherein the hydrogenated block copolymer or olefin copolymer is functionalised by reaction with a sulphonyl azide of formula RSO_2N_3 , R being as defined in Claim 2 or 3.

45 5. Composition as claimed in claim 4 wherein the functionalisation reaction between the hydrogenated block copolymer or olefin copolymer and the sulphonyl azide is effected by heating the reactants together at a temperature in the range of from 100°C to 300°C , optionally in the presence of a radical scavenger.

6. Composition as claimed in any one of the preceding claims wherein the hydrogenated block copolymer or olefin copolymer which is functionalised is (a) a diblock copolymer of the formula A-B wherein A is a mono-alkenylaromatic polymer block having a molecular weight between 5,000 and 50,000, and B is an olefin polymer block derived from mono- α olefins or conjugated dienes having an average molecular weight between 10,000 and 1,000,000, wherein hydrogenation has reduced at least 50% of the aliphatic unsaturation but less than 20% of the aromatic unsaturation; (b) a hydrogenated polyalkadiene of molecular weight between 10,000 and 1,000,000 wherein hydrogenation has reduced at least 80% of the aliphatic unsaturation but less than 20% of the aromatic unsaturation; (c) a hydrogenated star polymer comprising a poly(polyalkenyl coupling agent) nucleus bearing at least 4 arms derived from conjugated dienes and/or monoalkenylarenes, wherein hydrogenation has reduced at least 80% of the aliphatic unsaturation but less than 20% of the aromatic unsaturation.

55 7. Composition as claimed in claim 6 wherein in (a) block A is polystyrene and block B is derived from



ethylene, propylene, butylene, isoprene, butadiene, or mixtures thereof, in (b) olefin copolymer is polybutadiene or polyisoprene, and in (c) the star nucleus is derived from divinylbenzene and the polymeric arms are derived from isoprene or butadiene, optionally copolymerised with styrene.

8. An oil concentrate comprising a lubricating oil and between 10 and 30% w of a carboxyl functionalised block copolymer or olefin copolymer as defined in any one of claims 1-7.

9. Process for preparing a lubricating oil composition according to any one of Claims 1 to 7 which comprises adding a carboxyl functionalised block copolymer or olefin copolymer as defined in any one of Claims 1-7 to a major proportion of a mineral lubricating oil.

10. Process as claimed in Claim 9 wherein the carboxyl functionalised block copolymer or olefin copolymer is as defined in Claim 2 and is prepared by reacting a hydrogenated block copolymer or olefin copolymer with a sulphonyl azide of formula RSO_2N_3 , wherein R represents a carboxyl-containing organic group.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : BE, DE, FR, GB, IT, NL

1. Schmierölzusammensetzung, umfassend einen größeren Anteil eines Mineralschmieröls und, als Mittel zum Verbessern des Viskositätsindex, ein hydriertes Blockmischpolymer oder Olefincopolymer, das durch die Gegenwart von durch Sulfonamid-Bindung an die Polymerkette gebundenen Carboxylgruppen funktionalisiert ist.

2. Zusammensetzung nach Anspruch 1, in welcher der funktionelle Carboxylsubstituent die Struktur $\text{RSO}_2\text{NH-}$ aufweist, wobei R eine Carboxyl enthaltende organische Gruppe ist.

3. Zusammensetzung nach Anspruch 2, in welcher R eine Carboxyphenylgruppe darstellt.

4. Zusammensetzung nach Anspruch 2 oder 3, in welcher das hydrierte Blockmischpolymer oder Olefincopolymer durch Umsetzung mit einem Sulfonylazid der Formel RSO_2N_3 funktionalisiert ist, wobei R wie in Anspruch 2 oder 3 definiert ist.

5. Zusammensetzung nach Anspruch 4, in welcher die Funktionalisierungsreaktion zwischen dem hydrierten Blockmischpolymer oder Olefincopolymer und dem Sulfonylazid durch Erhitzen der Reaktanden bei einer Temperatur im Bereich von 100°C bis 300°C , gegebenenfalls in Gegenwart eines Radikalentferners(scavenger) durchgeführt wird.

6. Zusammensetzung nach einem der vorstehenden Ansprüche, in welcher das hydrierte Blockmischpolymer oder Olefincopolymer, welches funktionalisiert ist, (a) ein Zweiblockmischpolymer der Formel A-B ist, wobei A ein monoalkenylaromatischer Polymer-block mit einem Molekulargewicht zwischen 5000 und 50000, und B ein Olefinpolymerblock, abgeleitet von mono-alpha-Olefinen oder konjugierten Dienen mit einem Durchschnittsmolekulargewicht zwischen 10000 und 1 000000, ist, wobei die Hydrierung mindestens 50% der aliphatischen Nicht-Sättigung, aber weniger als 20% der aromatischen Nicht-Sättigung reduziert hat; (b) ein hydriertes Polyalkadien mit einem Molekulargewicht zwischen 10000 und 1 000000 ist, wobei die Hydrierung mindestens 80% der aliphatischen Nicht-Sättigung, aber weniger als 20% der aromatischen Nicht-Sättigung reduziert hat; (c) ein hydriertes Sternpolymer ist, umfassend einen Poly(polyalkenyl-Kupplungsmittel)Kern mit mindestens 4 Armen, abgeleitet von konjugierten Dienen und /oder Monoalkenylarenen, wobei die Hydrierung mindestens 80% der aliphatischen Nicht-Sättigung, aber weniger als 20% der aromatischen Nicht-Sättigung reduziert hat.

7. Zusammensetzung nach Anspruch 6, in welcher in (a) Block A Polystyrol ist und Block B von Äthylen, Propylen, Butylen, Isopren, Butadien, oder Mischungen davon abgeleitet ist, in (b) das Olefincopolymer Polybutadien oder Polyisopren ist, und in (c) der Sternkern von Divinylbenzol abgeleitet ist und die Polymerarme von Isopren oder Butadien, gegebenenfalls copolymerisiert mit Styrol, abgeleitet sind.

8. Ein Ölkonzentrat, umfassend ein Schmieröl und zwischen 10 und 30 Gewichtsprozent eines mit Carboxylgruppen funktionalisierten Blockmischpolymers oder Olefincopolymers, wie in einem der Ansprüche 1 bis 7 definiert.

Patentansprüche für folgenden Vertragsstaat: ES

1. Schmierölzusammensetzung, umfassend einen größeren Anteil eines Mineralschmieröls und, als Mittel zum Verbessern des Viskositätsindex, ein hydriertes Blockmischpolymer oder Olefincopolymer, das durch die Gegenwart von durch Sulfonamid-Bindung an die Polymerkette gebundenen Carboxylgruppen funktionalisiert ist.

2. Zusammensetzung nach Anspruch 1, in welcher der funktionelle Carboxylsubstituent die Struktur



RSO₂NH- aufweist, wobei R eine Carboxyl enthaltende organische Gruppe ist.

3. Zusammensetzung nach Anspruch 2, in welcher R eine Carboxyphenylgruppe darstellt.

4. Zusammensetzung nach Anspruch 2 oder 3, in welcher das hydrierte Blockmischpolymer oder Olefin-copolymer durch Umsetzung mit einem Sulfonylazid der Formel RSO₂N₃ funktionalisiert ist, wobei R wie in Anspruch 2 oder 3 definiert ist.

5. Zusammensetzung nach Anspruch 4, in welcher die Funktionalisierungsreaktion zwischen dem hydrierten Blockmischpolymer oder Olefin-copolymer und dem Sulfonylazid durch Erhitzen der Reaktanden bei einer Temperatur im Bereich von 100°C bis 300°C, gegebenenfalls in Gegenwart eines Radikalentferners (scavenger) durchgeführt wird.

6. Zusammensetzung nach einem der vorstehenden Ansprüche, in welcher das hydrierte Blockmischpolymer oder Olefin-copolymer, welches funktionalisiert ist, (a) ein Zweiblockmischpolymer der Formel A-B ist, wobei A ein monoalkenylaromatischer Polymerblock mit einem Molekulargewicht zwischen 5000 und 50000, und B ein Olefinpolymerblock, abgeleitet von mono- α -Olefinen oder konjugierten Dienen mit einem Durchschnittsmolekulargewicht zwischen 10000 und 1 000000, ist, wobei die Hydrierung mindestens 50% der aliphatischen Nicht-Sättigung, aber weniger als 20% der aromatischen Nicht-Sättigung reduziert hat; (b) ein hydriertes Polyalkadien mit einem Molekulargewicht zwischen 10000 und 1 000000 ist, wobei die Hydrierung mindestens 80% der aliphatischen Nicht-Sättigung, aber weniger als 20% der aromatischen Nicht-Sättigung reduziert hat; (c) ein hydriertes Sternpolymer ist, umfassend einen Poly(polyalkenyl-Kupplungsmittel)Kern mit mindestens 4 Armen, abgeleitet von konjugierten Dienen und/oder Monoalkenylarenen, wobei die Hydrierung mindestens 80% der aliphatischen Nicht-Sättigung, aber weniger als 20% der aromatischen Nicht-Sättigung reduziert hat.

7. Zusammensetzung nach Anspruch 6, in welcher in (a) Block A Polystyrol ist und Block B von Äthylen, Propylen, Butylen, Isopren, Butadien, oder Mischungen davon abgeleitet ist, in (b) das Olefin-copolymer Polybutadien oder Polyisopren ist, und in (c) der Sternnukleus von Divinylbenzol abgeleitet ist und die Polymerarme von Isopren oder Butadien, gegebenenfalls copolymerisiert mit Styrol, abgeleitet sind.

8. Ein Ölkonzentrat, umfassend ein Schmieröl und zwischen 10 und 30 Gewichtsprozent eines mit Carboxylgruppen funktionalisierten Blockmischpolymers oder Olefin-copolymers, wie in einem der Ansprüche 1 bis 7 definiert.

9. Verfahren zur Herstellung einer Schmierölzusammensetzung nach einem der Ansprüche 1 bis 7, welches das Zugabe eines durch Carboxylgruppen funktionalisierten Blockmischpolymers oder Olefin-copolymers, wie in einem der Ansprüche 1 bis 7 beansprucht, zu einem größeren Anteil eines Mineralschmieröls umfaßt.

10. Verfahren nach Anspruch 9, in welchem das durch Carboxylgruppen funktionalisierte Blockmischpolymer oder Olefin-copolymer wie in Anspruch 2 definiert ist und durch Umsetzen eines hydrierten Blockmischpolymers oder Olefin-copolymers mit einem Sulfonylazid der Formel RSO₂N₃, wobei R eine Carboxylgruppen enthaltende organische Gruppe ist, hergestellt wird.

Revendications

Revendications pour les Etats contractants suivants : BE, DE, FR, GB, IT, NL

1. Composition d'huile lubrifiante comportant une proportion prépondérante d'une huile lubrifiante minérale et, en tant qu'agent améliorant l'indice de viscosité, un copolymère séquencé hydrogéné ou un copolymère oléfinique fonctionnalisé par la présence de groupes carboxyle attachés à la chaîne polymère par une liaison sulfonamido.

2. Composition telle que revendiquée dans la revendication 1, dans laquelle le substituant carboxyle fonctionnel présente la structure RSO₂NH-, dans laquelle R représente un groupe organique renfermant du carboxyle.

3. Composition telle que revendiquée dans la revendication 2, dans laquelle R représente un groupe carboxyphényle.

4. Composition telle que revendiquée dans la revendication 2 ou 3, dans laquelle le copolymère séquencé hydrogéné ou le copolymère oléfinique est fonctionnalisé par réaction avec un sulfonylazide de formule RSO₂N₃, R étant tel que défini dans la revendication 2 ou la revendication 3.

5. Composition telle que revendiquée dans la revendication 4, dans laquelle la réaction de fonctionnalisation entre le copolymère séquencé hydrogéné ou le copolymère oléfinique et le sulfonylazide est réalisée en chauffant les réactifs ensemble à une température dans la gamme de 100°C à 300°C, facultativement en présence d'un intercepteur de radicaux.



6. Composition telle que revendiquée dans l'une quelconque des revendications précédentes, dans laquelle le copolymère séquencé hydrogéné ou le copolymère oléfinique qui est fonctionnalisé est (a) un copolymère diséquencé de la formule A-B, dans laquelle A est une séquence de polymère monoalcényl aromatique présentant un poids moléculaire entre 5000 et 50 000, et B est une séquence de polymère oléfinique dérivée de mono-alpha-oléfin ou de diènes conjugués présentant un poids moléculaire moyen entre 10 000 et 1 million, dans laquelle l'hydrogénation a réduit au moins 50 % de l'insaturation aliphatique mais moins de 20 % de l'insaturation aromatique ; (b) un polyalcadiène hydrogéné de poids moléculaire entre 10 000 et 1 million, dans lequel l'hydrogénation a réduit au moins 80 % de l'insaturation oléfinique mais moins de 20 % de l'insaturation aromatique ; (c) un polymère hydrogéné en étoile comportant un noyau poly(agent de couplage polyalcénylé) portant au moins quatre branches dérivées de diènes conjugués et/ou de monoalcénylarènes, dans lequel l'hydrogénation a réduit au moins 80 % de l'insaturation aliphatique mais moins de 20 % de l'insaturation aromatique.

7. Composition telle que revendiquée dans la revendication 6, dans laquelle, en (a), la séquence A est du polystyrène et la séquence B est dérivée de l'éthylène, du propylène, du butylène, de l'isoprène, du butadiène ou de mélanges de ceux-ci, en (b) le copolymère oléfinique est du polybutadiène ou de l'isoprène et en (c) le noyau en étoile est dérivé du divinylbenzène et les branches polymère sont dérivées de l'isoprène et du butadiène, facultativement copolymérisé avec du styrène.

8. Un concentré d'huiles comportant une huile lubrifiante et entre 10 et 30 % en poids d'un copolymère séquencé fonctionnalisé par des groupes carboxyle ou d'un copolymère oléfinique tel que défini dans l'une quelconque des revendications 1 à 7.

Revendications pour l'Etat contractant suivant: ES

1. Composition d'huile lubrifiante comportant une proportion prépondérante d'une huile lubrifiante minérale et, en tant qu'agent améliorant l'indice de viscosité, un copolymère séquencé hydrogéné ou un copolymère oléfinique fonctionnalisé par la présence de groupes carboxyle attachés à la chaîne polymère par une liaison sulfonamido.

2. Composition telle que revendiquée dans la revendication 1, dans laquelle le substituant carboxyle fonctionnel présente la structure RSO_2NH- , dans laquelle R représente un groupe organique renfermant du carboxyle.

3. Composition telle que revendiquée dans la revendication 2, dans laquelle R représente un groupe carboxyphényle.

4. Composition telle que revendiquée dans la revendication 2 ou 3, dans laquelle le copolymère séquencé hydrogéné ou le copolymère oléfinique est fonctionnalisé par réaction avec un sulfonlazide de formule RSO_2N_3 , R étant tel que défini dans la revendication 2 ou la revendication 3.

5. Composition telle que revendiquée dans la revendication 4, dans laquelle la réaction de fonctionnalisation entre le copolymère séquencé hydrogéné ou le copolymère oléfinique et le sulfonlazide est réalisée en chauffant les réactifs ensemble à une température dans la gamme de 100°C à 300°C, facultativement en présence d'un intercepteur de radicaux.

6. Composition telle que revendiquée dans l'une quelconque des revendications précédentes, dans laquelle le copolymère séquencé hydrogéné ou le copolymère oléfinique qui est fonctionnalisé est (a) un copolymère diséquencé de la formule A-B, dans laquelle A est une séquence de polymère monoalcényl aromatique présentant un poids moléculaire entre 5000 et 50 000, et B est une séquence de polymère oléfinique dérivée de mono-alpha-oléfin ou de diènes conjugués présentant un poids moléculaire moyen entre 10 000 et 1 million, dans laquelle l'hydrogénation a réduit au moins 50 % de l'insaturation aliphatique mais moins de 20 % de l'insaturation aromatique ; (b) un polyalcadiène hydrogéné de poids moléculaire entre 10 000 et 1 million, dans lequel l'hydrogénation a réduit au moins 80 % de l'insaturation oléfinique mais moins de 20 % de l'insaturation aromatique ; (c) un polymère hydrogéné en étoile comportant un noyau poly(agent de couplage polyalcénylé) portant au moins quatre branches dérivées de diènes conjugués et/ou de monoalcénylarènes, dans lequel l'hydrogénation a réduit au moins 80 % de l'insaturation aliphatique mais moins de 20 % de l'insaturation aromatique.

7. Composition telle que revendiquée dans la revendication 6, dans laquelle, en (a), la séquence A est du polystyrène et la séquence B est dérivée de l'éthylène, du propylène, du butylène, de l'isoprène, du butadiène ou de mélanges de ceux-ci, en (b) le copolymère oléfinique est du polybutadiène ou de l'isoprène et en (c) le noyau en étoile est dérivé du divinylbenzène et les branches polymère sont dérivées de l'isoprène et du butadiène, facultativement copolymérisé avec du styrène.

8. Un concentré d'huiles comportant une huile lubrifiante et entre 10 et 30 % en poids d'un copolymère séquencé fonctionnalisé par des groupes carboxyle ou d'un copolymère oléfinique tel que défini dans l'une



quelconque des revendications 1 à 7.

9. Procédé pour préparer une composition d'huile lubrifiante selon l'une quelconque des revendications 1 à 7, dans lequel on ajoute un copolymère séquencé ou un copolymère oléfinique fonctionnalisé au carboxyle tel que défini dans l'une quelconque des revendications 1 à 7, à une proportion prépondérante d'une huile minérale lubrifiante.

10. Procédé tel que revendiqué dans la revendication 9, dans lequel le copolymère séquencé ou le copolymère oléfinique fonctionnalisé au carboxyle est tel que défini dans la revendication 2 et est préparé en faisant réagir un copolymère séquencé hydrogéné ou un copolymère oléfinique avec un sulfonylazide de formule RSO_2N_3 , dans laquelle R représente un groupe organique renfermant du carboxyle.