

Description

This invention relates to modified polymers having useful properties as additives for lubricating oils.

The newer engines place increased demands on the lubricants to be employed. In the past a number of different additives has been added to lubricating oils to improve properties such as viscosity index and dispersancy. One such additive added to lubricating oils to improve viscosity index (VI) is a two-block copolymer having the general configuration A-B where A is styrene and B is hydrogenated isoprene, e.g. as described in U.S. Patents Nos. 3,763,044 and 3,772,196. A VI improver having greatly improved mechanical shear stability is the selectively hydrogenated star-shaped polymer disclosed in U.K. Patent Specification 1,575,507. Employing a single additive that improves a number of lubricant properties can achieve significant reductions in cost, and also circumvent the compatibility problems that can arise between the various additives and/or base oil. However, in attempting to improve more than a single lubricant property, care must be taken in not causing the deterioration of other properties. For example, the use of an oxidation step to attach polar groups to the polymer backbone in U.S. Patent No. 3,864,268 leads to reduced lubricant stability by introducing sites for oxidative attack.

US Patent No. 4,077,893 discloses ashless oil-soluble additives prepared by a process comprising:

(a) reacting selectively hydrogenated star-shaped polymer with an alpha-beta unsaturated carboxylic acid, anhydride or ester at a temperature of between about 150 °C and about 300 °C, for between about 1 hour and about 20 hours wherein said star-shaped polymer comprises a poly (polyalkenyl coupling agent) nucleus, and at least four polymeric arms linked to said nucleus wherein said polymeric arms are selected from the group consisting of:

- (i) hydrogenated homopolymers and hydrogenated copolymers of conjugated dienes;
- (ii) hydrogenated copolymers of conjugated dienes and monoalkenyl arenes; and
- (iii) mixtures thereof;

and wherein at least about 80% of the aliphatic unsaturation of the star-shaped polymer has been reduced by hydrogenation while less than 20% of the aromatic unsaturation has been reduced; and

(b) reacting the product of step (a) with an alkane polyol having at least two hydroxy groups at a temperature of between about 150 °C and about 250 °C.

EP-A-364 058 (Applicants' ref. T 5277 EPC) describes ashless, oil-soluble additives having both dispersant and viscosity-index (VI) improving properties produced by

1) reacting an alpha-beta unsaturated carboxylic acid or active derivative thereof, preferably at a temperature of between about 100 °C and about 300 °C for between about 1 hour and about 24 hours, with a selectively hydrogenated star-shaped polymer comprising a polyvinyl aromatic nucleus and at least 4 polymeric arms e.g. 4-25 arms, which arms each can have a number average molecular weight of e.g. 5,000 to 150,000 and which are linked to said nucleus wherein said polymeric arms are selected from the group consisting of:

- (i) hydrogenated homopolymers and hydrogenated copolymers of conjugated dienes;
- (ii) hydrogenated copolymers of conjugated dienes and monoalkenyl arenes; and
- (iii) mixtures thereof;

and wherein at least 80%, preferably 90 to 98%, of the aliphatic unsaturation of the star-shaped polymer has been reduced by hydrogenation while less than 20% of the aromatic unsaturation has been reduced; and

2) reacting the activated hydrogenated star polymer thus formed with:

- a) a long-chain alkane-substituted carboxylic acid or active derivative thereof, and
- b) with a C₁ to C₁₈ amine containing 1 to 8 nitrogen atoms and/or with an alkane polyol having at least two hydroxy groups;
- or with
- c) the preformed product of reactants a) and b).

According to the present invention there is provided a process for preparing a dispersant/VI improver which comprises

1) reacting an alpha-beta unsaturated carboxylic acid or active derivative thereof with a selectively hydrogenated star-shaped polymer comprising a polyvinylaromatic nucleus and at least 4 polymeric arms linked to said nucleus wherein said polymeric arms are selected from the group consisting of:

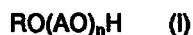
- (i) hydrogenated homopolymers and hydrogenated copolymers of conjugated dienes;
- (ii) hydrogenated copolymers of conjugated dienes and monoalkenyl arenes; and
- (iii) mixtures thereof;

and wherein at least 80% of the aliphatic unsaturation of the star-shaped polymer has been reduced by hydrogenation while less than 20% of the aromatic unsaturation has been reduced;

and

2) reacting the activated star polymer thus formed with:

(a) at least one compound of general formula



wherein R is a $\text{C}_4\text{--}20$ alkyl group, any A moiety is independently an ethylene or propylene moiety, and n is 0 to 10, optionally followed by reaction with

(b) a long chain alkane-substituted carboxylic acid or active derivative thereof, and/or

(c) a C_1 to C_{18} amine containing 1 to 8 nitrogen atoms and/or an alkane polyol having at least two hydroxy groups;

or with (d) the pre-formed product of reactants (b) and (c), optionally followed by esterifying any residual acid groups with a $\text{C}_1\text{--}6$ alkanol.

Step 1) above is essentially similar to step 1) of EP-A-364 058.

The star polymers employed in making the present dispersant VI improvers are generally produced by the process comprising the following reaction steps:

(i) polymerizing one or more conjugated dienes in solution in the presence of an ionic initiator to form a living polymer;

(ii) reacting the living polymer with a polyvinyl aromatic compound, preferably divinyl benzene, to form a star-shaped polymer; and

(iii) hydrogenating the star-shaped polymer to form a hydrogenated star-shaped polymer.

This preparation is described in detail in UK Patent Specification 1575507.

The living polymers produced in reaction step (i) of the above process are the precursors of the hydrogenated polymer chains which extend outwardly from the polyvinyl aromatic nucleus. Preferably each polymeric arm has a number average molecular weight between 5,000 to 150,000 and is a hydrogenated polyisoprene homopolymer.

The molecular weights of the star-shaped polymer to be hydrogenated in reaction step (iii) may vary between relatively wide limits. It is possible to produce star polymers having peak molecular weights between about 25,000 and about 1,250,000. Preferred molecular weights are 100,000 to 500,000. These peak molecular weights are determined by gel permeation chromatography (GPC) on a polystyrene scale.

In step (iii), the star-shaped polymers are hydrogenated by any suitable technique. Suitably at least 80%, preferably about 90 to about 98%, of the original olefinic unsaturation is hydrogenated. The amount of aromatic unsaturation which is hydrogenated, if any, will depend on the hydrogenation conditions used. However, preferably less than 20%, more preferably less than 5%, of such aromatic unsaturation is hydrogenated.

The molecular weights of the hydrogenated star-shaped polymers correspond to those of the unhydrogenated star-shaped polymers.

The hydrogenation can be carried out as described in UK Patent Specification 1,575,507, the preferred process being the selective hydrogenation process described in U.S. Patent 3,595,942. In that process hydrogenation is conducted, preferably in the same solvent in which the polymer was prepared, utilizing a catalyst comprising the reaction product of an aluminium alkyl and a nickel or cobalt carboxylate or alkoxide. A favoured catalyst is the reaction product formed from triethyl aluminium and nickel octoate.

The hydrogenated star-shaped polymer is then 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. Easily handleable concentrates are produced even when the amount of hydrogenated star-shaped polymer therein exceeds 10%w. Suitable concentrates contain from 10 to 25%w of the hydrogenated star-shaped polymer.

The selectively hydrogenated star polymers as prepared above do not in themselves have adequate dispersancy characteristics and are modified as explained below.

1) The star polymer is first activated by reaction with an alpha-beta unsaturated carboxylic acid or active derivative thereof. By "active derivative thereof" is meant anhydrides, esters and the like. Suitable unsaturated acids and derivatives include maleic acid, maleic anhydride, itaconic acid, dimethyl itaconate, acrylic acid, ethyl acrylate, methacrylic acid, methyl methacrylate, oleic acid, linoleic acid, etc., with maleic anhydride being especially preferred.

The unsaturated carboxylic compound and the hydrogenated star polymer may conveniently be reacted together at a temperature in the range 100°C to 300°C , preferably 130°C to 250°C . The contacting time may conveniently be from 1 hour to 24 hours, preferably from 4 hours to 8 hours. The

carboxylic compound reacts with the residual olefinic bonds available on the diene portion of the star polymer, and/or with the radicals initiated on the polymer chain; temperatures from 100°C to 150°C being suitable in the latter case.

Various solvents may be employed in the carboxylic acid derivative addition step 1) including generally olefin-free petroleum hydrocarbons, aromatics and halogenated hydrocarbons. A preferred solvent is a lubricating oil basestock. Preferably a concentration in the range of about 1% to about 20% by weight of the copolymer in solvent may conveniently be used for this conversion.

Generally the amount of unsaturated carboxylic compound is an excess over that stoichiometrically necessary to react with all the residual double bonds remaining in the diene portion of the selectively hydrogenated star polymer. Preferably, at least one mol of carboxylic compound is used for each olefinic unsaturation present in the selectively hydrogenated star polymer, with equivalent ratios of carboxylic compound to olefinic double bonds in the range from 1:1 to 2:1 being particularly suitable. However, less than stoichiometric amounts of carboxylic compound may also be used.

The above reaction may be carried out with or without the use of catalyst or radical initiators such as tert. butyl hydroperoxide or tert. butyl perbenzoate. Any excess carboxylic compound is typically removed either by vacuum distillation or through the use of a stripping gas stream.

2) The activated hydrogenated star polymer resulting from the above reaction with unsaturated carboxylic acid is then modified by reaction with:

(a) at least one compound of general formula



wherein R is a C₄₋₂₀ alkyl group, any A moiety is independently an ethylene or propylene moiety and n is 0 to 10, optionally followed by reaction with

(b) a long-chain alkane-substituted carboxylic acid or active derivative thereof, preferably succinic acid, anhydride or ester, and/or

(c) C₁ to C₁₈ amine containing 1 to 8 nitrogen atoms and/or with an alkane polyol having at least two hydroxy groups; or (d) the preformed product of reactants (b) and (c), optionally followed by esterifying any residual acid groups with a C₁₋₆ alkanol. Reaction of the activated star polymer with

the compound of general formula I (reactant (a)) is suitably effected by heating these reactants together, suitably at a temperature in the range from 100°C to 200°C, preferably from 140°C to 170°C. Subsequent reaction with an alkane carboxylic acid (reactant (b)), and/or an alkylamine or alkane polyol (reactant (c)), or a pre-formed reaction product of (a) and (b) (reactant (d)) is suitably effected in similar manner to reaction of the activated star polymer with reactant (a), but reactants (b) and (c) may be added in any order or together. Preferably however, when both reactants (b) and (c) are used, reactant (b) is added first. The reaction may be carried out in the presence of a solvent, conveniently the same solvent as that used in the star polymer activating step 1), a luboil basestock being particularly convenient for both process steps. It is desirable to operate under an inert atmosphere, suitably nitrogen.

Compounds of formula I are known. It will be appreciated that when n is 0, the compounds of formula I are C₄₋₂₀ alkanols, e.g. n-butanol or a C₉₋₁₅ detergent primary alkanol such as those sold by the Royal Dutch/Shell Group of companies under the "DOBANOL" trade mark, e.g. "DOBANOL 91", "DOBANOL 23", "DOBANOL 25", or "DOBANOL 45". It is preferred, however for n to be in the range 2 to 10, more preferably 3 to 7, very conveniently 5. A is preferably an ethylene moiety. R is preferably C₉₋₁₅ alkyl, more preferably C₉₋₁₁ alkyl. Suitable such compounds are "DOBANOL" (trade mark) ethoxylates sold by the Royal Dutch/Shell Group of companies, e.g. "DOBANOL 91-2.5", "DOBANOL 91-6", "DOBANOL 23-6.5", "DOBANOL 25-3", "DOBANOL 25-7", and very conveniently "DOBANOL 91-5".

The molar ratio of compound of formula I to carboxylic moieties in the activated star polymer product of step 1) preferably in the range 0.1:1 to 2:1. Thus when the alpha-beta unsaturated carboxylic acid or active derivative is maleic anhydride, as is preferred, the molar ratio of compound of formula I: maleic anhydride groups in the activated star polymer is preferably 0.2:1 to 4:1, and is more preferably 0.5:1 to 2:1. In the case where there is no subsequent reaction with any of reactants (b), (c) and (d), the preferred molar ratio of compound of formula I: maleic groups is 0.5:1 to 4:1, more preferably 1:1 to 2:1.

Long-chain alkane-substituted carboxylic acid/derivatives (reactant (b)) are preferably derived by reacting an alpha-beta unsaturated carboxylic acid or active derivative thereof with a polyolefin, suitably a homopolymer or copolymer of one or more olefin monomers having 2 to 16 preferably from 2 to 6, carbon atoms. The copolymers include random, block and tapered copolymers. Suitable monomers include ethene, propene, butenes, isobutene, pentenes, octenes, and also diolefines such as butadiene and isoprene. If a

diene is used as monomer the resulting polymer is preferably hydrogenated to saturate at least 90%, more preferably substantially all unsaturated bonds. It is especially preferred to use a polyolefin substituent derived from polyisobutylene.

The number average molecular weight of the polyolefin substituent is suitably not greater than 5000, since molecular weights above 5000 can impair the dispersancy properties of the final products, especially in crankcase lubricants. To reduce the risk of problems the number average molecular weight is preferably from 700 to 3000. The number average molecular weight (M_n) can easily be determined by vapour pressure osmometry or by gel permeation chromatography with calibration of the polymer, as will be appreciated by those skilled in the art. The weight average molecular weight (M_w) can also be determined by gel permeation chromatography. The quotient M_w/M_n , which is a measure indicating the width of molecular weight distribution, suitably has a value from 1.5 to 4.0.

The unsaturated acid reacting with the polyolefin may be any of those listed earlier as suitable for activating the hydrogenated star polymer, maleic acid or anhydride being particularly preferred. In the case of maleic acid/anhydride, the addition of the polyolefin to the unsaturated bonding yields a polyolefin-substituted succinic acid derivative.

The average number of unsaturated carboxylic acid groups per polyolefin moiety is normally in the range from 0.5 to 1.5. This means that some of the polyolefin moieties are connected to more than one succinic group. Preferably, the average number of succinic groups per polyolefin moiety is in the range from 0.9 to 1.1.

The polyolefin-substituted carboxylic acids may be prepared according to established procedures from an alkene of required molecular weight and an appropriate amount of the unsaturated carboxylic acid or active derivative. Thus, the polyolefin, e.g. polyisobutylene, may be mixed with maleic anhydride and chlorine passed through the mixture, yielding hydrochloric acid and polyolefin-substituted succinic anhydride, as described in e.g. GB-A-949,981. Another method for the preparation of polyolefin substituted succinic anhydride is described in US-A-3,172,892, according to which a halogenated, in particular chlorinated, polyolefin is reacted with maleic anhydride.

From e.g. GB-A-1,483,729 it is known to prepare hydrocarbon-substituted succinic anhydride by thermally reacting a polyolefin with maleic anhydride, a procedure which may be combined with that of GB-A-949,981, as is illustrated in GB-A-1,440,219 and GB-A-1,543,627. The products prepared in this way include compounds in which the polyolefin chain is connected to one or both of the alpha carbon atoms of the succinic group.

C_1 to C_{18} amines employed in the instant invention can be branched or unbranched, saturated, aliphatic, primary or secondary amines, containing 1 to 8 nitrogens, preferably mono- or diamines, such as ethylamine, butylamine, sec. butylamine, diethylamine, 3-dimethylamino propylamine etc., but including higher polyamines such as alkylene polyamines, wherein pairs of nitrogen atoms are joined by alkylene groups of 2 to 4 carbon atoms. Thus, polyamines of the formula:



are included where n is 2 to 4 and m is 0 to 6. Examples of such polyamines include tetraethylene pentamine, tripropylene tetramine, triethylene tetramine, diethylene triamine, N-aminoalkyl piperazines, e.g., N-(2-aminoethyl) piperazine, N,N'-di(2-aminoethyl) piperazine, etc. Preferred are diethylene triamine, triethylene tetramine or tetraethylene pentamine, as well as corresponding commercial mixtures such as "Polyamine H", and "Polyamine 500".

Alkane polyols useful in making the esters are alkane polyols having at least two and preferably at least four hydroxy groups such as the trihydroxyalkanes, e.g. ethylene glycol, propylene glycol, polymethylene glycols, trihydroxybutanes, pentanes, hexanes, heptanes, octanes, nonanes, dodecanes, etc., as well as tetrahydroxy alkanes, pentahydroxy alkanes, hexahydroxy alkanes, as well as the sugar alcohols such as erythritol, pentaerythritol, tetritols, pentitols, hexitols, mannitol, sorbitol, glucose and the like. Particularly preferred alcohols are pentaerythritol and mannitol. Especially preferred is pentaerythritol.

The molar ratio of amine or polyol to the balance of the carboxylic compounds taking into account the amount of compound of formula I employed is typically between about 0.1:1 and about 2:1, preferably between about 0.25:1 and about 2:1, most preferably about 0.5:1. The conditions during imide formation or esterification are typically about 150°C to 250°C for between about 1 hours and 20 hours.

In the reaction steps of 2) it is much preferred that the reactions take place in the absence of oxygen. A nitrogen blanket is often used to accomplish this result. The reason for performing the reaction in the absence of oxygen is that the resulting additive may be more oxidatively unstable if any oxygen is present during the formation of the additive.

In the event that amine or polyol is employed, and is employed in excess, then it may be desirable to remove the excess. One means of doing this is to first exchange the tri-chlorobenzene solvent for a lube base stock by vacuum distillation, and then add a volume of heptane equal to the volume of oil solution. Then an equal volume of methanol is added and mixed. Two separate layers are therein formed upon settling; one layer comprising predominantly wash solvent and the unreacted amine or polyol, and a second layer comprising predominantly oil, heptane, and the additive product. After separating the wash layer, the volatiles present in the product layer can then be removed by a distillation technique. Alternatively, the excess amine or polyol may be removed under a vacuum or with a stripping gas stream.

In the event that any residual acid groups are to be esterified with a C_{1-6} alkanol, esterification is effected in known manner, e.g. by addition of the alkanol and a suitable acid, e.g. p-toluenesulphonic acid, at elevated temperature e.g. at reflux temperature. The C_{1-6} alkanol may conveniently be, e.g. methanol, ethanol, n-propanol, isopropanol or, preferably, n-butanol.

The dispersant VI improvers of the present invention possess a useful combination of viscosity improving properties with oxidative stability, mechanical shear stability, and dispersancy. In particular, lubricating oils containing these VI improver/ dispersants possess a good combination of thickening efficiency and shear stability at high temperature and also good low temperature viscosity characteristics. A lower amount of the present VI improver/dispersants may be required in order to obtain the required thickening performance, as compared with the prior art VI improvers. Further, the VI improver/dispersants may also possess a superior combination of oxidative shear stability, permanent shear stability, and "temporary shear loss". Temporary shear loss refers to the temporary viscosity loss at high shear stress conditions resulting from the non-Newtonian character of the polymeric VI improvers. Still further, the dispersing power of the instant polymeric additive is excellent.

The reaction product of this invention can be incorporated in lubricating oil compositions, e.g. automotive crankcase oils, in concentrations e.g. within the range of about 0.1 to about 15, preferably about 0.1 to 3, weight percent based on the weight of the total compositions, if desired after treatment with base e.g. sodium hydroxide or, preferably, calcium hydroxide to neutralise any residual undesired acidity. The lubricating oils to which the additives of the invention can be added include not only mineral lubricating oils, but synthetic oils also. Synthetic hydrocarbon lubricating oils may also be employed, as well as non-hydrocarbon synthetic oils including dibasic acid esters such as di-2-ethyl hexyl sebacate, carbonate esters, phosphate esters, halogenated hydrocarbons, polysilicones, polyglycols, glycol esters such as C_{13} oxo acid diesters of tetraethylene glycol, etc. When used in gasoline or fuel oil, e.g. diesel fuel, No. 2 fuel oil, etc., then usually about 0.001 to 0.5 weight percent, based on the weight of the total composition of the reaction product will be used. Concentrations comprising a minor proportion, e.g. 15 to 45 weight percent, of said reaction product in a major amount of hydrocarbon diluent, e.g. 85 to 55 weight percent mineral lubricating oil, with or without other additives present, can also be prepared for ease of handling.

In the above compositions or concentrates, other conventional additives may also be present, including dyes, pour point depressants, antiwear agents, e.g. tricresyl phosphate, zinc dialkyl dithiophosphates of 3 to 8 carbon atoms, antioxidants such as phenyl-alpha-naphthylamine, tert-octylphenol sulphide, bis-phenols such as 4,4'-methylene bis(3,6-di-tert-butylphenol), viscosity index improvers such as the ethylene-higher olefin copolymer, polymethylacrylates, polyisobutylene, alkyl fumaratevinyl acetate copolymers, and the like as well as other ashless dispersants or detergents such as overbased sulphonates.

The invention is further illustrated by means of the following Examples, which are given for the purpose of illustration.

EXAMPLE 1

(a) A concentrate of "SHELLVIS 200" (trade mark) star polymer in "XHV-6" oil (13.8% m/m) was reacted under stirring with maleic anhydride (MALA) (2% m/m on star polymer) at 133°C during 18 hours in the presence of tert. butylperbenzoate, as radical initiator, in a N_2 -atmosphere (50 ppm O_2). The radical initiator was dosed (by pumping) over 41 minutes as a 50% m/m solution in oil.

		GRAMS	% m/m
5	Intake: "SHELLVIS 200"	340.94	13.66
	MALA	6.82	0.27 (= 2% m/m on starpolymer)
10	"Trigonox C" (trade mark)	9.21	0.37 (= 2% m/m tert. tert. butylperbenzoate on starpolymer)
15	(=75% tert. butylperbenzoate)		
	"XHVI-oil"	2138.87	85.70
20	Total	2495.84	100.0

25 "SHELLVIS 200" is a star-shaped polymer comprising hydrogenated polyisoprene arms having mol. wt. 35,000 coupled with divinylbenzene according to the procedure of UK Patent No. 1,575,507.

Then the reaction mixture was stripped at 110°C under high vacuum (0.06 mm Hg, 8Pa) to remove residual non-reacted maleic anhydride.

30 The maleic anhydride content of the thus obtained VI-improver concentrate was determined by titration with 0.1 mol/l sodium methoxide solution in methanol, using phenolphthalein as the indicator. The MALA content of the reaction product after high vacuum stripping was: 0.015 mmol/g product. Theoretical MALA-content assuming 100% grafting, would be 0.028 mmol/g. Grafting efficiency was therefore 54%.

35 (b) 1505.9 g (22.1 mmol grafted MALA content) of the stripped product of step (a) above was reacted under nitrogen with 8.41g (22.1 mmol) of a blend of C₉₋₁₁ alkanol ethoxylates of mean relative molecular mass 380 and containing 5 mol ethylene oxide/mol ("DOBANOL 91-5" (trade mark) ethoxylate available from the Royal Dutch/Shell Group of companies) by heating the stirred mixture at 150°C for 1 hour followed by 3 hours at 170°C. The resulting product (concentrate, Product A) contained 13.6%w star polymer and 0.014 mmol/g acid, according to titration.

40 A blend of 1.7%w of Product A in "HVI 60" oil had viscosity at 100°C of 15.8mm²/S (ASTM D445). "HVI 60" oil is a bright and clear high viscosity index base oil having viscosity at 100°C of 4.4 to 4.9 mm²/S (ASTM D445) and minimum flash point 200°C (ASTM D 92).

EXAMPLE 2

45 1567.0g (23.0 mmol grafted MALA content) of the stripped product of Example 1(a) was reacted in similar manner to Example 1(b) with 17.5g (46.1 mmol) of "DOBANOL 91-5" (trade mark) ethoxylate. The resulting product contained 0.0125 mmol/g acid, according to titration. In order to achieve exhaustive esterification, 14.1g (190.5 mmol) n-butanol 3.8g p-toluenesulphonic acid and 1 l toluene were added (acid content of resulting mixture 0.009 mmol/g) and the resulting mixture was heated under reflux for 22 hours. 50 The acid content of the mixture reduced to 0.004 mmol/g. The mixture was then treated with 20g calcium hydroxide for 1 hour at ambient temperature (20°C), filtered and evaporated in vacuo at 100°C to yield a product (concentrate, Product B) containing 13.6%w star polymer, which was acid-free, according to titration.

55 A blend of 1.7%w of Product B in "HVI 60" oil had viscosity at 100°C of 14.9 mm²/S (ASTM D445).

EXAMPLE 3

1700g (25.5 mmol grafted MALA content) of the stripped product of Example 1(a) was reacted under nitrogen with 4.84g (12.8 mmol) of "DOBANOL 91-5" (trade mark) ethoxylate by heating the stirred mixture at 150 °C for 2 hours. After cooling to ambient temperature (20 °C), a polyisobutylene-substituted succinic anhydride (PIB MALA) (39.2 g, containing 38.22 mmol succinic anhydride groups) was added. Diethylene triamine (DETA) (2.76 g, 2.90 ml, 26.78 mmol) was added with heating under nitrogen for 58 minutes at 150 °C, followed by heating at 180 °C for 3 hours, during the last hour of which nitrogen was passed through the reaction mixture to aid removal of volatile materials. The resulting product (concentrate, Product C) contained 13.3% w star polymer, 0.010 mmol/g basic N and 0.008 mmol/g acid, according to titration.

A blend of 1.7% w of Product C in "HVI 60" oil had viscosity at 100 °C of 19.33 mm²/S (ASTM D 445).

EXAMPLE 4

The procedure of Example 3 was followed except that the diethylamine was replaced by pentaerythritol (3.47 g, 25.5 mmol), and unreacted pentaerythritol was removed from final, viscous, reaction product by dilution with a volume of xylene equal to the volume of the final reaction product, filtration at 100 °C and evaporation of the xylene in vacuo. The resulting product (concentrate, Product D) contained 13.3% w star polymer and 0.024 mmol/g acid, according to titration.

A blend of 1.7% w of Product D in "HVI 60" oil had viscosity at 100 °C of 28.3 mm²/S (ASTM D445).

EXAMPLE 5

Samples of Products A, B, C, D and the commercially available VI-improver "SHELLVIS 200" were blended with a SAE 10w/40 luboil containing 6%w/w of an additive package comprising an overbased salicylate detergent, a succinimide ashless dispersant, a zinc-based anti-wear additive and a poly-methacrylate pour point depressant. The resulting oil was then evaluated according to the sequence VE (as described in "Sequence VE test procedure", 7th draft dated 19th May, 1988; ASTM Monitoring Center, 4400 5th Avenue Pittsburgh USA).

Results are given in Table I following:-

TABLE I

Sample	% w/w sample	VE Test Parameter		
		Average Engine Sludge (AES)	Average Engine Varnish (AEV)	Average Camlobe Wear (ACLM) (um)
SHELLVIS 200	9.50	5.4	4.3	34.3
SHELLVIS 200	7.64	4.5	5.0	8.0
Product A	7.48	6.3	4.3	14.0
Product B	8.10	6.7	4.1	21.6
Product C	7.52	6.3	4.3	18.0
Product D	4.89	5.6	5.0	88.1
SG Pass Limit		9 (min)	5.0 (min)	127 (max)

**Claims****Claims for the following Contracting States : BE, DE, FR, GB, IT, NL****1. Process for preparing a dispersant/VI improver which comprises**

5 1) reacting an alpha-beta unsaturated carboxylic acid or active derivative thereof with a selectively hydrogenated star-shaped polymer comprising a polyvinylaromatic nucleus and at least 4 polymeric arms linked to said nucleus wherein said polymeric arms are selected from the group consisting of:

(i) hydrogenated homopolymers and hydrogenated copolymers of conjugated dienes;

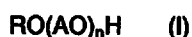
10 (ii) hydrogenated copolymers of conjugated dienes and monoalkenyl arenes; and

(iii) mixtures thereof;

and wherein at least 80% of the aliphatic unsaturation of the star-shaped polymer has been reduced by hydrogenation while less than 20% of the aromatic unsaturation has been reduced; and

2) reacting the activated star polymer thus formed with:

15 (a) at least one compound of general formula



20 wherein R is a C_4-20 alkyl group, any A moiety is independently an ethylene or propylene moiety, and n is 0 to 10, optionally followed by reaction with

(b) a long chain alkane-substituted carboxylic acid or active derivative thereof, and/or (c) a C_1 to C_{18} amine containing 1 to 8 nitrogen atoms and/or an alkane polyol having at least two hydroxy groups; or with (d) the pre-formed product of reactants (b) and (c), optionally followed by esterifying any residual acid groups with a C_1-6 alkanol.

25 2. Process as claimed in claim 1 wherein the number of polymeric arms is between 4 and 25, and the polyvinyl aromatic compound is divinyl benzene.

30 3. Process according to claim 1 or 2, wherein, in the star polymer, the number average molecular weight of each polymeric arm is between 5,000 and 150,000, and the peak molecular weight of the hydrogenated star-shaped polymer is between 25,000 and 1,250,000.

35 4. Process as claimed in any one of claims 1-3 wherein the star polymer and carboxylic acid or active derivative thereof are reacted at a temperature in the range 130°C to 250°C .

5. Process as claimed in any one of Claims 1 to 4 wherein R in formula I is C_9-15 alkyl.

6. Process as claimed in any one of Claims 1 to 5 wherein n in formula I is in the range of 3 to 7.

40 7. Process as claimed in any one of Claims 1 to 6 wherein the alpha-beta unsaturated carboxylic acid or active derivative thereof is maleic anhydride.

8. Process as claimed in Claim 7 wherein the molar ratio of compound of formula I: maleic anhydride groups in the activated star polymer is in the range of 0.2:1 to 4:1.

45 9. An ashless, oil-soluble dispersant/VI improver when prepared by a process as claimed in any one of the preceding claims.

50 10. A lubricating composition comprising a major amount of a lubricating oil and a minor amount of a dispersant/VI improver as claimed in claim 9.

Claims for the following Contracting State : ES**1. Process for preparing a dispersant/VI improver which comprises:**

55 (1) reacting an alpha-beta unsaturated carboxylic acid or active derivative thereof with a selectively hydrogenated star-shaped polymer comprising a polyvinylaromatic nucleus and at least 4 polymeric arms linked to said nucleus wherein said polymeric arms are selected from the group consisting of:

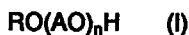
(i) hydrogenated homopolymers and hydrogenated copolymers of conjugated dienes;



(ii) hydrogenated copolymers of conjugated dienes and monoalkenyl arenes; and
 (iii) mixtures thereof;
 and wherein at least 80% of the aliphatic unsaturation of the star-shaped polymer has been reduced by hydrogenation while less than 20% of the aromatic unsaturation has been reduced;
 and

(2) reacting the activated star polymer thus formed with:

(a) at least one compound of general formula:



wherein R is a $\text{C}_4\text{--}20$ alkyl group, any A moiety is independently an ethylene or propylene moiety, and n is 0 to 10, optionally followed by reaction with

(b) a long chain alkane-substituted carboxylic acid or active derivative thereof, and/or

(c) a C_1 to C_{18} amine containing 1 to 8 nitrogen atoms and/or an alkane polyol having at least two hydroxy groups; or with

(d) the pre-formed product or reactants (b) and (c), optionally followed by esterifying any residual acid groups with a $\text{C}_1\text{--}6$ alkanol.

2. Process as claimed in claim 1 wherein the number of polymeric arms is between 4 and 25, and the polyvinyl aromatic compound is divinyl benzene.

3. Process according to claim 1 or 2, wherein, in the star polymer, the number average molecular weight of each polymeric arm is between 5,000 and 150,000, and the peak molecular weight of the hydrogenated star-shaped polymer is between 25,000 and 1,250,000.

4. Process as claimed in any one of claims 1-3 wherein the star polymer and carboxylic acid or active derivative thereof are reacted at a temperature in the range 130°C to 250°C .

5. Process as claimed in any one of Claims 1 to 4 wherein R in formula I is $\text{C}_3\text{--}15$ alkyl.

6. Process as claimed in any one of Claims 1 to 5 wherein n in formula I is in the range of 3 to 7.

7. Process as claimed in any one of Claims 1 to 6 wherein the alpha-beta unsaturated carboxylic acid or active derivative thereof is maleic anhydride.

8. Process as claimed in Claim 7 wherein the molar ratio of compound of formula I: maleic anhydride groups in the activated star polymer is in the range of 0.2:1 to 4:1.

Patentsprüche

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

1. Verfahren zur Herstellung eines Dispergiermittels/VI-Verbesserers, bei dem man

1) eine α,β -ungesättigte Carbonsäure oder eines ihrer aktiven Derivate mit einem selektiv hydrierten, sternförmig aufgebauten Polymer umsetzt, welches aus einem polyvinyl- aromatischen Kern und mindestens 4 an den Kern gebundenen Polymerästen besteht, wobei man die Polymeräste aus der Gruppe, bestehend aus

(i) hydrierten Homopolymeren und hydrierten Copolymeren von konjugierten Dienen,

(ii) hydrierten Copolymeren von konjugierten Dienen und Monoalkenylarenen und

(iii) Mischungen daraus, auswählt,

und wobei mindestens 80% der aliphatischen Ungesättigtheit des sternförmig aufgebauten Polymers durch Hydrieren reduziert wurde, während weniger als 20% der aromatischen Ungesättigtheit reduziert wurde,
 und man

2) das so gebildete aktivierte Sternpolymer mit

(a) mindestens einer Verbindung der allgemeinen Formel





in der R eine C₄-C₂₀-Alkylgruppe bedeutet, jeder Molekülteil A unabhängig eine Ethylen- oder eine Propyleneinheit bedeutet und n gleich 0 bis 10 ist, umgesetzt, gegebenenfalls gefolgt von einer Reaktion mit

(b) einer langkettigen, alkansubstituierten Carbonsäure oder einem ihrer aktiven Derivate und/oder (c) einem C₁- bis C₁₈-Amin mit 1 bis 8 Stickstoffatomen und/oder einem Polyhydroxyalkan mit mindestens zwei Hydroxygruppen, oder man es mit

(d) dem zuvor gebildeten Produkt der Reaktanden (b) und (c) umgesetzt, gegebenenfalls gefolgt von einer Veresterung restlicher Säuregruppen mit einem C₁-C₆-Alkanol.

2. Verfahren nach Anspruch 1, bei dem die Anzahl der Polymeräste zwischen 4 und 25 liegt und es sich bei der polyvinylaromatischen Verbindung um Divinylbenzol handelt.
3. Verfahren nach Anspruch 1 oder 2, bei dem das zahlenmittlere Molekulargewicht eines jeden Polymerastes in dem Sternpolymer zwischen 5000 und 150 000 liegt und das Molmassenmaximum des hydrierten, sternförmig aufgebauten Polymers zwischen 25 000 und 1 250 000 liegt.
4. Verfahren nach einem der Ansprüche 1-3, bei dem man das Sternpolymer und die Carbonsäure bzw. ihr aktives Derivat bei einer Temperatur im Bereich von 130 °C bis 250 °C umsetzt.
5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem es sich in Formel I bei R um C₃-C₁₅-Alkyl handelt.
6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem n in Formel I im Bereich von 3 bis 7 liegt.
7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem es sich bei der α,β -ungesättigten Carbonsäure bzw. ihrem aktiven Derivat um Maleinsäureanhydrid handelt.
8. Verfahren nach Anspruch 7, bei dem das Molverhältnis von der Verbindung der Formel I zu den Maleinsäureanhydridgruppen im aktivierten Sternpolymer im Bereich von 0,2:1 bis 4:1 liegt.
9. Aschefreies/-er, öllösliches/-er Dispergiermittel/VI-Verbesserer, hergestellt durch ein Verfahren nach einem der vorhergehenden Ansprüche.
10. Schmiermittelzusammensetzung, welche zu einem großen Teil aus einem Schmieröl und zu einem kleinen Teil aus einem Dispergiermittel/VI-Verbesserer nach Anspruch 9 besteht.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung eines Dispergiermittels/VI-Verbesserers, bei dem man

1) eine α,β -ungesättigte Carbonsäure oder eines ihrer aktiven Derivate mit einem selektiv hydrierten, sternförmig aufgebauten Polymer umsetzt, welches aus einem polyvinylaromatischen Kern und mindestens 4 an den Kern gebundenen Polymerästen besteht, wobei man die Polymeräste aus der Gruppe, bestehend aus

(i) hydrierten Homopolymeren und hydrierten Copolymeren von konjugierten Dienen,

(ii) hydrierten Copolymeren von konjugierten Dienen und Monoalkenylarenen und

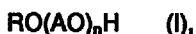
(iii) Mischungen daraus, auswählt,

und wobei mindestens 80% der aliphatischen Ungesättigtheit des sternförmig aufgebauten Polymers durch Hydrieren reduziert wurde, während weniger als 20% der aromatischen Ungesättigtheit reduziert wurde,

und man

- 2) das so gebildete aktivierte Sternpolymer mit

(a) mindestens einer Verbindung der allgemeinen Formel



in der R eine C₄-C₂₀-Alkylgruppe bedeutet, jeder Molekülteil A unabhängig eine Ethylen- oder eine Propyleneinheit bedeutet und n gleich 0 bis 10 ist, umgesetzt, gegebenenfalls gefolgt von einer Reaktion mit



- (b) einer langkettigen, alkansubstituierten Carbonsäure oder einem ihrer aktiven Derivate und/oder
 (c) einem C₁- bis C₁₈-Amin mit 1 bis 8 Stickstoffatomen und/oder einem Polyhydroxyalkan mit
 mindestens zwei Hydroxygruppen, oder man es mit
 (d) dem zuvor gebildeten Produkt oder Reaktanden (b) und (c) umsetzt, gegebenenfalls gefolgt
 von einer Veresterung restlicher Säuregruppen mit einem C₁-C₆-Alkanol.
- 5
2. Verfahren nach Anspruch 1, bei dem die Anzahl der Polymeräste zwischen 4 und 25 liegt und es sich
 bei der polyvinylaromatischen Verbindung um Divinylbenzol handelt.
- 10 3. Verfahren nach Anspruch 1 oder 2, bei dem das zahlenmittlere Molekulargewicht eines jeden Polyme-
 rastes in dem Sternpolymer zwischen 5000 und 150 000 liegt und das Molmassenmaximum des
 hydrierten, sternförmig aufgebauten Polymers zwischen 25 000 und 1 250 000 liegt.
- 15 4. Verfahren nach einem der Ansprüche 1-3, bei dem man das Sternpolymer und die Carbonsäure bzw.
 ihr aktives Derivat bei einer Temperatur im Bereich von 130 °C bis 250 °C umsetzt.
5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem es sich in Formel I bei R um C₉-C₁₅-Alkyl
 handelt.
- 20 6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem n in Formel I im Bereich von 3 bis 7 liegt.
7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem es sich bei der α,β-ungesättigten Carbonsäure
 bzw. ihrem aktiven Derivat um Maleinsäureanhydrid handelt.
- 25 8. Verfahren nach Anspruch 7, bei dem das Molverhältnis von der Verbindung der Formel I zu den
 Maleinsäureanhydridgruppen im aktivierten Sternpolymer im Bereich von 0,2:1 bis 4:1 liegt.

Revendications

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

- 30 1. Procédé de préparation d'un agent d'amélioration des propriétés dispersives/de l'indice de viscosité,
 caractérisé en ce que
- 35 1) on fait réagir un acide carboxylique alpha-bêta insaturé, ou un dérivé activé de celui-ci, avec un
 polymère étoilé sélectivement hydrogéné comprenant un noyau polyvinylaromatique et au moins 4
 bras polymériques liés audit noyau, où lesdits bras polymériques sont choisis dans le groupe
 constitué par :
- 40 (i) les homopolymères hydrogénés et les copolymères hydrogénés de diènes conjugués,
 (ii) les copolymères hydrogénés de diènes conjugués et les monoalcénylarènes et
 (iii) leurs mélanges
 et où au moins 80% de l'insaturation aliphatique du polymère étoilé ont été réduits par
 hydrogénation cependant que moins de 20% de l'insaturation aromatique ont été réduits
 et
- 45 2) on fait réagir le polymère étoilé activé ainsi formé
 avec
- (a) au moins un composé de la formule générale
- RO(AO)_nH (I)
- 50 dans laquelle R représente un radical alkyle en C₄ à C₂₀, n'importe quel groupement A est
 indépendamment un radical éthylène ou propylène et n a une valeur qui varie de 0 à 10, réaction
 éventuellement suivie d'une réaction avec
- (b) un acide carboxylique alcane substitué à longue chaîne, ou un dérivé activé de celui-ci et/ou
 (c) une amine en C₁ à C₁₈ contenant de 1 à 8 atomes d'azote et/ou un alcanepolyol possédant
 au moins deux radicaux hydroxyle, et/ou avec
- 55 (d) le produit préformé des réactifs (b) et (c), réaction éventuellement suivie de l'estérification des
 radicaux acide résiduels avec un alcool en C₁ à C₆.



2. Procédé suivant la revendication 1, caractérisé en ce que le nombre de bras polymériques varie de 4 à 25 et le composé polyvinylaromatique est le divinylbenzène.
3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que, dans le polymère étoilé, le poids moléculaire moyen en nombre de chaque bras polymérique varie de 5.000 à 150.000 et le poids moléculaire pic du polymère étoilé hydrogéné fluctue de 25.000 à 1.250.000.
4. Procédé suivant l'une quelconque des revendications 1 à 3, caractérisé en ce que le polymère étoilé et l'acide carboxylique ou son dérivé activé sont mis à réagir à une température qui varie de 130 °C à 250 °C.
5. Procédé suivant l'une quelconque des revendications 1 à 4, caractérisé en ce que R dans la formule I représente un radical alkyle en C₃ à C₁₅.
6. Procédé suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que n dans la formule I a une valeur qui varie de 3 à 7.
7. Procédé suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que l'acide carboxylique alpha-bêta insaturé ou son dérivé activé est l'anhydride maléique.
8. Procédé suivant la revendication 7, caractérisé en ce que le rapport molaire du composé de la formule I aux radicaux anhydride maléique dans le polymère étoilé activé varie de 0,2:1 à 4:1.
9. Agent d'amélioration de la dispersivité/indice de viscosité oléosoluble et sans cendre, préparé par mise en oeuvre d'un procédé suivant l'une quelconque des revendications précédentes.
10. Composition lubrifiante comprenant une quantité principale d'une huile lubrifiante et une quantité mineure d'un agent d'amélioration de la dispersivité/indice de viscosité suivant la revendication 9.

Revendications pour l'Etat contractant suivant : ES

1. Procédé de préparation d'un agent d'amélioration des propriétés dispersives/de l'indice de viscosité, caractérisé en ce que
 - 1) on fait réagir un acide carboxylique alpha-bêta insaturé, ou un dérivé activé de celui-ci, avec un polymère étoilé sélectivement hydrogéné comprenant un noyau polyvinylaromatique et au moins 4 bras polymériques liés audit noyau, où lesdits bras polymériques sont choisis dans le groupe constitué par :
 - (i) les homopolymères hydrogénés et les copolymères hydrogénés de diènes conjugués,
 - (ii) les copolymères hydrogénés de diènes conjugués et les monoalcénylarènes et
 - (iii) leurs mélanges
 et où au moins 80% de l'insaturation aliphatique du polymère étoilé ont été réduits par hydrogénation cependant que moins de 20% de l'insaturation aromatique ont été réduits et
 - 2) on fait réagir le polymère étoilé activé ainsi formé
 - (a) au moins un composé de la formule générale

$$RO(AO)_nH \quad (I)$$
 dans laquelle R représente un radical alkyle en C₄ à C₂₀, n'importe quel groupement A est indépendamment un radical éthylène ou propylène et n a une valeur qui varie de 0 à 10, réaction éventuellement suivie d'une réaction avec
 - (b) un acide carboxylique alcane substitué à longue chaîne, ou un dérivé activé de celui-ci et/ou
 - (c) une amine en C₁ à C₁₈ contenant de 1 à 8 atomes d'azote et/ou un alcanepolyol possédant au moins deux radicaux hydroxyle, et/ou
 - ou avec (d) le produit préformé des réactifs (b) et (c), réaction éventuellement suivie de l'estérification des radicaux acide résiduels avec un alcool en C₁ à C₆.



2. Procédé suivant la revendication 1, caractérisé en ce que le nombre de bras polymériques varie de 4 à 25 et le composé polyvinylaromatique est le divinylbenzène.
- 5 3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que, dans le polymère étoilé, le poids moléculaire moyen en nombre de chaque bras polymérique varie de 5.000 à 150.000 et le poids moléculaire pic du polymère étoilé hydrogéné fluctue de 25.000 à 1.250.000.
- 10 4. Procédé suivant l'une quelconque des revendications 1 à 3, caractérisé en ce que le polymère étoilé et l'acide carboxylique ou son dérivé activé sont mis à réagir à une température qui varie de 130 °C à 250 °C.
5. Procédé suivant l'une quelconque des revendications 1 à 4, caractérisé en ce que R dans la formule I représente un radical alkyle en C₃ à C₁₅.
- 15 6. Procédé suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que n dans la formule I a une valeur qui varie de 3 à 7.
7. Procédé suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que l'acide carboxylique alpha-bêta insaturé ou son dérivé activé est l'anhydride maléique.
- 20 8. Procédé suivant la revendication 7, caractérisé en ce que le rapport molaire du composé de la formule I aux radicaux anhydride maléique dans le polymère étoilé activé varie de 0,2:1 à 4:1.

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