

Description

This invention relates to an improved process for the preparation of a grafted hydrogenated star polymer, and to a lubricating oil composition containing the resultant polymer.

U.K. Patent Specification No. 1575507 describes hydrogenated star-shaped polymers comprising a poly-(poly-alkenyl coupling agent)nucleus having extending outwardly therefrom a plurality of hydrogenated polymer chains of one or more conjugated dienes and, optionally, one or more monoalkenyl aromatic compounds, wherein the poly-alkenyl coupling agent has at least two non-conjugated alkenyl groups and no halogen atoms together with the preparation of such polymers by

(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.

EP-A-113 138 discloses a product suitable as lubricating oil additive obtainable by polymerizing one or more C_1 - $_{30}$ -alkyl(meth)acrylates, and optionally at least one further monomer in a solvent, preferably a base oil, containing an at least partially hydrogenated polymer of a conjugated diene and optionally a monoalkenyl arene, characterized in that said polymer is a star-shaped polymer comprising a nucleus and polymeric arms linked to said nucleus wherein said arms are selected from the group consisting of:

(i) at least partially hydrogenated homopolymers and at least partially hydrogenated copolymers of conjugated dienes;

(ii) at least partially hydrogenated copolymers of conjugated dienes and monoalkenyl arenes;

(iii) homopolymers and copolymers of alkenyl arenes; and

(iv) mixtures thereof.

EP-A-171 167 discloses a process comprising grafting a hydrocarbon polymer of C_2 to C_{28} olefin, said polymer having a number average molecular weight in the range of from 5,000 to 500,000 with an unsaturated material selected from the group consisting of: (A) ethylenically unsaturated C_3 to C_{10} carboxylic acid having 1 to 2 carboxylic acid groups or an anhydride group, and (B) nitrogen-containing ethylenically unsaturated monomers containing 6 to 30 carbon atoms and 1 to 4 nitrogen atoms, in the presence of a free radical initiator and a chain stopping agent.

European Patent 0029622 describes how the properties of hydrogenated star-shaped polymers can be improved by grafting with nitrogen containing polymerizable organic compounds, especially 2-vinylpyridine or 4-vinylpyridine, together with the preparation of such grafted products by reacting the star polymer and the nitrogen-containing compound in the presence of a free radical initiator and in an inert solvent such as cyclohexane. Further work by the Applicants has now established that this grafting reaction can be carried out more simply in a mineral oil solvent, with particularly useful results being obtained when certain additives are used to reduce shear loss caused by the tendency of the nitrogen-containing compounds to couple with one another.

Accordingly, the present invention provides a process for preparing a grafted star polymer which consists of contacting a nitrogen-containing polymerisable organic polar compound with a star polymer comprising a nucleus bearing polymeric arms of

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

(ii) hydrogenated copolymers of conjugated dienes and mono-alkenyl arenes; or

(iii) mixture of i) and ii),

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, in the presence of a free radical polymerisation initiator, in a mineral oil solvent and, as coupling inhibitor, either anisole, or, as comonomer, N-vinylpyrrolidone.

The nucleus of the star polymer is preferably a poly(polyvinyl aromatic coupling agent), such as poly-(divinylbenzene), and suitably bears 4 to 25, especially 5 to 10, polymeric arms. Those polymeric arms are conveniently derived from one or more C_4 to C_{12} conjugated dienes, preferably being hydrogenated polybutadiene or polyisoprene chains, and suitably each arm has a number average molecular weight of from 5,000 to 150,000.

The star polymers which are grafted in the present process are generally produced by 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.

5 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 is a hydrogenated polyisoprene homopolymer.

10 The molecular weights of the star-shaped polymer to be hydrogenated in reaction step (iii) may vary between relatively wide limits. However, an important aspect of the present invention is that polymers possessing good shear stability may be produced even though the polymers have very high molecular weights. 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 600,000. These peak molecular weights are determined by gel permeation chromatography (GPC) on a polystyrene scale.

15 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.

20 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.

25 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 a concentrate. Easily handleable concentrates are produced even when the amount of hydrogenated star-shaped polymer therein exceeds 10%. Suitable concentrates contain from 10 to 25%W of the hydrogenated star polymer.

30 The nitrogen-containing organic polar compound is preferably a polymerizable nitrogen-containing heterocyclic compound selected from the group consisting of piperidine, morpholine, piperazine, pyridine, pyrrolidone, pyrrole, benzopyrrole, quinoline, indole, which are all alkenyl-substituted and 2-methyl vinylpyridine and N-vinylimidazole. Of the polar compounds 2-vinylpyridine and 4-vinylpyridine are most preferred.

35 The free radical initiator may be any of those compounds known for this purpose in graft polymerization, tert. butyl hydroperoxide, tert. butyl perbenzoate and di-tert. butyl peroxide generally being convenient materials. The mineral oil reaction medium is preferably a high viscosity index mineral oil such as "HVI 60" oil; a commercial product of kinematic viscosity (100 °C) 4.73 cSt.

40 The coupling inhibitor is, according to the present invention, present in order to inhibit the tendency of the grafting process to increase the shear loss properties of the final product, which is believed to arise mainly from a coupling side reaction between two nitrogen-containing polar (e.g. 4-vinyl pyridine) star shaped molecules.

45 The amount of nitrogen-containing compound grafted onto the star polymer is suitably between 1 and 20, preferably 2 to 12 and especially 4.5, % m/m, based on star polymer, whilst the amount of coupling inhibitor is dependent on the nature of the inhibitor selected. In the case of anisole, the amount is suitably between 5 to 15 and especially 9% m/m being preferred; and in the case of the comonomer, N-vinylpyrrolidone, an amount between 1 and 10%, especially 2 to 3% m/m, is preferred, all amounts based on star polymer.

50 The process for preparing the grafted hydrogenated star polymers may be carried out at a temperature from 70 ° to 180 °C, but is preferably between 110 ° and 130 °C, with grafting at 120 °C giving optimal results in respect of the shear loss characteristics of the final product. A convenient practical compromise between a short reaction time (requiring a higher reaction temperature) and satisfactory shear loss characteristics (optimal at 120 °C) can be attained by an initial reaction at 120 °C (e.g. for the first hour), followed by gradual heating to 130 °C (e.g. over 1-2 hours), concluding with several hours at 130 °C. The amount of free radical polymerization initiator is suitably chosen to balance the production of the necessary grafting sites on the star polymer and thereby the number of grafted chains, and the chain-length of the

grafted chains, amounts within the range of 1 to 10% m/m, generally 2.0% m/m on polymer, being generally suitable. In some cases, it may be convenient to dose both the free radical initiator and the grafting monomer gradually through the course of the reaction. In order to minimize undesirable side reactions, the process is preferably carried out under an inert atmosphere, conveniently nitrogen, with pressures between 1 (1×10^5 Pa) and 50 bars (50×10^5 Pa) being selected according to the constraints of the apparatus in use.

The grafted polymers of this invention are of particular value as additives for lubricating oils, functioning as viscosity index improvers; hence a further embodiment of the invention provides a lubricating oil composition comprising a minor proportion, suitably from 0.15 to 20%w, of the grafted star polymer. For convenience of formulation, it is often useful to incorporate the grafted polymer in the form of a luboil concentrate containing from 5 to 50%w of the polymer.

The invention is further illustrated in the following Examples, of which numbers 1-6 are included for comparative purposes.

15 Example 1

Following the procedure described in USP 4,077,893 there was prepared a star-shaped polymer, having hydrogenated polyisoprene arms having a number average molecular weight of 35,000 coupled with divinylbenzene ("Shellvis" 200). This was taken up in "HVI-oil Brent 60" to form a 13.6%w concentrate.

2595g of the concentrate was charged into a 5 litre stainless steel reactor fitted with a mechanical stirrer, gas inlet tube, manometer, thermometer and heating/cooling device.

The polymer solution was heated to 90 °C in the meantime replacing the air by nitrogen. As soon as the oxygen content in the reactor amounted to less than 100 ppm the concentrate was heated to 120 °C. A 20%w oxygen free solution of 15.88g of 4-vinyl pyridine in "HVI-oil Brent 60" was added to the polymer solution, followed after a few minutes of mixing, by a 50%w oxygen-free solution of 9.53g of "TRIGONOX C" (trade mark) (=75%w of tert. butylperbenzoate in oil) in "HVI-oil 60". Heating and stirring were continued for 18 hours to yield the desired grafted star polymer as a concentrate in the "HVI-oil" reaction medium.

30 Examples 2-6

Procedures similar to those of Example 1 were used to prepare further products, the detailed reaction conditions being varied as follows:-

Example 2	Reaction at 130 °C
Example 3	Reaction at 110 °C
Example 4	Reaction at 120 °C for 1 hour, 120-130 °C for 2 hours, 130 °C for 4 hours.
Example 5	Reaction at 120 °C, but half amount of initiator
Example 6	Reaction at 120 °C, but 4-vinyl pyridine and initiator added in 2 equal portions at 0 hours and 3 hours.

Examples 7 and 8

The general procedure of Example 1 was followed, but employing additionally a coupling inhibitor according to the present invention; the nature and amount of coupling inhibitor being set out in Table I.

Table I records also the relevant performance parameters on the products of each example (Examples 1-6 being included for comparative purposes) as determined after formulation into a 10W40 oil at 1.1% m/m polymer content. For further comparison, Example S denotes the comparable properties determined on the ungrafted hydrogenated star polymer ("Shellvis" 200) (trade mark).

TABLE I

Example No.	*Coupling Inhibitor	**Relative		Kinematic Viscosity (100_C) (c St) ($\times 10^{-6} \text{ m}^2/\text{s}$)	Sequence VD Engine Test Results ^x		
		Shear	Loss		AES	AEV	PSV
1	-	1.18		14.6	9.64	7.06	7.29
2	-	1.60		14.8	nd	nd	nd
3	-	1.45		14.8	nd	nd	nd
4	-	0.96		14.8	nd	nd	nd
5	-	0.66		14.2	nd	nd	nd
6	-	1.05		14.6	9.63	7.2	7.18
7	A 9%	0.85		14.4	nd	nd	nd

TABLE I

Example No.	*Coupling Inhibitor	**Relative Shear Loss	Kinematic Viscosity (100°C) (c St) ($\times 10^{-6} \text{ m}^2/\text{s}$)	Sequence VD Engine Test Results ^x		
				AES	AEV	PSV
8***	NVP 2.25%	0.71	14.4	9.58	7.61	7.24
S	-	0.25-0.28	13.7	9.54	5.33	7.14

* Coupling Inhibitor; A = anisole; NVP = N-vinyl pyrrolidone

** Shear Loss expressed as relative to "Shellvis" 250, determined in a 10W40 formulation of DIN 51382.

*** In Example No. 8 half the amount of 4-vinylpyridine, used in Example No. 1, was employed.

x AES = average engine sludge; AEV = average engine varnish; PSV = piston skirt varnish (ratings 0 - 10; 10 = clean).

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

- 5 1. Process for preparing a grafted star polymer which consists of contacting a nitrogen-containing polymerisable organic polar compound with a star polymer comprising a nucleus bearing polymeric arms of
 - (i) hydrogenated homopolymers and hydrogenated copolymers of conjugated dienes; or
 - (ii) hydrogenated copolymers of conjugated dienes and mono-alkenyl arenes; or
 - (iii) mixture of i) and ii),
- 10 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, in the presence of a free radical polymerisation initiator, in a mineral oil solvent and, as coupling inhibitor, either anisole, or, as comonomer, N-vinylpyrrolidone.
- 15 2. Process as claimed in Claim 1, wherein the nitrogen-containing polymerisable organic polar compound is a nitrogen-containing heterocyclic compound selected from the group consisting of piperidine, morpholine, piperazine, pyridine, pyrrolidone, pyrrole, benzopyrrole, quinoline, indole, which are all alkenyl-substituted and 2-methylvinylpyridine and N-vinylimidazole, preferably 2-vinylpyridine or 4-vinylpyridine.
- 20 3. Process as claimed in claim 1 or 2, wherein the free radical polymerisation initiator is tert. butyl perbenzoate or di-tert. butyl peroxide.
- 25 4. Process as claimed in any one of the preceding claims wherein the star polymer comprises a poly-(polyvinyl aromatic)nucleus bearing 4 to 25 polymeric arms, and has a number average molecular weight from 25,000 to 1,250,000.
- 30 5. Process as claimed in claim 4, wherein the star polymer comprises a poly(divinylbenzene)nucleus bearing 5 to 10 arms of hydrogenated polyisoprene, each of which arms has a number average molecular weight from 5,000 to 150,000.
- 35 6. Process as claimed in any one of the preceding claims wherein the amount of nitrogen-containing polar compound is between 1 and 20% m/m; and the amount of coupling inhibitor is between 5 and 15% m/m for anisole, or between 1 and 10% m/m for N-vinylpyrrolidone, all amounts based on star polymer.
7. A lubricating oil composition comprising an oil containing a minor proportion of a grafted star polymer obtained by a process according to any one of claims 1 to 6.

Claims for the following Contracting State : ES

- 40 1. Process for preparing a grafted star polymer which consists of contacting a nitrogen-containing polymerisable organic polar compound with a star polymer comprising a nucleus bearing polymeric arms of
 - (i) hydrogenated homopolymers and hydrogenated copolymers of conjugated dienes; or
 - (ii) hydrogenated copolymers of conjugated dienes and mono-alkenyl arenes; or
 - (iii) mixture of i) and ii),
- 45 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, in the presence of a free radical polymerisation initiator, in a mineral oil solvent and, as coupling inhibitor, either anisole, or, as comonomer, N-vinylpyrrolidone.
- 50 2. Process as claimed in Claim 1, wherein the nitrogen-containing polymerisable organic polar compound is a nitrogen-containing heterocyclic compound selected from the group consisting of piperidine, morpholine, piperazine, pyridine, pyrrolidone, pyrrole, benzopyrrole, quinoline, indole, which are all alkenyl-substituted and 2-methylvinylpyridine and N-vinylimidazole, preferably 2-vinylpyridine or 4-vinylpyridine.
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3. Process as claimed in claim 1 or 2, wherein the free radical polymerisation initiator is tert. butyl perbenzoate or di-tert. butyl peroxide.
- 5 4. Process as claimed in any one of the preceding claims wherein the star polymer comprises a poly-(polyvinyl aromatic)nucleus bearing 4 to 25 polymeric arms, and has a number average molecular weight from 25,000 to 1,250,000.
- 10 5. Process as claimed in claim 4, wherein the star polymer comprises a poly(divinylbenzene)nucleus bearing 5 to 10 arms of hydrogenated polyisoprene, each of which arms has a number average molecular weight from 5,000 to 150,000.
- 15 6. Process as claimed in any one of the preceding claims wherein the amount of nitrogen-containing polar compound is between 1 and 20% m/m; and the amount of coupling inhibitor is between 5 and 15% m/m for anisole, or between 1 and 10% m/m for N-vinylpyrrolidone, all amounts based on star polymer.
7. Process for the preparation of a lubricating oil composition which comprises mixing an oil with a minor proportion of a grafted star polymer obtained by a process according to any one of claims 1 to 6.

Patentansprüche

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

- 25 1. Verfahren zur Herstellung von gefropften, sternförmig aufgebauten Polymerisaten, die sich zusammensetzen aus Kontaktieren einer polymerisierbaren, polaren, Stickstoff enthaltenden organischen Verbindung mit einem sternförmig aufgebauten Polymerisat, umfassend einen Kern, der polymere, armähnliche Fortsätze von
 - (i) hydrierten Homopolymeren und hydrierten Copolymeren von konjugierten Dienen; oder
 - (ii) hydrierten Copolymeren von konjugierten Dienen und Monoalkenylarenen; oder
 - (iii) Gemischen von (i) und (ii)
 trägt, und wobei mindestens etwa 80% der aliphatischen Ungesättigtheit des sternförmig aufgebauten
 30 Polymerisats durch Hydrierung reduziert worden sind, während weniger als 20% der aromatischen Ungesättigtheit reduziert worden sind, in Gegenwart eines freie Radikale liefernden Polymerisationsinitiators, in einem Mineralöl-Lösungsmittel und, als Kupplungsinhibitor, entweder Anisol oder, als Comonomeres, N-Vinylpyrrolidon.
- 35 2. Verfahren wie in Anspruch 1 beansprucht, wobei die polymerisierbare polare, Stickstoff enthaltende organische Verbindung eine Stickstoff enthaltende heterocyclische Verbindung, ausgewählt aus der Gruppe, bestehend aus Piperidin, Morpholin, Piperazin, Pyridin, Pyrrolidon, Pyrrol, Benzopyrrol, Chinolin, Indol, die alle alkenylsubstituiert sind, und 2-Methylvinylpyridin und N-Vinylimidazol, vorzugsweise 2-Vinylpyridin oder 4-Vinylpyridin, ist.
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3. Verfahren wie in Anspruch 1 oder 2 beansprucht, wobei der freie Radikale liefernde Polymerisationsinitiator tert.-Butylperbenzoat oder Di-tert.-butylperoxid ist.
- 45 4. Verfahren wie in irgendeinem der vorstehenden Ansprüche beansprucht, wobei das sternförmig aufgebaute Polymerisat aus einem poly(polyvinylaromatischen) Kern, der 4 bis 25 polymere, armähnliche Fortsätze trägt, besteht, und eine durchschnittliche Molekulargewichtszahl von 25 000 bis 1 250 000 hat.
- 50 5. Verfahren wie in Anspruch 4 beansprucht, wobei das sternförmig aufgebaute Polymerisat aus einem Poly(divinylbenzol)-Kern besteht, der 5 bis 10 armähnliche Fortsätze von hydriertem Polyisopren trägt, von denen jeder armähnliche Fortsatz eine durchschnittliche Molekulargewichtszahl von 5000 bis 150 000 hat.
- 55 6. Verfahren wie in irgendeinem der vorstehenden Ansprüche beansprucht, wobei die Menge der polaren, Stickstoff enthaltenden Verbindung zwischen 1 und 20 Molprozent je Mol liegt und die Menge des Kupplungsinhibitors für Anisol zwischen 5 und 15 Molprozent je Mol und für N-Vinylpyrrolidon zwischen 1 und 10 Molprozent je Mol liegt, wobei sich alle Mengen auf das sternförmig aufgebaute Polymerisat beziehen.



7. Eine Schmierölzusammensetzung, bestehend aus einem Öl mit einem geringen Gehalt an einem gepropften, sternförmig aufgebauten Polymerisat, das nach irgendeinem der Ansprüche 1 bis 6 erhalten worden ist.

5 Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung von gepropften, sternförmig aufgebauten Polymerisaten, die sich zusammensetzen aus Kontaktieren einer polymerisierbaren, polaren, Stickstoff enthaltenden organischen Verbindung mit einem sternförmig aufgebauten Polymerisat, umfassend einen Kern, der polymere, armähnliche Fortsätze von
- 10 (i) hydrierten Homopolymeren und hydrierten Copolymeren von konjugierten Dienen; oder
(ii) hydrierten Copolymeren von konjugierten Dienen und Monoalkenylarenen; oder
(iii) Gemischen von (i) und (ii)
- 15 trägt, und wobei mindestens etwa 80% der aliphatischen Ungesättigtheit des sternförmig aufgebauten Polymerisats durch Hydrierung reduziert worden sind, während weniger als 20% der aromatischen Ungesättigtheit reduziert worden sind, in Gegenwart eines freie Radikale liefernden Polymerisationsin-
itiators, in einem Mineralöl-Lösungsmittel und, als Kupplungsinhibitor, entweder Anisol oder, als Comonomeres, N-Vinylpyrrolidon.
- 20 2. Verfahren wie in Anspruch 1 beansprucht, wobei die polymerisierbare polare, Stickstoff enthaltende organische Verbindung eine Stickstoff enthaltende heterocyclische Verbindung, ausgewählt aus der Gruppe, bestehend aus Piperidin, Morpholin, Piperazin, Pyridin, Pyrrolidon, Pyrrol, Benzopyrrol, Chino-
lin, Indol, die alle alkenylsubstituiert sind, und 2-Methylvinylpyridin und N-Vinylimidazol, vorzugsweise 2-Vinylpyridin oder 4-Vinylpyridin, ist.
- 25 3. Verfahren wie in Anspruch 1 oder 2 beansprucht, wobei der freie Radikale liefernde Polymerisationsin-
itiator tert.-Butylperbenzoat oder Di-tert.-butylperoxid ist.
4. Verfahren wie in irgendeinem der vorstehenden Ansprüche beansprucht, wobei das sternförmig
30 aufgebaute Polymerisat aus einem poly(polyvinylaromatischen) Kern, der 4 bis 25 polymere, armähnliche Fortsätze trägt, besteht, und eine durchschnittliche Molekulargewichtszahl von 25 000 bis 1 250 000 hat.
5. Verfahren wie in Anspruch 4 beansprucht, wobei das sternförmig aufgebaute Polymerisat aus einem
35 Poly(divinylbenzol)-Kern besteht, der 5 bis 10 armähnliche Fortsätze von hydriertem Polyisopren trägt, von denen jeder armähnliche Fortsatz eine durchschnittliche Molekulargewichtszahl von 5000 bis 150 000 hat.
6. Verfahren wie in irgendeinem der vorstehenden Ansprüche beansprucht, wobei die Menge der polaren,
40 Stickstoff enthaltenden Verbindung zwischen 1 und 20 Molprozent je Mol liegt und die Menge des Kupplungsinhibitors für Anisol zwischen 5 und 15 Molprozent je Mol und für N-Vinylpyrrolidon zwischen 1 und 10 Molprozent je Mol liegt, wobei sich alle Mengen auf das sternförmig aufgebaute Polymerisat beziehen.
- 45 7. Verfahren zur Herstellung einer Schmierölzusammensetzung, umfassend ein Mischen eines Öls mit einem geringen Gehalt an einem gepropften, sternförmig aufgebauten Polymerisat, das nach einem Verfahren irgendeines der Ansprüche 1 bis 6 erhalten worden ist.

Revendications

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

1. Procédé pour la préparation d'un polymère étoilé greffé qui consiste à mettre en contact un composé
polaire organique polymérisable contenant de l'azote avec un polymère étoilé comprenant un noyau
portant des bras polymères
- 55 (1) d'homopolymères hydrogénés et de copolymères hydrogénés de diènes conjugués ; ou
(2) de copolymères hydrogénés de diènes conjugués et de mono-alcényl arènes ; ou
(3) d'un mélange de (1) et (2),
et où au moins environ 80 % de l'insaturation aliphatique du polymère étoilé a été réduite par



hydrogénation tandis que moins de 20 % de l'insaturation aromatique a été réduite, en présence d'un initiateur de polymérisation radicalaire, dans un solvant huile minérale et, comme inhibiteur de couplage, de l'anisol, ou, comme comonomère, de la N-vinylpyrrolidone.

- 5 2. Procédé selon la revendication 1, dans lequel le composé polaire organique polymérisable contenant de l'azote est un composé hétérocyclique contenant de l'azote choisi dans le groupe constitué par la pipéridine, la morpholine, la pipérazine, la pyridine, la pyrrolidone, le pyrrole, le benzopyrrole, la quinoléine, l'indole, qui sont tous alcényles, et la 2-méthylvinylpyridine et le N-vinylimidazole, de préférence la 2-vinylpyridine ou la 4-vinylpyridine.
- 10 3. Procédé selon la revendication 1 ou 2, dans lequel l'initiateur de polymérisation radicalaire est le perbenzoate de tertiobutyle ou le peroxyde de di-tertiobutyle.
- 15 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polymère étoilé comprend un noyau poly(polyvinyl aromatique) portant 4 à 25 bras polymères et a un poids moléculaire moyen en nombre compris entre 25 000 et 1 250 000.
5. Procédé selon la revendication 4, dans lequel le polymère étoilé comprend un noyau de poly-(divinylbenzène) portant 5 à 10 bras de polyisoprène hydrogéné, chacun de ces bras ayant un poids moléculaire moyen en nombre compris entre 5 000 et 150 000.
- 25 6. Procédé selon l'une quelconque des revendications précédentes, dans lequel la quantité de composé polaire contenant de l'azote est comprise entre 1 et 20 moles % ; et la quantité d'inhibiteur de couplage est comprise entre 5 et 15 moles % pour l'anisol ou entre 1 et 10 moles % pour la N-vinylpyrrolidone, toutes les quantités étant indiquées par rapport au polymère étoilé.
7. Une composition d'huile lubrifiante comprenant une huile contenant une proportion mineure d'un polymère étoilé greffé obtenu par un procédé selon l'une quelconque des revendications 1 à 6.

30 Revendications pour l'Etat contractant suivant : ES

1. Procédé pour la préparation d'un polymère étoilé greffé qui consiste à mettre en contact un composé polaire organique polymérisable contenant de l'azote avec un polymère étoilé comprenant un noyau portant des bras polymères
 - 35 (1) d'homopolymères hydrogénés et de copolymères hydrogénés de diènes conjugués ; ou
 - (2) de copolymères hydrogénés de diènes conjugués et de mono-alcényl arènes ; ou
 - (3) d'un mélange de (1) et (2),
 et où au moins environ 80% de l'insaturation aliphatique du polymère étoilé a été réduite par hydrogénation tandis que moins de 20% de l'insaturation aromatique a été réduite, en présence d'un
 - 40 initiateur de polymérisation radicalaire, dans un solvant huile minérale et, comme inhibiteur de couplage, de l'anisol, ou, comme comonomère, de la N-vinylpyrrolidone.
2. Procédé selon la revendication 1, dans lequel le composé polaire organique polymérisable contenant de l'azote est un composé hétérocyclique contenant de l'azote choisi dans le groupe constitué par la
 - 45 pipéridine, la morpholine, la pipérazine, la pyridine, la pyrrolidone, le pyrrole, le benzopyrrole, la quinoléine, l'indole, qui sont tous alcényles, et la 2-méthylvinylpyridine et le N-vinylimidazole, de préférence la 2-vinylpyridine ou la 4-vinylpyridine.
3. Procédé selon la revendication 1 ou 2, dans lequel l'initiateur de polymérisation radicalaire est le
 - 50 perbenzoate de tertiobutyle ou le peroxyde de di-tertiobutyle.
4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le polymère étoilé comprend un noyau poly(polyvinyl aromatique) portant 4 à 25 bras polymères et a un poids moléculaire moyen en nombre compris entre 25 000 et 1 250 000.
 - 55 5. Procédé selon la revendication 4, dans lequel le polymère étoilé comprend un noyau de poly(divinylbenzène) portant 5 à 10 bras de polyisoprène hydrogéné, chacun de ces bras ayant un poids moléculaire moyen en nombre compris entre 5 000 et 150 000.



6. Procédé selon l'une quelconque des revendications précédentes, dans lequel la quantité de composé polaire contenant de l'azote est comprise entre 1 et 20 moles % ; et la quantité d'inhibiteur de couplage est comprise entre 5 et 15 moles % pour l'anisol ou entre 1 et 10 moles % pour la N-vinylpyrrolidone, toutes les quantités étant indiquées par rapport au polymère étoilé.

7. Procédé de préparation d'une composition d'huile lubrifiante comprenant le mélange d'une huile avec une faible proportion d'un polymère étoilé greffé obtenu par un procédé selon l'une quelconque des revendications 1 à 6.