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## Description

This invention is directed to an oil-soluble product useful in lubricating oil compositions. More particularly, this invention is directed to a star-shaped polymer having the properties of both a viscosity index improver and a dispersant, the preparation thereof and lubricating oil compositions containing it.

The newer engines place increased demands on the lubricants to be employed. In the past a number of different additives have been added to lubricating oils to improve such properties as viscosity index and dispersancy. One such additive added to lubricating oils to improve viscosity index is a two-block copolymer having the general configuration A—B where A is styrene and B is hydrogenated isoprene. See generally U.S. Patent 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.S. Patent No. 4,116,917.

Significant reductions in cost can be made by employing a single additive that improves a number of lubricant properties. For example, in U.S. Patent No. 4,141,847 a selectively hydrogenated star-shaped polymer is reacted first with an alpha-beta carboxylic acid, anhydride or ester, and then the product is reacted with an amine to form a dispersant-VI improver. Likewise, in U.S. Patent No. 4,077,893 a similar product is obtained where an alkane polyol reactant is employed in place of the amine reactant to form a dispersant-VI improver. Still further, in the copending European patent application 80200993 a hydrogenated star-shaped polymer is reacted with a nitrogen containing polymerizable organic polar compound to form a dispersant-VI improver. The processes to form the above three products all have certain shortcomings. In each of the above-described patents, the synthesis process involved an additional step whereby the star-shaped polymer is subjected to either free radical polymerization initiators, such as, tert-butyl hydroperoxide and tert-butyl benzoate or a high temperature condensation reaction between an α—β unsaturated carboxylic acid or derivative and the residual olefin bonds in the star-polymer. The acidic derivatized site would then be reacted with an amine or alkane polyol. The high temperatures required for the free radical process (140°C) and condensation processes (180—250°C) add higher energy requirements for their manufacture and the additional reaction time as well as high temperatures increase the likelyhood of unwanted side-reactions such as cross-linking and chain-scission of the polymer. In each case the addition of a polar molecule, and more specifically a nitrogen-based molecule to the star-polymer backbone allows for the attainment of dispersant properties. Further process difficulties are encountered in controlling the degree of grafting and reproduceability of the functionalization reaction.

A new lube additive has been found that has significantly improved property advantages over the prior art additives.

The present invention is directed to an oil-soluble, star-shaped product having the properties of both a viscosity index-improver and a dispersant, said oil soluble product comprising:

(a) a poly(polyalkenyl aromatic)nucleus;
(b) at least three hydrogenated polymeric arms linked to said nucleus, said hydrogenated polymeric arms being selected from the group consisting of:
  (i) hydrogenated homopolymers and hydrogenated copolymers of conjugated dienes;
  (ii) hydrogenated copolymers of conjugated dienes and mono-alkenyl arenes; and
  (iii) mixtures thereof; and wherein at least about 80% of the aliphatic unsaturation of the polymeric arms has been reduced by hydrogenation while preferably less than 20% of the aromatic unsaturation has been reduced, and
(c) at least one polymerized nitrogen containing polar compound arm linked to said nucleus.

The dispersant-VI improvers of the present invention possess excellent viscosity improving properties, oxidative stability, mechanical shear stability and dispersancy. The advantages of the above-described process include lower functionalization temperatures, better control of the process and the degree of functionalization, short reaction times, and less polymer degradation such as cross-linking and chain scission. In essence, this process involves terminating the poly(polyalkenyl aromatic)nucleus with a suitable polar compound. This added step is a simple addition to the process of forming the said star-polymers and requires no increased temperatures, extra catalysts or long reaction times to affect the functionalization. Likewise, control over the degree of added polar compound which becomes chemically bonded to the poly(polyalkenyl aromatic)nucleus can be achieved by adjusting the molar ratio of polar compound to organo lithium compound used to polymerize the arms of the star-polymer.

The process for preparing this product comprises:

(a) solution polymerizing one or more conjugated diene and optionally one or more monoalkenyl arene monomers under polymerization conditions with an organolithium compound, forming living polymeric arms;
(b) contacting said living polymeric arms with a polyalkenyl aromatic coupling agent forming a coupled polymer having a poly(polyalkenyl aromatic)nucleus and attached polymeric arms;
(c) contacting said coupled polymer with a nitrogen containing polar compound monomer attaching poly(nitrogen containing polar compound)arms to said nucleus, and

(d) reducing by hydrogenation at least 80% of the aliphatic unsaturation of the polymeric arms while preferably reducing less than 20% of the aromatic unsaturation.

As is well-known, living polymers may be prepared by anionic solution polymerization of conjugated dienes and, optionally, monoalkenyl arene 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. 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., $C_4$ to $C_{12}$ conjugated dienes and, optionally, one or more monoalkenyl arene compounds.

Preferred dienes are, butadiene and/or isoprene. Preferred monoalkenyl arene compounds are the monovinyl aromatic compounds such as styrene, as well as the alkylated derivatives thereof. If a monoalkenyl arene compound is used in the preparation of the living polymers it is preferred that the amount thereof be below about 50% by weight, preferably about 3% to about 50%.

The living polymers may be living homopolymers or living copolymers. E.g. the living homopolymers may be represented by the formula A—M, wherein M is an ionic group, e.g., lithium, and A is polybutadiene or polyisoprene. Living polymers of isoprene are the preferred living homopolymers.

The living copolymers may be living block copolymers, living random copolymers or living tapered copolymers.

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, such as a lubricating oil, may also be used.

The temperature at which the polymerization is carried out may vary between wide limits such as from −75°C to 150°C, preferably from 20°C 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.

The concentration of the initiator used to prepare 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 number average molecular weights from 15,000 to 100,000 being preferred. Consequently, the number average molecular weight of the hydrogenated polymers 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 a polyalkenyl coupling agent. Polyalkenyl coupling agents capable of forming star-shaped polymers are known. See generally U.S. Patent No. 3,985,830, Canadian Patent No. 716,645, and British Patent No. 1,025,295. They are usually compounds having at least two non-conjugated alkenyl groups. Such groups are usually attached to the same or different electron-with-drawing 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. 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. The preferred compounds are represented by the formula: $A\text{-}(CH{=}CH_2)_x$ wherein A is an optionally substituted aromatic nucleus and x is an integer of at least 2. Divinyl benzene, in particular metadivinyl 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 diene and monoalkenyl arene monomer has been converted to living polymers.

The amount of polyalkenyl coupling agent added may vary between wide limits but preferably 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 solvents as for reaction step (a). A list of suitable solvent is given above. In reaction step (b) the temperature may also vary between wide limits, e.g., from 0° to 150°C, preferably from 20° 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.

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 typically between 3 and 25, preferably from about 7 to about 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 2 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.

It has been found that the greater number of arms employed in the instant invention significantly improve both the thickening efficiency and the shear stability of the polymer since it is then possible to prepare a VI-improver having a high molecular weight (resulting in increased thickening efficiency) without the necessity of excessively long arms (resulting in improved shear stability).

In step (c), the star-shaped polymer is contacted with a nitrogen-containing polar compound monomer, resulting in the attachment of at least one polymer arm directly to the poly(polyvinyl aromatic)nucleus. The nitrogen containing polar compound is preferably selected from the group consisting of 2-vinylpyridine and 4-vinylpyridine, with 2-vinylpyridine being most preferred. However, other polymerizable nitrogen-bearing compounds are also contemplated in the present invention, including, by way of example: 2-methyl, 5-vinyl pyridine; acrylamide; methacrylamides; N-alkyl acrylamides; N,N-dialkyl acrylamides; N,N-dialkylmethacrylamides, where the alkyl group contains from one to seven carbon atoms. Other polymerizable nitrogen-bearing compounds are: N-vinyl imidazole and N-vinyl carbazole; ε-caprolactam; N-vinyloxazolidone; N-vinylcaprolactam; N-vinylthiocaprolactam; and N-vinyl-pyrrolidone. Non-polymerizable nitrogen heterocycles can also be added with the polymerizable nitrogen-containing polar compound to give the desired functionality including: piperidine, pyrrolidine, morpholine, pyridine, aziridine, pyrrole, indole, pyridazine, quinoline and isoquinoline, pyridazine, pyrimidine, pyrazine, and derivatives and poly-pyridines having less than 20 pyridyl groups such as 2,2′-bipyridine and tripyridine, etc.

In the interests of simplicity, the remainder of the specification shall refer to vinylpyridine instead of nitrogen-containing polar compound.

After contacting the star-shaped polymer with the vinylpyridine monomer, the resulting star-shaped copolymer contains about 0.1 to about 10 per cent by weight vinylpyridine, preferably about 0.1 to about 5.0 per cent by weight. The number of poly(vinylpyridine)arms is typically between one and about 10, preferably between one and about 5. Accordingly, the molecular weight of the poly(vinylpyridine)arms is between about 105 and about 10,000, preferably between about 105 and about 1000.

The addition of the polar compound, preferably 2-vinylpyridine, to the poly(polyalkenyl aromatic)nucleus occurs at temperatures between −78°C and +80°C, preferably between 25°C and 60°C.

The molecular weights of the star-shaped polymer to be hydrogenated 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 500,000. These peak molecular weights are determined by gel permeation chromotography (GPC) on a polystyrene scale.

In step (d), the star-shaped polymers are hydrogenated by any suitable technique. Suitably at least 80%, preferably 90 to about 98% of the original olefinic unsaturation is hydrogenated. If the star-shaped polymer is partly derived from a monoalkenyl arene compound, then 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. If the poly(polyalkenyl coupling agent)nucleus is a poly(polyalkenyl aromatic coupling agent)nucleus, then the aromatic unsaturation of the nucleus may or may not be hydrogenated again depending upon the hydrogenation conditions used. The molecular weights of the hydrogenated star-shaped polymers correspond to those of the unhydrogenated star-shaped polymers.

The hydrogenation of the olefinic unsaturation is important with the regard to the thermal and oxidative stability of the product. This hydrogenation may be carried out in any desired way.

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.

A much preferred hydrogenation process is the selective hydrogenation process shown in U.S. Patent No. 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.

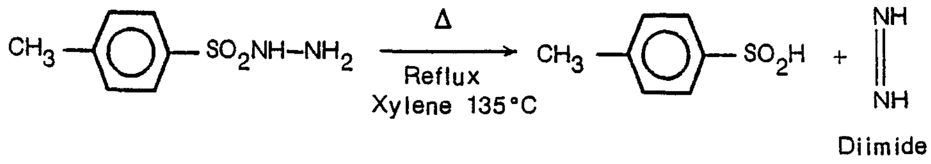
Another suitable process is a stoichiometric hydrogenation process wherein the polymer is contacted with a hydrazine or p-toluenesulphonylhydrazide reactant forming $N_2H_2$, which reduces the polymer by hydrogenation.

The advantage of the p-toluenesulphonylhydrazide and hydrazine hydrogenation technique is the ability to selectively reduce olefin saturation within the block copolymers without excessive degradation (chain-scission, cross-linking) of the polymer chain. Likewise, hydrogenation by this technique is mild and can be achieved in the presence of various functional groups. Specifically the unsaturated portion of the polymer chains containing primary, secondary or tertiary amines can be reduced to at least about 80%. Other functional groups which are rather inert toward the diimide reduction process are double-bonds which possess a polar character such as: (—C≡N, =C=N—, =C=O). Hence the major advantage of the diimide reduction procedure is the selectivity, allowing for the reduction of the olefinic sites within the block-polymer chain, while leaving other polar functional groups intact. Preferred solvents are cyclohexane, hexane, benzene, toluene, meta-, ortho- and para-xylenes or mixtures thereof. Most preferably, xylenes are used as the hydrogenation solvent.

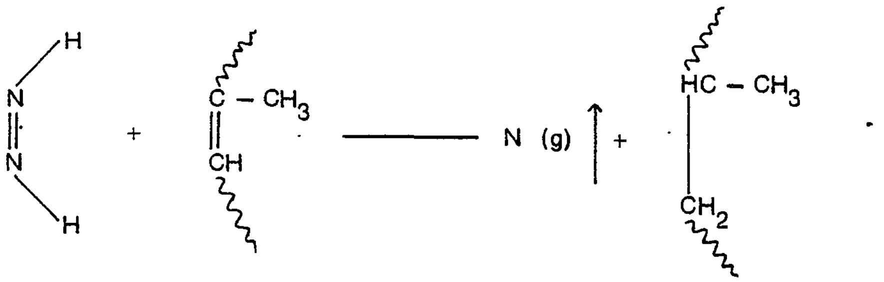
Without wishing to be bound to a particular theory, it is considered that in this stoichiometric hydrogenation, the reactant thermally decomposes, resulting in the formation of a diimide which serves as the actual hydrogenating agent. Next, the diimide quickly undergoes a concerted cis-addition to the polymer aliphatic double bonds affecting the hydrogenation, while releasing nitrogen as the gaseous by-product. The reactants employed herein include p-toluenesulfphonylhydrazide (PTSH) and hydrazine, with PTSH being preferred.

The mechanism of the hydrogenation step can be envisioned as follows, with PTSH as the reactant:

(1)



(2)



The temperature during the reactant decomposition stage is e.g. between 50°C and 150°C, preferably between 80°C and 135°C. The molar ration of PTSH or hydrazine reactant to conjugated diene units (aliphatic unsaturation bonds) is typically between 5:1 and 1:1, preferably between 3:1 and 1:1.

The hydrogenated star-shaped polymer is then recovered in solid form from the solvent in which it it hydrogenated by any convenient tecnique 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 reaction product of this invention can be incorporated in lubrication oil compositions, e.g., automotive crankcase oils, in concentrations within the range of about 0.1 to about 15, preferably about 0.1 to 3, %w based on the weight of the total compositions. The lubricating oils to which the additives of the invention can be added include not only mineral lubricating oils by synthetic oils also. Synthetic hydrocarbon lubricating oils may also be employed, as well asnon-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%w, 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 %w of said reaction product in a major amount of hydrocarbon diluent, e.g., 85 to 55 %w 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, e.g., tricresyl phosphate, zinc dialkyl dithiophosphates of 3 to 8 carbon atoms, antioxidants such as phenyl-alpha-naphthyl-amine, tert-octylphenol sulphide, bisphenols 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 the following Examples.

## Example 1

A 2-litre glass-bowl reactor equipped with a stirrer and appropriate temperature control was utilized for the synthesis of the star-shaped poly(isoprene) and the dispersant VI-improver. Anionic polymerization techniques were employed and all reagents such as: monomers, solvents, initiators, etc. were dry and of high purity. The polymerization was achieved under an inert gas such as argon or nitrogen in order to avoid contamination with the atmosphere.

The reactor was charged with 1170 grams of cyclohexane and heated to 35°C. A small amount of 1,1-diphenylethylene was then added to serve as an indicator for the subsequent tritration.

Incremental additions of sec-butyllithium were introduced into the reactor until a permanent yellow colour was reached. This served as an indicator that all impurities had been scavaged from the system. The solution was then back titrated with solvent until the yellow colour had just disappeared. The required amount of initiator was then charged, which was calculated to be $5.7 \times 10^{-3}$ moles of sec-butyllithium. To this solution was then added 294 mls of isoprene monomer. The temperature was allowed to increase to 60°C, where the polymerization continued for 2 hours. To the living poly(isoprene) was next added 0.028 moles of commercial divinylbenzene, such that the molar ratio of divinylbenzene to sec-RLi was 5:1. The reaction was allowed to proceed to 1—2 hours at 60°C. The solution turned deep red after addition of the divinylbenzene. This divinylbenzene coupling formed the star-shaped poly(isoprene). After the coupling step, 0.87 grams of 2-vinylpyridine was added to the solution giving the polymer a chemically bonded polar group. The polymer was then precipitated into a large excess of isopropanol, filtered, and dried in a vacuum oven until a constant weight was obtained.

Analysis of the polymer by Kjeldahl nitrogen analysis indicated that the polymer contained from 350 to 450 ppm nitrogen. This corresponds to around 0.5 %w 2-vinylpyridine in the polymer.

G.P.C. analysis of the polymer revealed the number-average arm molecular weight to be 38,000 and the functionality was observed to be around 9—10 arms. The polymer was stabilized with Ionol and stored until needed for subsequent hydrogenation.

### Stoichiometric Hydrogenation

Hydrogenation of the 2-vinylpyridine functionalized starshaped poly(isoprene) was achieved with para-toluenesulphonylhydrazide in refluxing xylene. A one-litre, four necked reaction flask, fitted with a condenser, nitrogen inlet, thermometer, and sample port was assembled and heated with a silicone oil bath.

The reaction flask was charged with 300 mls of xylene, to which was added 5 grams of polymer. The reactor was heated to 60°C to aid polymer dissolution. Once the temperature had stabilized, 0.304 moles of para-toluenesulphonylhydrazide was added through a powder funnel to the reaction. This amounts to a 4 to 1 molar ratio of para-toluenesulphonyl-hydrazide to polymer double bonds. The reaction medium was then heated to the reflux temperature of xylene (130—135°C) and allowed to react for 5 hours. The hydrogenated product was recovered by filtering the hot xylene solution, followed by coagulation of the polymer solution in isopropanol. The polymer was washed several times with hot water and isopropanol to remove any unreacted by-products. The polymer was then dried overnight in a vacuum oven at 50°C.

Analysis of the polymer by an $O_3$ titration technique, resulted in a 98% yield for the degree of hydrogenation. G.P.C. analysis of the polymer after hydrogenation likewise indicated that no polymer degradation took place during the reaction.

## Example 2

A 20-gallon (76-litre) stainless steel batch reactor was employed for the synthesis of the dispersant VI-improver. To the reactor was charged 8.8 gallons (33 litre) of cyclohexane, followed by 7.8 pounds (3.5 kg) of isoprene monomer. This solution was titrated with sec-butyllithium, and then the required amount of sec-butyllithium was added (0.118 moles) to initiate the polymerization. The reaction was allowed to proceed at 60°C for 2 hours, at which point 64.4 grams of commercial divinylbenzene was added. The star-coupling reaction was allowed to continue for 1—2 hours at 60°C. Next, was added 18.5 grams of 2-vinylpyridine to the solution to form the chemically bonded polar group. The polymer cement was terminated with methanol, and then stabilized with an anti-oxidant and stored until needed for subsequent hydrogenation.

Kjeldahl nitrogen analysis indicated 460 ppm nitrogen, which amounts to 0.3—0.4 %wt 2-vinylpyridine.

G.P.C. analysis of the polymer revealed the number average arm molecule weight to be 32,000, and the functionality was observed to be around 9—10 arms.

Catalytic Hydrogenation

To hydrogenate the star-polymer as described above, a catalytic hydrogenation technique was employed. This method involves subjecting the polymer cement to catalyst comprising the reaction product of an aluminium alkyl and anickel carboxylate, more specifically triethyl-aluminium and nickel octoate.

To a 10 gallon (38 litre) stainless steel autoclave reactor, equipped with a stirrer, hydrogen inlet, and appropriate temperature control, was charged 42 pounds (18.9 kg (6.5 gallons) (24.7 litre) of a 12%w polymer solution in cyclohexane. The reactor was then heated to 40°C. This charge amounts to 5.04 pounds (2.27 kg) of neat polymer.

The autoclave was then pressurized with hydrogen to 750 psi (52.5 bar) followed by the addition of 5,959 ml of the catalyst solution of a 6,000 ppm nickel concentration. The catalyst solution was added in three increments (i.e., 1,986 ml per increment) being careful not to allow the temperature to increase beyond 70°C. (The overall amount of catalyst added was 1,500 ppm). The reaction temperature was maintained within 60—70°C for 4 hours at which point the conversion, as determined by $O_3$ titration, was found to be 98%.

The reaction was allowed to continue overnight resulting in a final degree of hydrogenation of 98.4%. After completion of the hydrogenation step, the polymer cement was subjected to several citric-acid wash cycles to remove the residual nickel from the polymer. Analysis of the polymer by an atomic absorption technique indicated the remaining nickel concentration to be on the order of 155—160 ppm nickel based on the weight of neat polymer. Ionol anti-oxidant was added to the cement and the polymer cement was stored until needed. The polymer could be easily isolated by coagulation into isopropanol, followed by vacuum drying.

Product Evaluation

The dispersancy of the star-shaped polymer was assessed by a spot dispersancy test (SDT). The new dispersant VI-improvers were evaluated and compared to known commercial dispersant VI-improvers such as: Amoco 9250, Lubrizol 6401 and Acryloid 1155. Acryloid 1155 is a nitrogen functionalized ethylene-propylene random copolymer. Lubrizol 6401, an ashless dispersant, is a polyisbutylene-maleic anhydride graft copolymer functionalized with pentaerythritol. Amoco 9250 is a poly-isobutylene-amine ashless dispersant also containing boron. The spot dispersancy test is a qualitative measure of the ability of an oil to disperse sludge. In these tests a 2%w solution of the additive was added to a common lubricating oil base stock, is mixed with a sludge-containing oil and heated to 149°C for 15 minutes and shaken for one hour. The samples were then left in an oven overnight at 149°C. The samples were next allowed to cool to room temperature and two drops of the solution were placed, with an eye dropper, on separate 12 cm diameter No. 1 whatman filter papers. The diameters of the spots were measured after 24 hours. The longitudinal and latatudinal diameters of the inner sludge spot were measured in millimeters (mm) and an average diameter was taken. In a similar fashion, the average outer diameters of the oil spot was measured. The ratio of the inner spot diameter to the outer spot diameter is known as the SDT ratio, a larger ratio indicated better dispersancy. Table I summerizes the data, comparing the commercially known dispersant VI-improvers to a blank control, and the 2-vinylpyridine functionalized star-shaped hydrogenated poly(isoprene).

TABLE I

SPOT DISPERSANCY TEST

| | SAMPLE | (SDT RATIO %) |
|---|---|---|
| (1) | Blank | 76 |
| (2) | Blank + Amoco 9250 (2 %w) | 79 |
| (3) | Blank + Lubrizol 6401 (2 %w) | 83 |
| (4) | Blank + Acryloid 1155 (1.2 %w) | 81 |
| (5) | Blank + Acryloid 1155 (2.4 %w) | 81 |
| (6) | Blank + Star–PI–(2vp) (1.2 %w) | 87 |
| (7) | Blank + Star–PI–(2vp) (2.4 %w) | 94 |

As observed from Table I, the dispersancy of the hydrogenated 2-vinylpyridine-star-poly(isoprene) is excellent, being much higher than the commercial dispersant VI-improvers used for comparison.

A viscometric comparison of the dispersant VI-improver and a similar star-shaped poly(isoprene) without 2-vinylpyridine functionality was made and the data are summarized in Table II.

TABLE II

VISCOMETRIC COMPARISON

| TEST | DISPERSANT VI | NON-DISPERSANT VI |
|---|---|---|
| $V_k$, cSt, 40°C | 117 | 84.2 |
| $V_k$, cSt, 100°C | 18.58 | 13.9 |
| Viscosity Index | 178 | 172 |
| $V_d$, −18°C, cP | 2,100 | 2,060 |
| $V_d$, −25°C, cP | 19,691 | 15,132 |

The kinematic viscosity data as measured at both high and low temperatures indicate the polymer has good thickening capability, qualifying this polymer as a suitable VI-improver as well as a dispersant. These superior properties make the hydrogenated star-poly(isoprene) with 2-vinylpyridine groups an excellent dispersant VI-improver.

**Claims**

1. An oil-soluble, star-shaped product having the properties of both viscosity index-improver and a dispersant, said oil soluble product comprising:

(a) a poly(alkenyl aromatic)nucleus;

(b) at least three hydrogenated polymeric arms linked to said nucleus, said hydrogenated polymeric arms being selected from the group consisting of:

(i) hydrogenated homopolymers and hydrogenated compolymers 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 polymeric arms has been reduced by hydrogenation while preferably less than 20% of the aromatic unsaturation has been reduced; and

(c) at least one polymerized nitrogen containing polar compound arm linked to said nucleus.

2. A product as claimed in claim 1, wherein said poly(polyalkenyl aromatic)nucleus is a poly(divinyl benzene)nucleus.

3. A product as claimed in claim 1 or 2, wherein the number average molecular weight of said each hydrogenated polymeric arm is between 1,000 and 100,000.

4. A product as claimed in any one of claims 1—3, wherein the weight percentage of nitrogen-containing polar compound is between 0.1 and 10.0.

5. A product as claimed in any one of claims 1—4, wherein said nitrogen-containing polar compound is 2-vinylpyridine or 4-vinylpyridine.

6. A process for preparing a product as claimed in any one of claims 1—5, comprising:

(a) solution polymerizing one or more conjugated diene and optionally one or more monoalkenyl arene monomers under polymerization conditions with an organolithium compound, forming living polymeric arms;

(b) contacting said living polymeric arms with a polyalkenyl aromatic coupling agent forming a coupled polymer having a poly(polyalkenyl aromatic)nucleus and attached polymeric arms;

(c) contacting said coupled polymer with a nitrogen-containing polar compound monomer attaching poly(nitrogen-containing polar compound)arms to said nucleus, and

(d) reducing by hydrogenation at least 80% of the aliphatic unsaturation of the polymeric arms while preferably reducing less than 20% of the aromatic unsaturation.

7. A process as claimed in claim 6, wherein the monomers of step (a) are butadiene and/or isoprene and optionally styrene.

8. A process as claimed in claim 6 or 7, wherein said nitrogen-containing polar compound is 2-vinylpyridine or 4-vinylpyridine.

9. A process as claimed in any one of claims 6—8, wherein said nitrogen-containing polar compound is contacted with said coupled polymer at a temperature between −78°C and +80°C.

10. A process as claimed in any one of claims 6—9, wherein in step (d) the resulting polymer is contacted with hydrogen and hydrogenation catalyst under hydrogenation conditions.

11. A process as claimed in claim 10, wherein said hydrogenation catalyst comprises the reaction product of an aluminium alkyl and a nickel carboxylate or nickel alkoxide.

12. A process as claimed in any one of claims 6—9, wherein in step (d) the resulting polymer is

contacted with a hydrazine or p-toluenesulphonylhydrazide reactant forming $N_2H_2$, which reduces the polymer by hydrogenation.

13. A process as claimed in claim 12, wherein the molar ratio of reactant to conjugated diene units is between about 5:1 and about 1:1.

14. A lubricating composition comprising a lubricating oil and 0.1—45%w of a product as claimed in any one of claims 1—5.

**Patentansprüche**

1. Ein öllösliches, sternförmig ausgebildetes Produkt mit den Eigenschaften sowohl eines Verbesserungsmittels für den Viskositätsindex als auch eines Dispergiermittels, welches öllösliche Produkt die nachstehenden Struktureinheiten umfaßt:

(a) einen Poly(polyalkenylaromatischen)Kern;

(b) mindestens drei hydrierte polymere Arme, welche mit besagtem Kern verknüpft sind, wobei besagte hydrierte polymere Arme ausgewählt sind 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, und wobei mindestens etwa 80% der aliphatischen Ungesättigtheit der polymeren Arme durch Hydrierung reduziert sind, während vorzungsweise weniger als 20% der aromatischen Ungesättigtheit reduziert worden sind;

(c) mindestens einen aus einer polymerisierten stickstoffhaltigen polaren Verbindung aufgebauten Arm, der mit besagtem Kern verknüpft ist.

2. Ein Produkt wie in Anspruch 1 beansprucht, in welchem besagter Poly(polyalkenylaromatischer)-Kern ein Poly(divinylbenzol)Kern ist.

3. Ein Produkt wie in Anspruch 1 oder 2 beansprucht, in welchem das Zahlenmittel des Molekulargewichts jedes hydrierten polymeren Arms zwischen 1000 und 100 000 liegt.

4. Ein Produkt wie in irgendeinem der Ansprüche 1 bis 3 beansprucht, in welchem der Gewichtsprozentsatz an der stickstoffhaltigen polaren Verbindung zwischen 0,1 und 10,0 liegt.

5. Ein Produkt wie in irgendeinem der Ansprüche 1 bis 4 beansprucht, in welchem besagte stickstoffhaltige polare Verbindung 2-Vinylpyridin oder 4-Vinylpyridin ist.

6. Ein Verfahren zur Herstellung eines Produktes wie in irgendeinem der Ansprüche 1 bis 5 beansprucht, umfassend:

(a) eine Lösungspolymerisation eines oder mehrerer konjugierten(r) Diens(e) und gegebenenfalls eines oder mehrerer Monoalkenylarenmonomer(e) unter Polymerisationsbedingungen mit einer Organolithiumverbindung unter Bildung reaktionsfähiger (living) polymerer Arme;

(b) Kontaktieren besagter reaktionsfähiger polymerer Arme mit einem polyalkenylaromatischen Kupplungsmittel unter Bildung eines gekuppelten Polymeren mit einem Poly(polyalkenylaromatischen)-Kern und daran gebundenen polymeren Armen;

(c) Kontaktieren besagten gekuppelten Polyumers mit einer monomeren stick-stoffhaltigen polaren Verbindung unter Anknüpfung von Armen, aufgebaut aus der polymeren stickstoffhaltigen polaren Verbindung, an besagten Kern und

(d) Reduzieren von mindestens 80% der aliphatischen Ungesättigtheit der polymeren Arme durch Hydrieren und vorzugsweise Reduzieren von weniger als 20% der aromatischen Ungesättigtheit.

7. Ein Verfahren wie in Anspruch 6 beansprucht, in welchem die Monomeren der Verfahrensstufe (a) Butadien und/oder Isopren und wahlweise Styrol sind.

8. Ein Verfahren wie in Anspruch 6 oder 7 beansprucht, in welchem besagte stickstoffhaltige polare Verbindung 2-Vinylpyridin oder 4-Vinylpyridin ist.

9. Ein Verfahren wie in irgendeinem der Ansprüche 6 bis 8 beansprucht, in welchem besagte stickstoffhaltige polare Verbindung mit besagtem gekuppeltem Polymer bei einer Temperatur zwischen −78°C und +80°C kontaktiert wird.

10. Ein Verfahren wie in irgendeinem der Ansprüche 6 bis 9 beansprucht, in welchem in Verfahrensstufe (d) das erhaltene Polymer mit Wasserstoff und einem Hydrierungskatalysator unter Hydrierungsbedingungen kontaktiert wird.

11. Ein Verfahren wie in Anspruch 10 beansprucht, in welchem besagter Hydrierungskatalysator das Reaktionsprodukt eines Aluminiumalkyls und eines Nickelcarboxylates oder Nickelalkoxyds umfaßt.

12. Ein Verfahren wie in irgendeinem der Ansprüche 6 bis 9 beansprucht, in welchem in Verfahrensstufe (d) das erhaltene Polymer mit einem Hydrazin- oder p-Toluolsulfonylhydrazid- Reaktionsmittel unter Bildung der Verbindung $N_2H_2$ kontaktiert wird, welche das Polymer durch Hydrierung reduziert.

13. Ein Verfahren wie in Anspruch 12 beansprucht, in welchem das molare Verhältnis der Reaktionsmittels zu den Einheiten des konjugierten Diens zwischen etwa 5:1 und etwa 1:1 liegt.

14. Eine Schmiermittelzusammensetzung, enthaltend ein Schmieröl und 0,1 bis 45 Gewichtsprozent eines Produktes, wie in irgendeinem der Ansprüche 1 bis 5 beansprucht.

**Revendications**

1. Un produit en étoile, soluble dans l'huile, ayant les propriétés à la fois d'un agent améliorant l'indice de viscosité et d'un dispersant, ce produit soluble dans l'huile comprenant:

(a) un noyau poly(polyalcényl aromatique);

(b) au moins trois branches polymères hydrogénées liées à ce noyau, ces branches polymères hydrogénées étant choisies dans le groups constitué par:

(1) des homopolymères hydrogénés et des copolymères hydrogénés de diènes conjugués;

(2) des compolymères hydrogénés de diènes conjugués et de monoalcényl arènes; et

(3) leurs mélanges; et où au moins environ 80% de l'insaturation aliphatique des branches polymères a été réduit par hydrogénation tandis que de préeférence moins de 20% de l'insaturation aromatique a été réduite; et

(c) au moins une branche de composé polaire azoté polymérisé liée au noyau.

2. Un produit selon la revendication 1, dans lequel le noyau poly(polyalcényl aromatique) est un noyau poly(divinyl benzène).

3. Un produit selon la revendication 1 ou 2, dans lequel le poids moléculaire moyen en nombre de chaque branche polymère hydrogénée est compris entre 1 000 et 100 000.

4. Un produit selon l'une quelconque des revendications 1—3, dans lequel le pourcentage en poids de composé polaire azoté est compris entre 0,1 et 10,0.

5. Un produit selon l'une quelconque des revendications 1—4, dans lequel le composé polaire azoté est de la 2-vinylpyridine ou de la 4-vinylpyridine.

6. Un procédé pour la préparation d'un produit tel que revendiqué dans l'une quelconque des revendications 1—5, comprenant:

(a) la polymérisation en solution d'un ou plusieurs monomères diènes conjugués et éventuellement d'un ou plusieurs monomères monoalcényle arènes dans des conditions de polymérisation avec un composé organo-lithium, formant des branches polymères vivantes;

(b) la mise en contact de ces branches polymères vivantes avec un agent de couplage polyalcényl aromatique formant un polymère couplé ayant un noyau poly(polyalcényl aromatique) et des branches polymères attachées;

(c) la mise en contact de ce polymère couplé avec un monomère polaire contenant de l'azote attachant des branches de poly(composé polaire azoté) au noyau, et

(d) la réduction par hydrogénation d'au moins 80% de l'insaturation aliphatique des branches polymères tout en réduisant de préference moins de 20% de linsaturation aromatique.

7. Un procédé selon la revendication 6, dans lequel les monomères de l'étape (a) sont du butadiène et/ou de l'isoprène et éventuellement du styrène.

8. Un procédé selon la revendication 6 ou 7, dans lequel le composé polaire azoté est de la 2-vinylpyridine ou de la 4-vinylpyridine.

9. Un procédé selon l'une quelconque des revendications 6—8, dans lequel le composé polaire azoté est mis en contact avec le polymère couplé à une température comprise entre −78°C et +80°C.

10. Un procédé selon l'une quelconque des revendications 6—9, dans lequel dans l'étape (d) le polymère résultant est mis en contact avec de l'hydrogène et un catalyseur d'hydrogénation dans des conditions d'hydrogénation.

11. Un procédé selon la revendication 10, dans lequel le catalyseur d'hydrogénation comprend le produit de réaction d'un aluminium-alcoyle et d'un carboxylate de nickel ou alcoolate de nickel.

12. Un procédé selon l'une quelconque des revendications 6—9, dans lequel dans l'étape (d) le polymère résultant est mis en contact avec un corps en réaction hydrazine ou p-toluènesulfonylhydrazide formant $N_2H_2$, qui réduit le polymère par hydogénation.

13. Un procédé selon la revendication 12, dans lequel le rapport molaire du corps en réaction aux mailles de diène conjugué est compris entre environ 5:1 et environ 1:1.

14. Une composition lubrifiante comprenant une huile lubrifiante et 0,1—45% en poids d'un produit selon l'une quelconque des revedications 1—5.