

Description

The present invention relates to the use of a (D) reaction product of (B) an unsaturated carboxylic acid reagent with (A) a hydrogenated block copolymer in the presence of (C) free radical initiators, manufactured
 5 in a solvent or in a solvent-free environment, as a lubricant additive concentrate additive concentrate or composition. The present invention further relates to preparation of (E) dispersant derivatives of said (D) reaction product with a primary amine containing compound.

Heretofore various solution reactions have been carried out between a polymer and an anhydride.

For example, U. S. Patent 2,524,424 to Buret relates to the treatment of the rubber-like polymers from
 10 butadiene hydrocarbons with carboxylic acid anhydrides.

U. S. Patent No. 2,845,403 to Gunberg relates to making rubbery adducts by chemical reaction of maleic anhydride with butyl rubber.

U.S. Patent No. 2,993,057 to Gleason relates to copolymers prepared from multiolefins and vinyl aromatic compounds which have a hydrocarbon group attached to the alpha position of the vinyl group.

15 U. S. Patent No. 3,240,762 to Wilks, et al. relates to a maleic anhydride hydrogenated polycyclopentadiene reaction product.

U.S. Patent No. 3,365,411 to Mertzweiller relates to a blend of (1) a polymeric half ester of a hydroxylated polymer and a saturated or unsaturated polycarboxylic acid or anhydride or its amination product with (2) a polymeric adduct of a polymer or copolymer of a conjugated diolefin and an unsaturated
 20 polycarboxylic acid anhydride or its amination product.

U. S. Patent No. 3,527,736 to Averink, et al. relates to the improvement of green strength of synthetic diene polymers (lithium-polyisoprene) by the reaction with an olefinic unsaturated 1,2-dicarboxylic acid (maleic anhydride) in a solvent.

U. S. Patent No. 3,567,691 to van Breen, et al. relates to a process for the preparation of reaction
 25 products of a synthetic diene rubber with maleic anhydride.

U.S. Patent No. 3,766,215 to Hesse, et al. relates to a process for the preparation of adducts from maleic anhydride and liquid, low-molecular weight polybutadienes.

U. S. Patent No. 3,887,527 to Okamura, et al. relates to modifying cis-1,4-polyisoprene rubber with maleic anhydride with substantially no increase in gel.

30 U. S. Patent No. 3,935,140 to Go, et al. relates to an aqueous coating composition having a water soluble or dispersible material prepared by the addition reaction of at least one alpha-beta unsaturated dicarboxylic compound with a mixture of a natural drying oil and a specific liquid copolymer containing 1,3-pentadiene and 1,3-butadiene units therein.

U.S. Patent No. 3,952,023 to Kaiya relates to preparing an adduct of (A) a butadiene lower polymer or
 35 butadiene lower copolymer and (B) an alpha-beta ethylenically unsaturated dicarboxylic acid compound by a method characterized in that said (A) and (B) are caused to react in the presence of one or more compounds selected from (C) p-phenylenediamine derivatives.

U. S. Patent No. 3,953,541 to Fuji relates to a process for the preparation of polyolefin graft copolymers.

40 U. S. Patent No. 3,998,912 to Zeitler, et al. relates to grafting carboxylic acids onto copolymers of ethylene and carboxylates.

U.S. Patent No. 4,033,888 to Kiofsky relates to lubricating oil additives allegedly having both dispersant and viscosity index improving properties which are prepared by reacting a block copolymer with maleic anhydride and an alkane polyol.

45 British Patent 1,548,464 to Shell relates to reacting a hydrogenated block copolymer with maleic anhydride and the subsequent reaction thereof with an amine containing compound.

U.S. Patent No. 4,082,817 to Imaizumi, et al. relates to a process for producing a maleic anhydride adduct of high molecular weight 1,2-polybutadiene.

U.S. Patent No. 4,073,737 to Elliott relates to hydrogenated copolymers of conjugated dienes and
 50 optionally, vinyl aromatic monomers which are useful as oil additives.

U.S. Patent No. 4,410,656 to Coran, et al. relates to a method of masticating diene rubber in the presence of maleic acid or maleic anhydride together with sulfur or an organic sulfur compound capable of generating a thiyl radical.

U.S. Patent No. 4,010,223 to Caywood relates to an adduct containing succinic groups attached to an
 55 elastomeric copolymer of an EPDM type copolymer. The reaction is carried out free of any free radical initiators.

U. S. Patent No. 4,080,493 to Yasui, et al. relates to a process for the production of the maleic anhydride adduct of a liquid polymer.

U. S. Patent No. 4,089,794 to Engle, et al. relates to polymeric dispersant additives for lubricating oils comprising ethylene and one or more C₃ to C₂₈ alpha-olefins which have been solution-grated in the presence of a free radical initiator with an ethylenically unsaturated carboxylic acid material in elevated temperatures and thereafter reacted with a polyfunctional material reactive with carboxylic groups such as polyamine, or a polyol.

U. S. Patent No. 4,117,036 to Honda, et al. relates to functional high polymeric substances having alpha, beta, unsaturated carboxylate and the compositions therefrom.

U. S. Patent Nos. 4,160,739 and 4,161,452 to Stambaugh, et al. relate to polyolefinic copolymer additives for lubricants and fuels wherein the backbone can be styrene-butadiene copolymers and the grafted units are the residues of a monomer system comprising maleic acid or anhydride with one or more other monomers copolymerizable therewith. Further reaction with amine compounds are disclosed.

U. S. Patent No. 4,161,571 to Yasui, et al. relates to a process for the production of the maleic anhydride adduct of a liquid polymer.

U. S. Patent No. 4,284,414 to Bryant relates to mixed alkyl esters of interpolymers for use in crude oils.

U. S. Patent No. 4,292,414 to Saito, et al. relates to a process for preparing modified block copolymers by graft reacting at least one maleic acid compound with an aromatic vinyl compound/conjugated diene compound block copolymer.

U. S. Patent No. 4,505,834 to Papay relates to lubricating oil compositions containing graft copolymers as a viscosity index improver-dispersant.

U. S. Patent Nos. 4,077,893 and 4,141,847 to Klovsky relate to lubricating oil additives allegedly having both dispersant and viscosity index improving properties which are prepared by hydrogenating star-shaped polymers of at least four arms of polymers or copolymers of dienes and monoalkenyl arenes with an alpha-beta unsaturated carboxylic acid and then reacting the resulting intermediate with either a polyol or an amine.

U.S. Patent No. 4,145,298 to Trepka relates to nitrogen-containing copolymers which are prepared by the reaction of lithiated hydrogenated conjugated diene-vinylarene copolymers with nitrogen-containing organic compounds.

U.S. Patent No. 4,320,019 to Hayashi relates to reaction products prepared by reacting EPDM type copolymers with olefinic carboxylic acid acylating agents to form an acylating reaction intermediate which is further reacted with an amine.

U.S. Patent No. 4,486,573 to Hayashi relates to hydrocarbyl substituted carboxylic acid reagents containing from about 2 to about 20 carbon atoms, exclusive of the carboxyl-based groups with one more more high molecular weight olefin polymers having 1 to 20 carbon atoms.

Accordingly, it is an aspect of the present invention to provide a composition which has been formed by reacting a hydrogenated block copolymer with unsaturated carboxylic reagents in the presence of free radical initiators in a solvent-free system for use as a lubricant additive concentrate or lubricant composition.

According to one aspect of the present invention, there is therefore provided use of a composition comprising a diluent oil and from 1% to 40% by weight of the oil-soluble (D) reaction product of:

(A) a hydrogenated linear block copolymer containing no more than about 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages comprising a normal block copolymer or a random block copolymer, said normal block copolymer made from a vinyl substituted aromatic and an aliphatic conjugated diene, said normal block copolymer having from two to five polymer blocks with at least one polymer block of said vinyl substituted aromatic and at least one polymer block of said aliphatic conjugated diene, said random block copolymer made from vinyl substituted aromatic and aliphatic conjugated diene monomers, the total amount of said vinyl substituted aromatic blocks in said block copolymer being in the range of from 20 percent to 70 percent by weight and the total amount of said diene blocks in said block copolymer being in the range of from 30 percent to 80 percent by weight; the number average molecular weight of said normal block copolymer and said random block copolymer being in the range of 10,000 to 500,000;

(B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups in an amount of from 0.20 percent to 20 percent by weight based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent; and

from 0.01 to 5 percent by weight of (C) a free radical initiator, based upon the weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent;

as a lubricant additive concentrate.

According to another aspect of the present invention there is therefore provided use of a composition comprising a major amount of an oil of lubricating viscosity and a minor amount of the oil-soluble (D) reaction product of;

- (A) a hydrogenated linear block copolymer containing no more than about 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages comprising a normal block copolymer or a random block copolymer, said normal block copolymer made from a vinyl substituted aromatic and an aliphatic conjugated diene, said normal block copolymer having from two to five polymer blocks with at least one polymer block of said vinyl substituted aromatic and at least one polymer block of said aliphatic conjugated diene, said random block copolymer made from vinyl substituted aromatic and aliphatic conjugated diene monomers, the total amount of said vinyl substituted aromatic blocks in said block copolymer being in the range of from 20 percent to 70 percent by weight and the total amount of said diene blocks in said block copolymer being in the range of from 30 percent to 80 percent by weight; the number average molecular weight of said normal block copolymer and said random block copolymer being in the range of 10,000 to 500,000;
- (B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups in an amount of from 0.20 percent to 20 percent by weight based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent; and
- from 0.01 to 5 percent by weight of (C) a free radical initiator, based upon the weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent;
- as a lubricant composition.

It is a further aspect of the present invention to produce a composition, as above, wherein said reaction product can further be reacted with a primary amine containing compound.

- According to a further aspect of the present invention there is provided a reaction product for use in an additive composition, of a component (D) with a component (E), the reaction product (D) being the solvent free reaction product of
- (A) a hydrogenated linear block copolymer containing no more than about 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages comprising a normal block copolymer or a random block copolymer, said normal block copolymer made from a vinyl substituted aromatic and an aliphatic conjugated diene, said normal block copolymer having from two to five polymer blocks with at least one polymer block of said vinyl substituted aromatic and at least one polymer block of said aliphatic conjugated diene, said random block copolymer made from vinyl substituted aromatic and aliphatic conjugated diene monomers, the total amount of said vinyl substituted aromatic blocks in said block copolymer being in the range of from 20 percent to 70 percent by weight and the total amount of said diene blocks in said block copolymer being in the range of from 30 percent to 80 percent by weight; the number average molecular weight of said normal block copolymer and said random block copolymer being in the range of 10,000 to 500,000;
- (B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups in an amount of from 0.20 percent to 20 percent by weight based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent; and
- and from 0.01 to 5 percent by weight of (C) a free radical initiator, based upon the weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent;
- and the component (E) being a primary amine containing compound, wherein said primary amine containing compound is ammonia or a compound having only one primary amine group therein.

Various preferred features and embodiments of the invention will now be described by way of non-limiting example.

- According to the present invention, a composition suitable for use as a viscosity improver/dispersant is made by reacting a (A) hydrogenated block copolymer and (B) an alpha-beta olefinically unsaturated reagent in the presence of (C) free radical initiators. The reaction product of (A), (B) and (C) is referred to as acylating reaction product (D) which can be further reacted with (E) a primary amine containing compound. The manufacture of reaction product (D) can be carried out in a solvent such as mineral oil or in a solvent-free environment.

- Considering the (A) hydrogenated linear block copolymer, it comprises either a normal block copolymer, that is, a true block copolymer or a random block copolymer. Considering the true or normal block copolymer, it is generally made from conjugated dienes having from 4 to 10 carbon atoms and preferably from 4 to 6 carbon atoms as well as from vinyl substituted aromatics having from 8 to 12 carbon atoms and preferably 8 or 9 carbon atoms.

- Examples of vinyl substituted aromatics include styrene, alpha-methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, para-tertiary-butylstyrene, with styrene being preferred. Examples of such conjugated dienes include piperylene, 2,3-dimethyl-1,3-butadiene, chloroprene, isoprene and 1,3-butadiene, with isoprene and 1,3-butadiene being particularly preferred. Mixtures of such conjugated dienes are useful.

The normal block copolymers have a total of from 2 to 5, and preferably 2 or 3, polymer blocks of the vinyl substituted aromatic and the conjugated diene with at least one polymer block of said vinyl substituted aromatic and at least one polymer block of said conjugated diene being present. The conjugated diene block is hydrogenated as more fully set forth hereinbelow. The linear normal block copolymers have a substantially long sequence of one monomeric unit (Block I) is linked with another substantially long sequence of a second (Block II), third (Block III), fourth (Block IV), or fifth (Block V) monomeric unit. For example, if A is a styrene monomeric unit and D is a conjugated diene monomeric unit, a tri-block copolymer of these monomeric units can be represented by the formula:



Block I

Block II

Block III

Linear ada Block

In practice, the number of repeat units involved in each polymer block usually exceeds about 500, but it can be less than about 500. The sequence length in one block should be long enough so that the block copolymer exhibits the inherent homopolymeric physical properties such as glass transition temperature and polymer melt temperature.

The vinyl substituted aromatic content of these copolymers, that is the total amount of vinyl substituted aromatic blocks in the normal block copolymer, is in the range of from 20 percent to 70 percent by weight and preferably from 40 percent to 60 percent by weight. Thus, the aliphatic conjugated diene content, that is, the total diene block content, of these copolymers is in the range of from 30 percent to 80 percent by weight and preferably from 40 percent to 60 percent by weight.

These normal block copolymers can be prepared by conventional methods well known in the art. Such copolymers usually are prepared by anionic polymerization using, for example, an alkali metal hydrocarbon (e.g., sec-butyllithium) as a polymerization catalyst.

Examples of suitable normal block copolymers as set forth above include Shellvis-40, and Shellvis-50, both hydrogenated styrene-isoprene block copolymers, manufactured by Shell Chemicals.

Considering the random block copolymer which can be utilized separately, in combination with the normal block copolymers set forth above, it is generally defined as a block copolymer having one or more block polymer portions therein. More specifically, the random block copolymers can be defined as an indeterminate number of A and D blocks of indeterminate lengths. These random copolymers are generally made from conjugated dienes of the type noted above and hereby incorporated by reference with butadiene or isoprene being preferred. The remaining monomer utilized to make the random block copolymer comprises vinyl substituted aromatics of the type set forth hereinabove. A suitable type of aromatic monomer is styrene. The random block copolymer can be made by simultaneously feeding a mixture of monomers to a polymerization system rather than feeding the monomers in a sequential manner. The amount of the various blocks by weight are the same as set forth above, that is, from 20 to 70 percent by weight of vinyl substituted aromatic blocks with 40 to 60 percent by weight of such blocks being preferred. Accordingly, the amount of the diene blocks is the difference. The number average molecular weight and the weight average molecular weight of the random block copolymers are the same as set forth above. The random block copolymers contain significant blocks of a vinyl substituted aromatic repeating unit and/or significant blocks of a conjugated diene repeating unit therein and/or blocks of random or random tapered conjugated diene/vinyl substituted aromatic. These copolymers also can be represented as by A'-B'-A'-B' wherein A' is a block of vinyl substituted aromatic compound, B' is a block of conjugated diene, and the length of A' and B' blocks vary widely and, are substantially shorter than the A and B blocks of a normal block polymer.

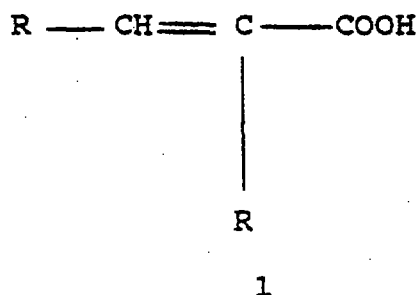
Examples of such commercially available random block copolymers include the various Glissoviscal block copolymers manufactured by BASF. A previous available random block copolymer was Phil-Ad viscosity improver, manufactured by Phillips Petroleum.

Regardless of whether a true or normal block copolymer or a random block copolymer, or combinations of both are utilized, they are hydrogenated before use in this invention so as to remove virtually all of their olefinic double bonds. Techniques for accomplishing this hydrogenation are well known to those of skill in the art and need not be described in detail at this point. Briefly, hydrogenation is accomplished by
 5 contacting the copolymers with hydrogen at super-atmospheric pressures in the presence of a metal catalyst such as colloidal nickel, palladium Supported on charcoal.

These block copolymers, for reasons of oxidative stability, contain no more than about 0.5% residual olefinic unsaturation on the basis of the total number of carbon-to-carbon covalent linkages within the average molecule. Such unsaturation can be measured by a number of means well known to those of skill
 10 in the art, such as infrared, NMR. Most preferably, these copolymers contain no discernible unsaturation, as determined by the aforementioned analytical techniques.

The (A) block copolymers typically have number average molecular weights in the range of 10,000 to 500,000, preferably 30,000 to 200,000. The weight average molecular weight for these copolymers is generally in the range of 30,000 to 500,000, preferably 30,000 to 300,000.

15 The unsaturated carboxylic reagent (B) contains an alpha-beta olefinic unsaturation. By the term alpha-beta olefinic unsaturated carboxylic acids reagent, it is meant to include alpha-beta olefinic unsaturated carboxylic acids (B) per se and functional derivatives thereof, such as anhydrides, esters, amides, imides, salts, acyl halides, nitriles, and other nitrogen containing compounds. These carboxylic acid reagents may be either monobasic or polybasic in nature. When they are polybasic they are preferably dicarboxylic acids,
 20 although tri- and tetracarboxylic acids can be used. Exemplary of the monobasic alpha-beta olefinically unsaturated carboxylic acid reagents are the carboxylic acids corresponding to the formula:



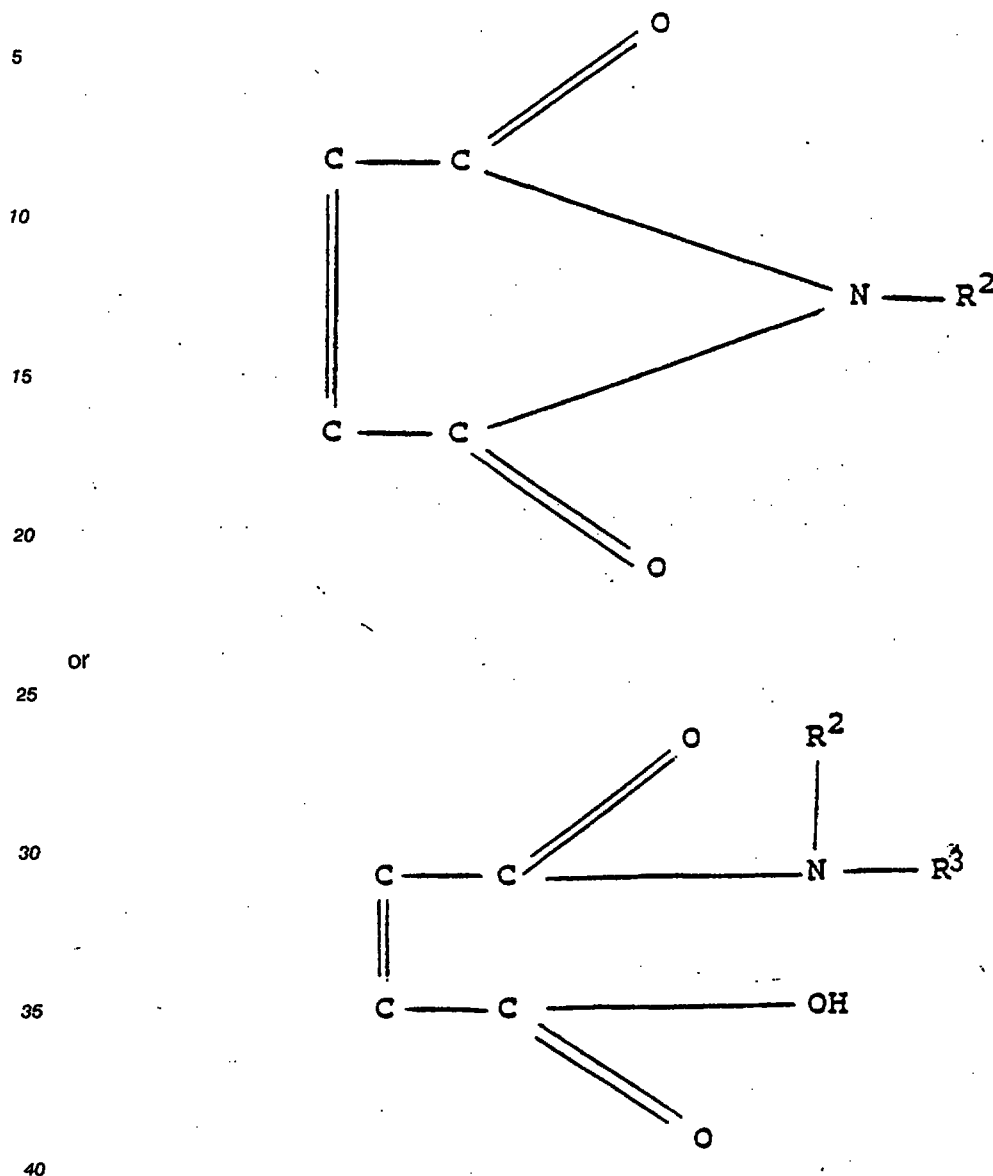
35 wherein R is hydrogen, or a saturated aliphatic or alicyclic, aryl, alkylaryl or heterocyclic group, preferably hydrogen or a lower alkyl group, and R₁ is hydrogen or a lower alkyl group. By lower alkyl it is meant from 1 to 10 carbon atoms. The total number of carbon atoms in R and R₁ should not exceed 18 carbon atoms. Specific examples of useful monobasic alpha-beta olefinic unsaturated carboxylic acids are acrylic acid,
 40 methacrylic acid, cinnamic acid, crotonic acid, 2-phenyl propenoic acid, etc. Exemplary polybasic acids include maleic acid, fumaric acid, mesaconic acid, itaconic acid and citraconic acid.

The alpha-beta olefinic unsaturated reagents (B) also include functional derivatives of the foregoing acids, as noted. These functional derivatives include the anhydrides, esters, amides, imides, salts, acid
 45 halides, and nitriles of the aforescribed acids. A preferred alpha-beta olefinic unsaturated carboxylic acid reagent (B) is maleic anhydride.

Especially preferred reagents (B) include maleic anhydride, citraconic anhydride, itaconic anhydride, glutaconic anhydride, chloromaleic anhydride, methyl maleic anhydride, acrylic acid, methacrylic acid, C₁₋₁₀ alkyl esters of such acids, and combinations thereof

50 Methods of preparing such functional derivatives are well known to those of ordinary skill in the art and they can be satisfactorily described by noting the reactants used to produce them. Thus, for example, derivative esters for use in the present invention can be made by esterifying monohydric or polyhydric alcohols or epoxides with any of the aforescribed acids. Amines and alcohols described hereinafter can be used to prepare these functional derivatives. The nitrile functional derivatives of the aforescribed carboxylic acid useful in making the products of the present invention can be made by the conversion of a
 55 carboxylic acid to the corresponding nitrile by dehydration of the corresponding amine. The preparation of the latter is well known to those skilled in the art and is described in detail in The Chemistry of the Cyano Group edited by Zvi Rappoport, Chapter 2, which discloses methods for preparing nitriles. Specific examples of such nitrogen containing functional derivatives include maleimide and maleamic acid. More

specifically, such amine functional derivatives of the alpha-beta olefinic unsaturated reagent (B) can have the formula:



wherein R₂ and R₃, independently, can be hydrogen, an alkyl having from 1 to 12 carbon atoms and preferably from 1 to 6 carbon atoms, an alkyl substituted aromatic having from 7 to 12 carbon atoms and preferably from 7 to 9 carbon atoms, or a moiety containing N, O or S as hereto atoms. Examples of highly preferred compounds include N-(3,6-dioxaheptyl)maleimide, N-(3-dimethylaminopropyl)maleimide, and N-(2-methoxyethoxyethyl)maleimide.

Ammonium salt derivatives can also be made from any of the amines described hereinafter as well as from tertiary amino analogs of them, ammonia or its derivatives, (e.g., NH₄Cl, NH₄OH, (NH₄)₂CO₃) by conventional techniques well known to those of ordinary skill in the art.

The acid halide functional derivative of the aforescribed olefinic carboxylic acid (B) can be prepared by the reaction of the acids and their anhydrides with a halogenation agent such as phosphorus tribromide, phosphorus pentachloride, or thionyl chloride. Esters can be prepared by the reaction of the acid halide with the aforesaid alcohols or phenolic compounds such as phenol, naphthol, octylphenol. Also, amides and imides and other acylated nitrogen derivatives can be prepared by reacting the acid halide with the above-described amino compounds. These esters and acylated nitrogen derivatives can be prepared from the acid halides by conventional techniques well known to those of ordinary skill in the art.

It is important that an effective amount of the (B) reagent be utilized such that sufficient dispersancy is imparted to the (D) acylated reaction product. According to the invention an amount of (B) reagent of from

0.20 to 20 percent by weight and desirably from 0.5 to 5 percent by weight based upon the total weight of said (A) block copolymer and said (B) reagent is utilized. Generally, such amounts are sufficient to ensure that from 0.1 percent to 3 percent by weight of the (D) reaction product is said (B) reagent.

With regard to the solvent-free reaction, the reaction temperature between the (A) hydrogenated block copolymer and the (B) reagent will depend to some extent upon the type of block copolymer as well as the type of the initiator system utilized. Generally, the reaction temperature is from 100 to 300 °C, desirably from 160 to 260 °C, preferably from 220 to 260 °C. Although not necessary, the reaction can be carried out in an inert atmosphere such as nitrogen.

The solvent-free reaction between the hydrogenated block copolymers and the unsaturated carboxylic acids or derivatives thereof can generally take place in any suitable vessel, device or apparatus without the presence of any solvent. Desirably, the reaction occurs in a blending device such as an extruder, an Banbury, or a two-roll mill.

As an optional and important aspect of the present invention, the blending device imparts high mechanical energy to such an extent that sufficient force is applied to the (A) block copolymer chains to cause scission or breakage thereof. The use of such high mechanical energy to cause chain scission is usually not desired. However, it is optionally desired in situations wherein the molecular weight of the block copolymer is greater than desired and hence, is broken down to a suitable range or the viscous nature of the block copolymer requires a high mechanical energy mixing system for processing. Such high mechanical energy devices can be the same type of mixing devices as noted above and generally impart high torque or masticate the ingredients therein. As a side reaction, it is thought that the block copolymer chains so broken produce terminal chain ends which serve as reaction sites for the (B) reagent. Thus, besides causing actual chain scission, it is speculated that the high mechanical energy imparting devices create reaction sites in addition to those created by the (C) free radical initiators. However, it is to be understood that such chain scission creates very few reaction sites compared with the free radical reaction.

In order to promote the reaction and to create reaction sites, free radical initiators are generally utilized. Two types of initiators include the various organic peroxides as well as the various organic azo compounds. The amount of initiators based upon the amount of the (A) block copolymers and the (B) reagent utilized is from 0.01 percent to 5.0 percent by weight and desirably from 0.05 percent to 2.0 percent by weight. Typical organic peroxides include benzoyl peroxide; *t*-butyl peroxyvalate; 2,4-dichlorobenzoyl peroxide; decanoyl peroxide; propionyl peroxide; hydroxyheptyl peroxide; cyclohexanone peroxide; *t*-butyl perbenzoate; dicumyl peroxide; 2,5-dimethyl-2,5-di(*t*-butylperoxy)-3-hexyne; 2,5-dimethyl-2,5-di(*t*-butylperoxy)-hexane; 2,5-dimethyl-2,5-dibenzoylperoxyhexane; *t*-butyl peroxide; cumene hydroperoxide; 2,5-dimethyl-2,5-di(hydroperoxy)hexane; *t*-butyl hydroperoxide; lauroyl peroxide; *t*-amyl perbenzoate; and mixtures thereof. Preferred organic peroxides are benzoyl peroxide and *t*-butyl perbenzoate. Mixtures of two or more of the above peroxides can also be used.

Naturally, handling of the peroxides should be done with the utmost care due to their tendency to decompose or violently react. Hence, the user should be thoroughly familiar with their properties as well as proper handling procedures before any contact therewith.

Examples of suitable organic azo initiators include 2,2'-azobis(2-methylpropionitrile) and 2,2'-azobis(2-methylvaleronitrile) and 4,4'-azobis(4-cyanovaleric acid).

The extent of the reaction of the (B) reagent such as maleic anhydride as incorporated onto the block copolymers is generally measured by a total acid number or TAN. The TAN number desirably is from 0.1 to 60 with from 0.5 to 20 being preferred. The definition of the TAN number is the mg of KOH required to neutralize the acid functional groups in one gram of the reaction product of (A) block copolymer and (B) alpha-beta olefinically unsaturated carboxylic reagent.

The (D) reaction products of the present invention are useful as intermediates as well as viscosity improvers for multigrade oils.

The present invention will be understood by reference to the following examples.

50 EXAMPLES I-III

Three commercial viscosity index improvers (VI improvers) were functionalized with maleic anhydride in a laboratory scale extruder. The extruder used in these experiments was a single-screw type driven by a C. W. Brabender Plasti-Corder torque rheometer. No die was used.

To ensure homogeneous extruder feeds, the crumb VI improving polymer was coated with maleic anhydride and *tert*-butyl peroxide prior to extrusion. This was done by dissolving both maleic anhydride and *tert*-butyl peroxide in acetone, spraying the acetone solution evenly over the crumb polymer, and allowing the acetone solvent to evaporate. This procedure leaves only the maleic anhydride- and peroxide-coated

crumb polymer behind as a residue. More specifically, a homogeneous extruder feed composed of 96.5 percent wt crumb polymer, 3.2 percent wt maleic anhydride, and 0.3 percent wt di-tert-butyl peroxide was charged to the extruder feed zone.

The reaction mixture is conveyed through the three heating zones of the extruder barrel by a single screw. The barrel length of the lab-scale extruder used herein was 18.75 inches (0.47m). The residence time in each of the three zones of the extruder barrel is given by the following relationship:

$$\text{Approximate Residence Time} = \frac{500 \text{ seconds}}{\text{RPM}}$$

In Each Zone

In each of the following three examples the first zone was used only to preheat the extruder feed to a 160°C initiation temperature. Although reaction of the components commenced, it was at a low rate with most of the reaction occurring in the last two zones. The approximate reaction times are given in the examples.

20 Example I

Maleinized Shellvis 40

Extruder feed: 760 gm Shellvis 40
26 gm Maleic Anhydride
3 gm di-tert-Butyl Peroxide

Extruder screw speed = 75 rpm

Residence time at temperature:

7 seconds at 160°C (Zone 1)

7 seconds at 240°C (Zone 2)

7 seconds at 260°C (Zone 3)

Approximate reaction time = 21 seconds TAN 10-15

Example II

35 Maleinized BASF Glissoviscal CE 5260

Extruder feed: 626 gm Glissoviscal CE
21 gm Maleic Anhydride
2 gm di-tert-Butyl Peroxide

Extruder screw speed = 50 rpm

40 Residence time at temperature:

10 seconds at 160°C (Zone 1)

10 seconds at 240°C (Zone 2)

10 seconds at 260°C (Zone 3)

Approximate reaction time = 30 seconds TAN 10-15

45

Example III

Maleinized Shellvis 50

Extruder feed: 626 gm Shellvis 50
21 gm Maleic Anhydride
2 gm di-tert-Butyl Peroxide

Extruder screw speed = 50 rpm

Residence time at temperature:

10 seconds at 160°C (Zone 1)

55 10 seconds at 240°C (Zone 2)

10 seconds at 260°C (Zone 3)

Approximate reaction time = 30 seconds TAN 10-15

In a similar manner, the same blending experiments were carried out at different temperatures as of

about 160, 180, 200 and 220 °C.

The reaction mixture is dissolved as a 10 percent solution in toluene. It is then poured slowly into methyl alcohol with rapid agitation to precipitate the polymer. The polymer is isolated by decantation and dried in an open dish at about 60 °C.

5 An alternative process is to carry out the above reaction in the presence of one or more solvents to form the (D) acylating reaction product. The solvent used can be any common or conventional solvent such as those known to the art and literature. Convenient and suitable solvents include the various oils which are lubricant base stocks such as natural and/or synthetic lubricating oils set forth hereinbelow. Briefly, natural
10 lubricating oils of the paraffinic-naphthenic or mixed paraffinic-naphthenic types. Animal and vegetable oils can also be used. Synthetic lubricating oils utilized are alkylated aromatics, poly-alpha-olefins, alkyl-phosphates and the esters derived from polybasic acids, polyols and fatty acids. Examples of solvents include solvent refined 100 to 200 Neutral mineral paraffinic and/or naphthenic oils, diphenyldodecanes, didodecylbenzenes, hydrogenated decene, oligomers, and mixtures of the above. The amount of oil should
15 be adjusted so that the viscosity of the reaction mixture is suitable for mixing. Typically, from about 70 percent to about 99 percent by weight of the total reaction mixture as oil can be utilized.

Although in this embodiment of the invention, the reactants are carried out in the presence of a solvent, the various reactants of the same are set forth hereinabove. For example, the various (A) hydrogenated
20 block copolymers can be either the normal block copolymer set forth hereinabove containing from 2 to 5 total block portions or the random block copolymer. The random block copolymer can also have the same number average molecular weight range as set forth hereinabove. The unsaturated carboxylic reagent (B) is the same as set forth hereinabove. The reagent can thus contain alpha-beta olefinic unsaturated carboxylic acids including various functional derivatives thereof having from 2 to 20 carbon atoms exclusive of the
25 carboxyl-base groups. The (C) initiators are also the same as set forth hereinabove with regard to the solvent-free reaction and include the organic peroxides and the various organic azo compounds. The various reaction parameters, conditions and methods are also the same as set forth hereinabove unless otherwise stated below to be different.

The preparation of the (D) acylating reaction product generally conforms to the procedure set forth above except that a solvent, for example a Neutral mineral oil is utilized. Any conventional or suitable
30 reaction vessel or container is utilized such as a reaction flask.

The mineral oil is initially added to the reaction vessel in a desired amount and heated. Inasmuch as the reaction is desirably carried out in an inert atmosphere, the vessel can be initially purged with an inert gas such as nitrogen. Longer resident times are generally required to react the generally larger amount of
35 reactants contained in the reaction vessel. Thus, although the temperatures can be from 100 °C to 300 °C, they are desirably somewhat lower as from 130 °C to 180 °C with from about 140 °C to 175 °C being preferred. The process is generally carried out by heating the solvent to a suitable reaction temperature. The (A) block copolymer is then added and allowed to dissolve over a matter of hours as for example a few hours. The (B) alpha-beta olefinic unsaturated carboxylic reagent is then added. The (C) free radical initiator
40 is subsequently added and the reaction conducted at a suitable temperature, as for example, from 140 °C to 170 °C. Desirably, the initiator is added in a slow manner, for example, dropwise over a period of time as many minutes and even hours. Upon completion of the addition of the (C) initiator, the solvent is held at the reaction temperature for a period of time until a desired yield is obtained, typically for 1/2 to 2 hours. Naturally, much shorter or greater periods of time can be utilized. The (D) acylating reaction product so
45 produced can be utilized as a viscosity improver or as an intermediate for further reaction with a (E) primary amine-containing compound.

The invention will be better understood by reference to the following examples.

EXAMPLE IV

50 A 1750g sample of a hydrogenated styrene/butadiene copolymer (BASF Glissoviscal CE5260) is charged to a 12-1 flask containing 5250g Sun HPO 100N oil which has been heated to 150 °C. During this step and throughout the entire reaction sequence, a N₂ blanket and mechanical stirring are maintained. Within 3 hrs. a homogeneous solution is obtained. Thirty-five (35g) grams of maleic anhydride is charged to
55 the flask and thoroughly dissolved while increasing the reaction temperature to 160 °C. A dropwise addition of 14.1g of the t-butyl peroxide initiator is charged into the reaction mixture over 1 hour. The solution is stirred at 160 °C for 1.5 additional hours. The N₂ blanket is then changed to a subsurface purge (2.0 SCFH) (1.5 x 10⁻⁵ m³/s). The reaction mixture is heated to 170 °C and held 2.0 hours to remove unreacted maleic anhydride and peroxide decomposition products. Infrared assay of the polymer solution confirms the

presence of succinic anhydride groups in the product. Treatment of a 50g aliquot of product with 0.1g DETA (Diethylenetriamine) at 110°C causes instantaneous gelation. This confirms that on the average each polymer molecule contains more than one succinic anhydride group. Titration of a toluene solution of the product, with 0.1 N NaOCH₃, indicates a TAN = 5.4 (95% maleic anhydride reacted). Dialysis of the polymer solution shows that 20-30% of the TAN is succinic anhydride attached to the polymer substrate, while 70-80% of the TAN is succinic anhydride attached to the 100N oil.

EXAMPLE V

In a similar manner, a reaction product is prepared utilizing Shellvis 40, a hydrogenated styrene-isoprene block copolymer produced by Shell Chemicals. The amount of Shellvis 40 is 10.0% by weight, the amount of maleic anhydride is 0.50 weight percent and the amount of neutral oil is 89.5 weight percent. These components are charged to a flask in a manner as set forth in Example IV and heated while a dropwise addition of 0.5 weight percent of t-butyl peroxide is charged over a period of 1 hours. The solution is stirred at 160°C for an additional 1.5 hours. The nitrogen blanket is then changed to a subsurface purge. The reaction mixture is heated to 170°C and held for 2 hours to remove unreacted maleic anhydride and peroxide of composition products. Infrared assay of the polymer solution confirms the presence of succinic anhydride groups in the product. Treatment of a 50g aliquot of product with 0.1g of diethylenetriamine at 110°C causes a dramatic viscosity increase thus confirming that a significant amount of succinic anhydride groups are attached to the polymer substrate. The TAN was 5.4 (theoretical 5.5). The number average molecular weight is approximately 160,000 and the weight average molecular weight is approximately 200,000.

EXAMPLE VI

In a manner similar to example IV, a reaction product is prepared utilizing Shellvis 50, a hydrogenated styrene-isoprene block copolymer produced by Shell Chemicals, with a lower molecular weight than Shellvis 40. The amount of Shellvis 50 is 14.9 weight percent, the amount of maleic anhydride is 0.3% and the amount of 100 Neutral oil is 84.8 weight percent. The reactants are heated in a manner as set forth in Example IV and then 0.2 weight percent of t-butyl peroxide initiator is charged to the reaction mixture over a period of 1 hour and the solution is stirred at 160°C for an additional 1.5 hours. As before, the nitrogen blanket is changed to a subsurface purge. The reaction mixture is heated at 170°C and held for 2 hours to remove unreacted maleic anhydride and peroxide decomposition products. Infrared assay of the polymer solution confirms the presence of succinic anhydride groups in the product. Treatment of a 50g aliquot of product with 0.1g of diethylenetriamine at 110°C causes a significant viscosity increase. This confirms that a significant amount of succinic anhydride groups are attached to the polymer. The TAN was 3.5 (theoretical 3.4) and the polymer solution was clear.

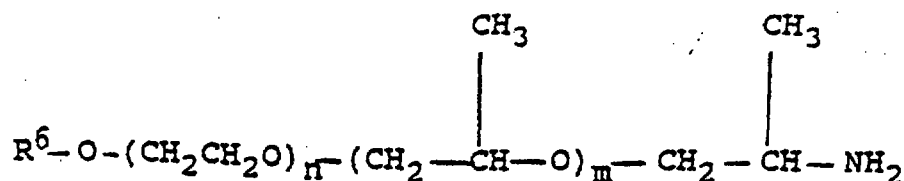
Regardless of whether a solvent-free process is utilized as carried out in an extruder or other apparatus or whether a solution process is utilized, the (D) reaction product is reacted with a (E) primary amine-containing compound. By the term "primary amine-containing compound" is meant ammonia or a compound which contains only one primary amino group therein. That is, although the compound can contain a plurality of nitrogen atoms therein, only one such nitrogen atom forms a primary amine group. Otherwise, undesirable gel is often obtained.

The (E) primary amine-containing compounds of the present invention can broadly be represented by the formula R⁴-NH₂ where R⁴ is hydrogen, an alkyl, a cycloalkyl, an aromatic, and combinations thereof, e.g., an alkyl substituted cycloalkyl. Furthermore, R⁴ can be an alkyl, an aromatic, a cycloalkyl group, or combination thereof containing one or more secondary or tertiary amine groups therein. R⁴ can also be an alkyl, a cycloalkyl, an aromatic group, or combinations thereof containing one or more heteroatoms (for example, oxygen, nitrogen, sulfur). R⁴ can further be an alkyl, a cycloalkyl, an aromatic, or combinations thereof containing sulfide or oxy linkages therein. Generally, R⁴ is hydrogen or said various R⁴ groups containing from 1 to 25 carbon atoms with from 1 to 6 or 7 carbon atoms being desirable. Exemplary of such (E) primary amine-containing compounds are the following wherein R⁴ is as set forth immediately hereinabove: ammonia, N,N-dimethylhydrazine, methylamine, ethylamine, butylamine, 2-methoxyethylamine, N,N-dimethyl-1,3-propanediamine, N-ethyl-N-methyl-1,3-propanediamine, N-methyl-1,3-propanediamine, N-(3-aminopropyl)morpholine, 3-alkoxypropylamines wherein the alkoxy group contains from 1 to 18 carbon atoms, usually an alkoxy group having from 1 to 8 carbon atoms and which have the formula R⁵-O-CH₂CH₂CH₂-NH₂ such as 3-methoxypropylamine, 3-isobutoxypropylamine and 3-(alkoxypolyethoxy)propylamines having the formula R⁵ O(CH₂CH₂O)_xCH₂CH₂CH₂NH₂ wherein R⁵O is alkoxy group as

immediately set forth above and where x is 1 to 50, 4,7-dioxactylamine, N-(3-aminopropyl)-N'-methylpiperazine, N-(2-aminoethyl)piperazine, the various (2-aminoethyl)-pyridines, aminopyridines, 2-aminomethylpyridines, 2-aminomethylfuran, 3-amino-2-oxotetrahydrofuran, N-(2-aminoethyl)pyrrolidine, 2-aminomethylpyrrolidine, 1-methyl-2-aminomethylpyrrolidine, 1-aminopyrrolidine, 1-(3-aminopropyl)-2-methylpyrrolidine, 4-aminomethylpiperidine, N-(2-aminoethyl)morpholine, 1-ethyl-3-aminopiperidine, 1-aminopiperidine, N-aminomorpholine.

Of these compounds, N-(3-aminopropyl)morpholine and N-ethyl-N-methyl-1,3-propanediamine are preferred with N,N-dimethyl-1,3-propanediamine being highly preferred.

Another group of (E) primary amine-containing compounds are the various amine terminated polyethers. A specific example of such a polyether is given by the formula:



wherein n is from 0 to 50 with from 5 to 25 being preferred, m is from 0 to 35 with from 2 to 15 being preferred, and R⁶ is an alkyl having from 1 to 18 carbon atoms.

The reaction between the (E) primary amine-containing compound and the (D) acylating reaction product can be carried out free of solvent or in a solvent system such as in a lubricating oil.

In the formation of the (D) reaction product, any suitable vessel or device can be utilized such as an extruder, or a Banbury. The blending device desirable imparts a suitable high mechanical energy to the compounds, that is the (D) acylating reaction product and the (E) primary amine-containing compound, such that a solvent-free reaction can be conducted with good mixing of the components. The reaction between the (D) acylating reaction product and the (E) primary amine-containing compound generally takes place upon heating and is from 50 to 250°C with from 140 to 180°C being preferred. Desirably, the reaction takes place in the presence of an inert gas such as nitrogen or argon. The time to carry out the reaction generally depends on for example the reaction temperature, desired yield. When a blending device such as an extruder is utilized having a relatively small amount reactants therein, the reaction time is generally quite short.

The reaction with the (E) primary amine-containing compound can also be carried out in the presence of one or more solvents. The solvent utilized in the solvent or solution-type reaction can be any common or conventional solvent known to the art or literature. More specifically, the solvent can be the same as set forth hereinabove with regard to the solvated formation of the (D) acylating reaction product. That is, conventional oils generally of lubricating viscosity such as natural and/or synthetic lubricating oils set forth hereinabove can be utilized. A more detailed description of such oils is also set forth hereinbelow. Generally, a neutral lubricating oil is utilized.

The solvent, e.g., lubricating oil, can be added to the reaction vessel, heated and the (D) acylating reaction product added thereto. The (E) primary amine-containing compound can then be added. Although this order of addition is somewhat desirable, it can be varied. Another source of oil is to utilize the solution of (D) acylating reaction product which is carried out in a substantial amount of oil.

The reaction conditions of the (D) acylating reaction product with the (E) primary amine-containing compounds in a solution are essentially the same as that set forth hereinabove with regard to the solvent-free reaction conditions. However, the temperature of reaction is from 50°C to 250°C and preferably from 150°C to 190°C. The reaction is carried out desirably in an inert gas. The amount of the various reactants is also the same as set forth hereinabove.

In any event, it is an important aspect of the present invention that essentially only (E) primary amine-containing compounds be utilized, that is, compounds which contain only one primary amine group therein as described hereinabove.

An effective amount of the (E) primary amine-containing compound is utilized so that an oil-soluble dispersant VI improver is formed. Generally, an amount of the (E) primary amine-containing compound is utilized such that from 0.1 to 3.0 primary amine groups exist for each two carbonyl groups or for each anhydride group of said (D) acylating reaction product. Desirably from 0.5 to 1.5 primary amine-containing groups exists for each two carbonyl groups or each anhydride group and preferably from 0.9 to 1.1 primary

amine groups for each two carbonyls or each anhydride group. Naturally, higher or lower amounts can be utilized but tend to be inefficient and/or costly.

The invention will be better understood by reference to the following examples.

5 EXAMPLE VII

A 3000g sample of the 24.9% polymer solution prepared in Example IV is charged to a 12-1 flask equipped with a mechanical stirrer, thermometer, N₂ inlet, addition funnel, Dean-Stark water trap, condenser, and heating mantle. Wibarco Heavy Alkylate (Wibarco GmbH; 3212.9g) is charged and the mixture is stirred and heated to 150°C under a N₂ blanket to obtain a homogeneous solution (approx. 2.0 h). When this solution has been obtained, 14.9g of N,N-dimethyl-1,3-propanediamine (Eastman Kodak Co.) is added dropwise to the mixture from the addition funnel over 0.5 hour. After all the amine has been charged, the reaction mixture is heated to 170°C and held 3.0 hours. The N₂ blanket is changed to a subsurface purge (1.0 SCFH) (7.8×10^{-6} m³/s) over the last hour of the reaction period to remove by-product water. This 12% weight polymer solution is the final product. Analytical assay of the final product gives an ANA nitrogen content of 0.065%. Infrared analysis of the product confirms imide formation with no residual anhydride absorptions. The kinematic viscosity at 100°C of this dispersant-VI concentrate is 240cSt (2.4×10^{-4} m²/s).

An API SF/CC, SAE 15W40 oil was prepared by blending 12.5% weight of the final product from Example VII, 10.6% weight of performance additive A^a), 0.4% weight Acryloid 156, in a lubricating oil base stock. This oil thereby contains 1.5% weight of the product copolymer. When evaluated in the Caterpillar 1G-2 engine test a TGF = 73; WTD = 217.6 rating is observed after a 480 hour test period.

An API SF/CC SAE 10W30 oil was prepared by blending 11% weight of the product dispersant-VI, 8.45% weight of Performance Additive B^b), 0.2% weight Acryloid 156 in a lubricating oil base stock. This oil thus contains 1.32% weight of the product copolymer. When evaluated in the Ford Sequence VD engine test, a merit rating of 9.5 sludge, 7.2 varnish and 6.8 piston skirt varnish is achieved after 192 test hours.

a) Performance additive A: %SA = 13.44, %Zn = 1.12, %P = 1.02, %Ca = 2.04, %Mg = 0.99, %N = 0.25, %S = 3.47, TBN = 96.9.

b) Performance additive B: %SA = 12.29, %Zn = 1.56, %P = 1.41, %Ca = 1.23, %Mg = 1.16, %N = 0.52, %S = 4.27, TBN = 85.8.

EXAMPLE VIII

In a manner similar to Example VII, 5500g of the 10% by wt polymer solution prepared in Example V is charged to a reactor. Diphenylalkane (Vista Chemical Co.; 2332.1g) is charged and the mixture stirred and heated to 150°C under a N₂ blanket. Once a homogeneous solution has been obtained, 27.3g of N,N-dimethyl-1,3-propanediamine (Eastman Kodak Co.) is added dropwise to the mixture over 0.5 hours. After all the amine has been charged, the reaction mixture is heated to 170°C and held for 3.0 hours. The nitrogen blanket is changed to a subsurface purge over the last hour of the reaction period to remove by-product water and yield a final product. Analytical assay of the final product gives an ANA nitrogen content of 0.094% (0.094% theoretical). Infrared analysis of the product confirms imide formation with no residual anhydride absorptions. The kinematic viscosity at 100°C of this dispersant-VI concentrate is 4353cSt (4.353×10^{-3} m²/s). The product is clear.

An API SF/CC, SAE 10W30 oil is prepared by blending 9.5% weight of the product dispersant-VI, 4.2% weight of performance additive C^c), in a lubricating oil base stock. This oil thus contains 0.67% weight of the product copolymer. When evaluated in the Ford Sequence VD engine test, a merit rating of 9.55 sludge, 7.1 varnish, 6.7 piston skirt varnish is achieved after 192 test hours.

c) Performance additive C: %SA = 17.4, %Zn = 2.45, %P = 2.21, %Ca = 1.36, %Mg = 0.87, %N = .62, %S = 5.22, %Na = 1.56, TBN = 115.9.

EXAMPLE IX

7000g of the 14.9% by wt polymer solution prepared in Example VI was charged to a flask equipped in a manner as set forth in Example VII. 6067g Wibarco Heavy Alkylate (Wibarco GmbH) is added and the mixture is heated to 150°C. Once a homogeneous solution is obtained, 22.5g of N,N-dimethyl-1,3-propanediamine was added dropwise over a 1/2 hour period. After all the amine had been charged, the reaction vessel is heated to 170°C and held for 3.0 hours. The nitrogen blanket is changed to a subsurface purge over the last hour of the reaction period to remove by-product water. The 8.0% weight polymer

solution gives the final product. Analytical assay of this final product gives an ANA nitrogen content of 0.05% (0.05% theoretical). Infrared analysis of the product confirms imide formation with no residual anhydride absorptions. The appearance of the concentrate was clear.

5 EXAMPLE X

A maleic anhydride functionalized solvent free polymer as obtained from Example II is reacted with a primary amine compound in the following manner: The solvent free polymer in an amount of 2 carbonyl equivalents (based upon the TAN number) is reacted with one equivalent of a primary amine group in the same type of extruder, that is, a single screw type extruder driven by a C. W. Brabender Plastic-Corder torque rheometer. The temperature of the extruder is approximately 180°C. The primary amine containing compound, N,N-dimethyl-1,3-propanediamine in the above noted amount was premixed with the solvent free polymer and both added to the feed portion of the extruder. Residence time of the extruder was approximately 20 seconds. The imidized neat polymer in an amount of 12% by weight was dissolved into Wibarco Heavy Akylate. The kinematic viscosity at 100°C of the dispersant-VI concentrate was 760cSt ($7.6 \times 10^{-4} \text{ m}^2/\text{s}$).

Should relatively small amounts of polyamines containing two or more primary amino groups be utilized to react with the (D) acylating reaction product containing an acid group or anhydride group, viscosity of the product increases dramatically and gel is often formed thereby yielding an insoluble material.

The number of the anhydride groups attached to each molecule of (D) depends upon the average molecular weight of the (A) block copolymer and the TAN of (D) copolymer. The following table illustrates this aspect.

Number Average Mol. Wt. of (A)	Total Acid Number (TAN) of (D)					
	2.2	3.4	4.5	5.6	22	44
50,000	2.2	3.4	4.5	5.6	22	44
70,000	1.6	2.4	3.2	4.0	16	32
100,000	1.12	1.7	2.2	2.8	11	22
150,000	0.75	1.1	1.5	1.9	7.5	15
200,000	0.56	0.84	1.1	1.4	5.6	11.2
300,000	0.37	0.56	0.75	0.93	3.7	7.5
Number Average Functionality* of (D)	1.0	1.5	2.0	5.0	10	20

*Number of anhydride groups attached to each polymer molecule.

On the other hand, a compound (E) containing only one primary amine group as set forth above, will form an oil soluble product regardless of the functionality of (D).

According to the present invention, it is required that the VI improvers/dispersants of the present invention be oil-soluble so that they can be utilized in various lubricating applications as set forth hereinbelow. As illustrative of this fact, examples are presented showing the criticality of utilizing essentially only compounds containing one primary amine group therein.

As previously indicated, the products of the present invention are suitable as VI improvers/dispersants. Accordingly, the composition of the present invention can be effectively employed in a variety of lubricating compositions formulated for a variety of uses. These lubricating compositions are based on diverse oils of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. These lubricating compositions containing the subject additive concentrates are effective as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, including automobile and truck engines, two-cycle engines, aviation piston engines, marine and low-load diesel engines. Also, automatic transmission fluids, transaxle lubricants, gear lubricants, metal-working lubricants, hydraulic fluids, and the other lubricating oil and grease compositions can benefit from the incorporation of the subject additive concentrates.

The following description with regard to the natural as well as synthetic lubricating oils in which the VI improver/dispersant can be utilized are also applicable solvents for either the (D) acylating reaction product formation or the subsequent reaction of the reaction product with the (E) primary amine-containing compound. Accordingly, it is to be understood that the following list of compounds can be utilized as a solvent in the above-described reactions. Examples of natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types.

Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., oligobutylenes, oligopropylenes, and propylene-ethylene oligomers, chlorinated polybutylenes); oligo-(1-hexenes), oligo(1-octenes), oligo(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by for example esterification, or etherification, constitute another class of known synthetic lubricating oils that can be used. These are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having an average molecular weight of 500-1000, diethyl ether of polypropylene glycol having an average molecular weight of 1000-1500) or mono- and polycarboxylic esters thereof. For example, the acetic acid esters, mixed C₃-C₈ fatty acid esters, or the C₁₃ oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkylsuccinic acid, alkenylsuccinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenylmalonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of these esters include butyl adipate, (2-ethylhexyl) sebacate, n-hexyl fumarate, octyl sebacate, isooctyl azelate, isodecyl azelate, octyl phthalate, decyl phthalate, eicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, tripentaerythritol.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-hexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxyl)-disiloxane, poly(methylsiloxanes), poly(methylphenylsiloxanes)).

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the concentrates of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated with one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation. Rerefined oils are obtained by processes similar to those used to obtain refined oils and to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

Generally the lubricants of the present invention contain an amount of one or more of the viscosity improver compositions of this invention sufficient to provide them with suitable viscosities. Normally the amount employed will be 0.01 percent to 20 percent, preferably 0.1 percent to 4 percent of the weight of the (d) reaction product or the (E) dispersant derivatives thereof based upon the total weight of the lubricating composition.

The invention also contemplates the use of other additives in combination with the viscosity improver compositions of this invention. Such additives include, for example, detergents and dispersants of the ash-producing or ashless type, corrosion- and oxidation-inhibiting agents, pour point depressing agents, extreme pressure agents, anti-wear agents, color stabilizers and anti-foam agents.

The ash-producing detergents are exemplified by oil-soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, or organic phosphorus acids characterized by at least one direct carbon-to-phosphorus linkage such as those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a number average molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur,

white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are those of sodium, potassium, lithium, calcium, magnesium, strontium and barium.

The term "basic salt" is used to designate metal salts wherein the metal is present in stoichiometrically larger amounts than the organic acid radical. The commonly employed methods for preparing the basic salts involve heating a mineral oil solution of an acid with a stoichiometric excess of a metal neutralizing agent such as the metal oxide, hydroxide, carbonate, bicarbonate, or sulfide at a temperature of about 50 °C and filtering the resulting mass. The use of a "promoter" in the neutralization step to aid the incorporation of a large excess of metal likewise is known. Examples of compounds useful as the promoter include phenolic substances such as phenol, naphthols, alkylphenols, thiophenol, sulfurized alkylphenols, and condensation products of formaldehyde with phenolic substance; alcohols such as methanol, 1-propanol, octyl alcohol, cellosolve, carbitol, ethylene glycol, stearyl alcohol, and cyclohexyl alcohol; and amines such as aniline, phenylenediamine, phenothiazine, N-phenylbeta-naphthylamine, and dodecylamine. A particularly effective method for preparing the basic salts comprises mixing an acid with an excess of a basic alkaline earth metal neutralizing agent and at least one alcohol promoter, and carbonating the mixture at an elevated temperature such as 60-200 °C.

Ashless detergents and dispersants are so called despite the fact that, depending on its constitution, the dispersant may upon combustion yield a non-volatile material such as boric oxide or phosphorus pentoxide; however, it does not ordinarily contain metal and therefore does not yield a metal-containing ash on combustion. Many types are known in the art, and any of them are suitable for use in the lubricant compositions of this invention. The following are illustrative:

(1) Reaction products of carboxylic acids (or derivatives thereof) containing at least 34 and preferably at least 54 carbon atoms with nitrogen containing compounds such as amine, organic hydroxy compounds such as phenols and alcohols, and/or basic inorganic materials. Examples of these "carboxylic dispersants" are described in British Patent 1,306,529 and in many U.S. patents including the following:

3,163,603	3,351,552	3,541,012
3,184,474	3,391,022	3,542,678
3,215,707	3,399,141	3,542,680
3,219,666	3,415,750	3,567,637
3,271,310	3,433,744	3,574,101
3,272,746	3,444,170	3,576,743
3,281,357	3,448,048	3,630,904
3,306,908	3,448,049	3,632,510
3,311,558	3,451,933	3,632,511
3,316,177	3,454,607	3,697,428
3,340,281	3,467,668	3,725,441
3,341,542	3,501,405	4,234,435
3,346,493	3,522,179	Re 36,433

(2) Reaction products of relatively high molecular weight aliphatic or alicyclic halides with amines, preferably oxyalkylene polyamines. These may be characterized as "amine dispersants" and examples thereof are described. For example, in the following U.S. patents:

3,275,554	3,454,555
3,438,757	3,565,804

(3) Reaction products of alkylphenols in which the alkyl group contains at least 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines), which may be characterized as "Mannich dispersants". The materials described in the following U.S. Patents are illustrative:

2,459,112	3,442,808	3,591,598
2,962,442	3,448,047	3,600,372
2,984,550	3,454,497	3,634,515
3,036,003	3,459,661	3,649,229
3,166,516	3,461,172	3,697,574
3,236,770	3,493,520	3,725,277
3,355,370	3,539,633	3,725,480
3,368,972	3,558,743	3,726,882
3,413,347	3,586,629	3,980,569

(4) Products obtained by post-treating the carboxylic, amine or Mannich dispersants with such reagents as urea, thiourea, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds. Exemplary materials of this kind are described in the following U.S. patents:

3,036,003	3,282,955	3,493,520	3,639,242
3,087,936	3,312,619	3,502,677	3,649,229
3,200,107	3,366,569	3,513,093	3,649,659
3,216,936	3,367,943	3,533,945	3,658,836
3,254,025	3,373,111	3,539,633	3,697,574
3,256,185	3,403,102	3,573,010	3,702,757
3,278,550	3,442,808	3,579,450	3,703,536
3,280,234	3,445,831	3,591,598	3,704,308
3,281,428	3,455,832	3,600,372	3,708,422

(5) Interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides and poly-(oxyethylene)-substituted acrylates. These may be characterized as "polymeric dispersants" and examples thereof are disclosed in the following U.S. patents:

3,329,658	3,666,730
3,449,250	3,687,849
3,519,565	3,702,300

The above-noted patents disclose ashless dispersants. Extreme pressure agents and corrosion- and oxidation-inhibiting agents which may be included in the lubricants of the invention are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyl disulfide, (chlorobenzyl) disulfide, butyl tetrasulfide, sulfurized methyl ester of oleic acid, sulfurized alkylphenols, sulfurized dipentene, and sulfurized terpenes; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with turpentine or methyl oleate, phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentyl phenyl phosphite, dipentyl phenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)- substituted phenyl phosphite, diisobutyl-substituted phenyl phosphite; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium heptylphenyldithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl)-phosphorodithioate, cadmium dinonylphosphorodithioate, and the zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

Many of the above-mentioned auxiliary extreme pressure agents and corrosion-oxidation inhibitors also serve as anti-wear agents. Zinc dialkylphosphorodithioates are well known examples.

Pour point depressants are particularly useful types of additive often included in the lubricating oils described herein. The use of such pour point depressants in oil-based compositions are well known in the art. See, for example, page 8 of Lubricant Additives by C. V. Smalheer and R. Kennedy Smith Lezius-Hiles Co. publishers, Cleveland, Ohio, 1967.

Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkyl fumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in
 5 U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715.

Anti-foam agents are used to reduce or prevent the formation of stable foam. Typical anti-foam agents include silicones or organic polymers. Additional anti-foam compositions are described in Foam Control Agents, by Henry T. Kerner, Noyes Data Corporation, 1976, pages 125-162.

10 The compositions of this invention can be added directly to the lubricant. Preferably, however, they are diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually contain from 1 percent to 40 percent by weight and desirably from 4 percent to 25 percent by weight of the dispersant-VI improvers of the present invention, that is, the (D) reaction product or the (E) dispersant derivatives thereof based upon
 15 the total weight of the lubricating compositions. Moreover, the lubricating composition can contain, in addition, one or more other additives known in the art or described hereinabove. The remainder of the concentrate is the substantially inert liquid diluent.

Claims

20 **Claims for the following Contracting States : DE, FR, IT, BE, CH, GB, LU, NL, SE**

1. Use of a composition comprising a diluent oil and from 1% to 40% by weight of the oil-soluble (D) reaction product of:

25 (A) a hydrogenated linear block copolymer containing no more than about 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages comprising a normal block copolymer or a random block copolymer, said normal block copolymer made from a vinyl substituted aromatic and an aliphatic conjugated diene, said normal block copolymer having from two to five polymer blocks with at least one polymer block of said vinyl substituted aromatic and at least one polymer block of said aliphatic conjugated diene, said random block copolymer
 30 made from vinyl substituted aromatic and aliphatic conjugated diene monomers, the total amount of said vinyl substituted aromatic blocks in said block copolymer being in the range of from 20 percent to 70 percent by weight and the total amount of said diene blocks in said block copolymer being in the range of from 30 percent to 80 percent by weight; the number average molecular weight of said normal block copolymer and said random block copolymer being in the range of 10,000 to 500,000;
 35 (B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups in an amount of from 0.20 percent to 20 percent by weight based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent; and
 from 0.01 to 5 percent by weight of (C) a free radical initiator, based upon the weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent;
 40 as a lubricant additive concentrate.

2. Use of a composition comprising a major amount of an oil of lubricating viscosity and a minor amount of the oil-soluble (D) reaction product of;

45 (A) a hydrogenated linear block copolymer containing no more than about 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages comprising a normal block copolymer or a random block copolymer, said normal block copolymer made from a vinyl substituted aromatic and an aliphatic conjugated diene, said normal block copolymer having from two to five polymer blocks with at least one polymer block of said vinyl substituted aromatic and at least one polymer block of said aliphatic conjugated diene, said random block copolymer
 50 made from vinyl substituted aromatic and aliphatic conjugated diene monomers, the total amount of said vinyl substituted aromatic blocks in said block copolymer being in the range of from 20 percent to 70 percent by weight and the total amount of said diene blocks in said block copolymer being in the range of from 30 percent to 80 percent by weight; the number average molecular weight of said normal block copolymer and said random block copolymer being in the range of 10,000 to 500,000;
 55 (B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups in an amount of from 0.20 percent to 20 percent by weight based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent; and
 from 0.01 to 5 percent by weight of (C) a free radical initiator, based upon the weight of said (A)



Examples of useful pour point depressants are polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkyl fumarates, vinyl esters of fatty acids and alkyl vinyl ethers. Pour point depressants useful for the purposes of this invention, techniques for their preparation and their uses are described in U.S. Patents 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 2,666,746; 2,721,877; 2,721,878; and 3,250,715.

Anti-foam agents are used to reduce or prevent the formation of stable foam. Typical anti-foam agents include silicones or organic polymers. Additional anti-foam compositions are described in Foam Control Agents, by Henry T. Kerner, Noyes Data Corporation. 1976, pages 125-162.

The compositions of this invention can be added directly to the lubricant. Preferably, however, they are diluted with a substantially inert, normally liquid organic diluent such as mineral oil, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually contain from 1 percent to 40 percent by weight and desirably from 4 percent to 25 percent by weight of the dispersant-VI improvers of the present invention, that is, the (D) reaction product or the (E) dispersant derivatives thereof based upon the total weight of the lubricating compositions. Moreover, the lubricating composition can contain, in addition, one or more other additives known in the art or described hereinabove. The remainder of the concentrate is the substantially inert liquid diluent.

Claims

Claims for the following Contracting States : DE, FR, IT, BE, CH, GB, LU, NL, SE

1. Use of a composition comprising a diluent oil and from 1% to 40% by weight of the oil-soluble (D) reaction product of:

(A) a hydrogenated linear block copolymer containing no more than about 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages comprising a normal block copolymer or a random block copolymer, said normal block copolymer made from a vinyl substituted aromatic and an aliphatic conjugated diene, said normal block copolymer having from two to five polymer blocks with at least one polymer block of said vinyl substituted aromatic and at least one polymer block of said aliphatic conjugated diene, said random block copolymer made from vinyl substituted aromatic and aliphatic conjugated diene monomers, the total amount of said vinyl substituted aromatic blocks in said block copolymer being in the range of from 20 percent to 70 percent by weight and the total amount of said diene blocks in said block copolymer being in the range of from 30 percent to 80 percent by weight; the number average molecular weight of said normal block copolymer and said random block copolymer being in the range of 10,000 to 500,000;

(B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups in an amount of from 0.20 percent to 20 percent by weight based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent; and from 0.01 to 5 percent by weight of (C) a free radical initiator, based upon the weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent;

as a lubricant additive concentrate.

2. Use of a composition comprising a major amount of an oil of lubricating viscosity and a minor amount of the oil-soluble (D) reaction product of;

(A) a hydrogenated linear block copolymer containing no more than about 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages comprising a normal block copolymer or a random block copolymer, said normal block copolymer made from a vinyl substituted aromatic and an aliphatic conjugated diene, said normal block copolymer having from two to five polymer blocks with at least one polymer block of said vinyl substituted aromatic and at least one polymer block of said aliphatic conjugated diene, said random block copolymer made from vinyl substituted aromatic and aliphatic conjugated diene monomers, the total amount of said vinyl substituted aromatic blocks in said block copolymer being in the range of from 20 percent to 70 percent by weight and the total amount of said diene blocks in said block copolymer being in the range of from 30 percent to 80 percent by weight; the number average molecular weight of said normal block copolymer and said random block copolymer being in the range of 10,000 to 500,000;

(B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups in an amount of from 0.20 percent to 20 percent by weight based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent; and from 0.01 to 5 percent by weight of (C) a free radical initiator, based upon the weight of said (A)



block copolymer and said (B) unsaturated carboxylic reagent;
as a lubricant composition.

3. Use of a composition according to either of claims 1 and 2, wherein said conjugated diene has from 4
5 to 10 carbon atoms and wherein said mono-vinyl substituted aromatic has from 8 to 12 carbon atoms,
and wherein said (B) unsaturated carboxylic reagent is selected from anhydride, ester, acylated
nitrogen, acyl halide, nitrile and metal salt derivatives thereof, and an acid having the formula



- 15 wherein R is hydrogen or a saturated aliphatic or alicyclic, aryl, alkylaryl or heterocyclic group, R₁ is
hydrogen or an alkyl group containing 1 to 10 carbon atoms and the total number of carbon atoms in R
and R₁ does not exceed 18 carbon atoms.

4. Use of a composition according to any preceding claim, wherein said (A) block copolymer has a total of
20 two or three polymer blocks, wherein the number average molecular weight of said block copolymer is
from 30,000 to 200,000, wherein in said block copolymer the total amount of said conjugated diene is
from 40 percent to 60 percent and the total amount of said vinyl substituted aromatic is from 40
percent to 60 percent by weight.

- 25 5. Use of a composition according to any preceding claim, wherein said (B) unsaturated carboxylic
reagent is selected from maleic anhydride, citraconic anhydride, itaconic anhydride, glutaconic anhy-
dride, chloromaleic anhydride, methyl maleic anhydride, acrylic acid, methacrylic acid, C₁₋₁₀ alkyl
esters of such acids, and combinations thereof, and wherein the amount of said (B) unsaturated
carboxylic reagent is from 0.5 to 5 percent by weight.

- 30 6. Use of a composition according to any preceding claim, wherein said conjugated diene is isoprene or
butadiene, wherein said mono-vinyl substituted aromatic is styrene, and wherein said reaction product
has a total acid number of from 0.1 to 60.

- 35 7. Use of a composition according to any one of claims 1 to 4 or 6, in which the reaction product has a
total acid number of from 0.5 to 20 and wherein said (B) unsaturated carboxylic reagent is selected
from fumaric acid, maleic acid and maleic anhydride.

8. A process for the preparation of the composition used according to claim 1 comprising the steps of:
40 placing into a reactor (A) a hydrogenated linear block copolymer containing no more than about
0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent
linkages having a number average molecular weight 10,000 to 500,000 which is made from a vinyl
substituted aromatic and an aliphatic conjugated diene, which copolymer is a normal block copolymer
45 having two to five polymer blocks with at least one block of vinyl substituted aromatic and at least one
block of aliphatic conjugated diene, or is a random block copolymer made from vinyl substituted
aromatic and aliphatic conjugated diene monomers, having 20 to 70 percent by weight vinyl substituted
aromatic blocks and 30 to 80 percent by weight aliphatic conjugated diene blocks;

- adding from 0.20 percent to 20 percent by weight of (B) an alpha-beta olefinic unsaturated
carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups based upon the
50 total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent, adding from 0.01
to 5 percent by weight of a free radical initiator based upon the weight of said (A) block copolymer and
said (B) unsaturated carboxylic reagent;

- and reacting said (A) block copolymer with said (B) unsaturated carboxylic reagent and said (C)
free radical initiator in a solvent-free system to form an (D) oil-soluble reaction product;

- 55 and mixing the reaction product with a diluent oil.

9. A process for the preparation of the composition used according to claim 2 comprising the steps of:
placing into a reactor (A) a hydrogenated linear block copolymer containing no more than about

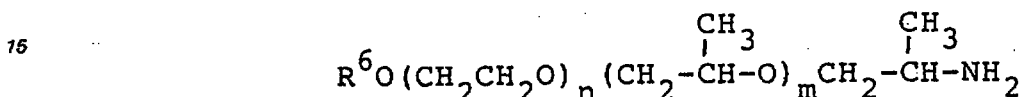


- 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages having a number average molecular weight 10,000 to 500,000 which is made from a vinyl substituted aromatic and an aliphatic conjugated diene, which copolymer is a normal block copolymer having two to five polymer blocks with at least one block of vinyl substituted aromatic and at least one block of aliphatic conjugated diene, or is a random block copolymer made from vinyl substituted aromatic and aliphatic conjugated diene monomers, having 20 to 70 percent by weight vinyl substituted aromatic blocks and 30 to 80 percent by weight aliphatic conjugated diene blocks;
- adding from 0.20 percent to 20 percent by weight of (B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent, adding from 0.01 to 5 percent by weight of a free radical initiator based upon the weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent;
- and reacting said (A) block copolymer with said (B) unsaturated carboxylic reagent and said (C) free radical initiator in a solvent-free system to form an (D) oil-soluble reaction product;
- and mixing the reaction product with an oil of lubricating viscosity.
10. The process according to either of claims 8 and 9, wherein said (A) block copolymers and said (B) unsaturated carboxylic reagent and said (C) free radical initiator are reacted at temperatures from 100°C to 300°C, wherein said number average molecular weight of said (A) normal block copolymer and said random block copolymer is from 30,000 to 200,000, wherein in said block copolymer the total amount of said conjugated diene is from 40 percent to 60 percent by weight, and wherein the total amount of said vinyl substituted aromatic is from 40 percent to 60 percent by weight.
11. The process according to any one of claims 8 to 10, wherein said normal block copolymer has two or three polymer blocks therein and wherein the total acid number of said reaction product is from 0.1 to 60.
12. The process according to any one of claims 8 to 11, wherein said (B) unsaturated carboxylic reagent is selected from acrylic acid, methacrylic acid, fumaric acid, maleic acid, C₁₋₁₀ alkyl esters of such acids, maleic anhydride, maleimide, maleamic acid and mixtures of two or more of any of these, and wherein said free radical initiator is an organic peroxide or an organic azo initiator.
13. The process according to any one of claims 8 to 12, wherein said (B) unsaturated carboxylic reagent is maleic anhydride, wherein said conjugated diene is isoprene or butadiene, wherein said mono-vinyl substituted aromatic is styrene, and wherein said free radical initiator is benzoyl peroxide or t-butyl perbenzoate.
14. The process according to any of claims 8 to 13, including causing scission of said (A) block copolymers and said (B) unsaturated carboxylic reagent in a high mechanical energy imparting device.
15. A reaction product for use in an additive composition, of a component (D) with a component (E), the reaction product (D) being the solvent free reaction product of
- (A) a hydrogenated linear block copolymer containing no more than about 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages comprising a normal block copolymer or a random block copolymer, said normal block copolymer made from a vinyl substituted aromatic and an aliphatic conjugated diene, said normal block copolymer having from two to five polymer blocks with at least one polymer block of said vinyl substituted aromatic and at least one polymer block of said aliphatic conjugated diene, said random block copolymer made from vinyl substituted aromatic and aliphatic conjugated diene monomers, the total amount of said vinyl substituted aromatic blocks in said block copolymer being in the range of from 20 percent to 70 percent by weight and the total amount of said diene blocks in said block copolymer being in the range of from 30 percent to 80 percent by weight; the number average molecular weight of said normal block copolymer and said random block copolymer being in the range of 10,000 to 500,000;
- (B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups in an amount of from 0.20 percent to 20 percent by weight based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent; and
- and from 0.01 to 5 percent by weight of (C) a free radical initiator, based upon the weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent;



and the component (E) being a primary amine containing compound, wherein said primary amine containing compound is ammonia or a compound having only one primary amine group therein.

- 5 16. A reaction product according to claim 15, wherein said primary amine containing compound is a compound having the formula R^4-NH_2 or an amine terminated polyether, wherein R^4 is hydrogen, or an alkyl, a cycloalkyl, an aromatic, or combinations thereof having from 1 to 25 carbon atoms; or said alkyl, said cycloalkyl, said aromatic, or said combinations thereof containing at least one secondary or tertiary amino group; or said alkyl, said cycloalkyl, said aromatic, or said combinations thereof containing at least one heteroatom moiety, or said alkyl, said cycloalkyl, said aromatic, or combinations thereof containing at least one sulfide or at least one oxy linkage, and wherein said amine terminated polyether has the formula:



- 20 wherein n is from 0 to 50, wherein m is from 0 to 35, and wherein R^6 is an alkyl containing from 1 to 18 carbon atoms.

- 25 17. A reaction product according to claim 16, wherein R^4 of said R^4-NH_2 has from 1 to 7 carbon atoms and wherein the amount of said (E) primary amine containing compound is such that from 0.1 to 3.0 primary amine groups exist for each two carbonyl groups and for each anhydride group of said (D) solvent free reaction product.

- 30 18. A reaction product according to claim 16, wherein said (E) primary amine containing compound is selected from ammonia, methylamine, ethylamine, butylamine, 2-methoxyethylamine, 3-methylethylaminopropylamine, 3-(N,N-dimethylamino)-propylamine, N-(3-aminopropyl)-morpholine, 3-alkoxy-propylamine having the formula $R^5-O-CH_2CH_2CH_2-NH_2$ wherein R^5 has from 1 to 18 carbon atoms, and said amine terminated polyether wherein said n is from 5 to 25, and wherein said m is from 2 to 15.

- 35 19. A reaction product according to anyone of claims 16 - 17, wherein the amount of said (E) primary amine containing compound is such that from 0.5 to 1.5 primary amine groups exist for each two carbonyl groups and for each anhydride groups of said (D) solvent free reaction product and wherein said (E) primary amine containing compound is selected from N,N-dimethyl-1,3-propanediamine, N-(3-aminopropyl)morpholine, and N-ethyl-N-methyl-1,3-propanediamine.

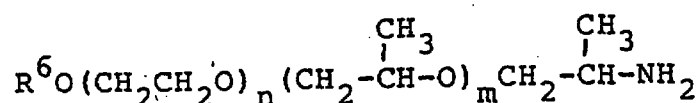
40 **Claims for the following Contracting State : AT**

1. A process for the preparation of an oil-soluble (D) reaction product comprising the steps of:
 45 placing into a reactor (A) a hydrogenated linear block copolymer containing no more than about 0.5% residual olefinic unsaturation therein based upon the total number of carbon-to-carbon covalent linkages, having a number average molecular weight of from 10,000 to 500,000 which is made from a vinyl substituted aromatic and an aliphatic conjugated diene, which copolymer is a normal block copolymer having two to five polymer blocks with at least one block of vinyl substituted aromatic and at least one block of aliphatic conjugated diene, or is a random block copolymer made from vinyl substituted aromatic and aliphatic conjugated diene monomers, having 20 to 70 percent by weight vinyl substituted aromatic blocks and 30 to 80 percent by weight aliphatic conjugated diene blocks;
 50 adding from 0.20 percent to 20 percent by weight of (B) an alpha-beta olefinic unsaturated carboxylic reagent containing 2 to 20 carbon atoms exclusive of the carboxy groups based upon the total weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent, adding from 0.01 to 5 percent by weight of a free radical
 55 initiator, based upon the weight of said (A) block copolymer and said (B) unsaturated carboxylic reagent;
 and reacting said (A) block copolymer with said (B) unsaturated carboxylic reagent and said (C)



free radical initiator in a solvent-free system to form the (D) oil-soluble reaction product.

2. The process according to claim 1 wherein said (A) block copolymers and said (B) unsaturated carboxylic reagent and said (C) free radical initiator are reacted at temperatures from 100° to 300° C, wherein said number average molecular weight of said (A) normal block copolymer and said random block copolymer is from 30,000 to 200,000, wherein in said block copolymer the total amount of said conjugated diene is from 40 percent to 60 percent by weight, and wherein the total amount of said vinyl substituted aromatic is from 40 percent to 60 percent by weight.
3. The process according to either of claims 1 and 2, wherein said normal block copolymer has two or three polymer blocks therein and wherein the total acid number of said reaction product is from 0.1 to 60.
4. The process according to any preceding claim, wherein said (B) unsaturated carboxylic reagent is selected from acrylic acid, methacrylic acid, fumaric acid, maleic acid, C₁₋₁₀ alkyl esters of such acids, maleic anhydride, maleimide, maleamic acid and mixtures of two or more of any of these, and wherein said free radical initiator is an organic peroxide or an organic azo initiator.
5. The process according to any preceding claim, wherein said (B) unsaturated carboxylic reagent is maleic anhydride, wherein said conjugated diene is isoprene or butadiene, wherein said mono-vinyl substituted aromatic is styrene, and wherein said free radical initiator is benzoyl peroxide or t-butyl perbenzoate.
6. The process according to any preceding claim, including causing scission of said (A) block copolymers and said (B) unsaturated carboxylic reagent in a high mechanical energy imparting device.
7. A process for the preparation of a reaction product for use in an additive composition, comprising: admixing the reaction product of the (D) solvent free reaction product of any one of claims 1 to 6 and a (E) primary amine containing compound, wherein said primary amine containing compound is ammonia or a compound having only one primary amine group therein.
8. The process according to claim 7, wherein said primary amine containing compound is a compound having the formula R⁴-NH₂ or an amine terminated polyether, wherein R⁴ is hydrogen, or an alkyl, a cycloalkyl, an aromatic, or combinations thereof having from 1 to 25 carbon atoms; or said alkyl, said cycloalkyl, said aromatic, or said combinations thereof containing at least one secondary or tertiary amino group; or said alkyl, said cycloalkyl, said aromatic, or said combinations thereof containing at least one heteroatom moiety, or said alkyl, said cycloalkyl, said aromatic, or combinations thereof containing at least one sulfide or at least one oxy linkage, and wherein said amine terminated polyether has the formula:



wherein n is from 0 to 50, wherein m is from 0 to 35, and wherein R⁶ is an alkyl containing from 1 to 18 carbon atoms.

9. The process according to claim 8, wherein R⁴ of said R⁴-NH₂ has from 1 to 7 carbon atoms and wherein the amount of said (E) primary amine containing compound is such that from 0.1 to 3.0 primary amine groups exist for each two carbonyl groups and for each anhydride group of said (D) solvent free reaction product.
10. The process according to claim 8, wherein said (E) primary amine containing compound is selected from ammonia, methylamine, ethylamine, butylamine, 2-methoxyethylamine, 3-methylethylaminopropylamine, 3-(N,N-dimethylamino)-propylamine, N-(3-aminopropyl)-morpholine, 3-alkoxy-propylamine having the formula R⁵O-CH₂CH₂CH₂NH₂ where R⁵ has from 1 to 18 carbon atoms,



and said amine terminated polyether wherein said n is from 5 to 25, and wherein said m is from 2 to 15.

- 5 11. The process according to any one of claims 7 to 9, wherein the amount of said (E) primary amine containing compound is such that from 0.5 to 1.5 primary amine groups exist for each two carbonyl groups and for each anhydride group of said (D) solvent free reaction product and wherein said (E) primary amine containing compound is selected from N,N-dimethyl-1, 3-propanediamine, N-(3-aminopropyl) morpholine, and N-ethyl-N-methyl-1,3 propanediamine.
- 10 12. A process for the preparation of a lubricant additive concentrate comprising admixing 1% to 40% by weight of the reaction product of the process of any of claims 1 to 11 with a diluent oil.
- 15 13. A process for the preparation of a lubricant composition comprising admixing a minor amount of the reaction product of the process of any of claims 1 to 11 with a major amount of an oil of lubricating viscosity.

Patentansprüche

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

- 20 1. Verwendung einer Zusammensetzung, umfassend ein Verdünnungsöl und 1 bis 40 Gew.-% des öllöslichen Reaktionsprodukts (D) aus:
 - (A) einem hydrierten linearen Blockcopolymer mit einem Gehalt von nicht mehr als etwa 0,5% an verbliebener olefinischer Ungesättigtheit, bezogen auf die Gesamtzahl der kovalenten Kohlenstoff-Kohlenstoff-Bindungen, umfassend ein normales Blockcopolymer oder statistisches Blockcopolymer,

25 wobei das normale Blockcopolymer aus einem vinylsubstituierten Aromaten und einem aliphatischen konjugierten Dien hergestellt ist und zwei bis fünf Polymerblöcke mit mindestens einem Polymerblock aus vinylsubstituierten Aromaten und mindestens einem Polymerblock aus dem aliphatischen konjugierten Dien enthält, wobei das statistische Blockcopolymer aus vinylsubstituierten aromatischen Monomeren und aliphatischen konjugierten Dienmonomeren hergestellt ist und die Gesamtmenge der vinylsubstituierten Aromatenblöcke im Blockcopolymer im Bereich von 20 bis 70 Gew.-% und die Gesamtmenge der Dienblöcke im Blockcopolymer im Bereich von 30 bis 80 Gew.-% liegt; wobei das Zahlenmittel des Molekulargewichts des normalen Blockcopolymers und des statistischen Blockcopolymers im Bereich von 10.000 bis 500.000 liegt;

30 (B) einem alpha-beta olefinisch ungesättigten carboxylischen Reaktanden mit 2 bis 20 C-Atomen ausschließlich der Carboxylgruppen in einer Menge von 0,20 bis 20 Gew.-%, bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B); und 0,01 bis 5 Gew.-% eines freie Radikale bildenden Initiators (C), bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B);

35 als Schmiermitteladditiv-Konzentrat.
- 40 2. Verwendung einer Zusammensetzung, umfassend einen Hauptbestandteil eines Öls mit Schmierviskosität und eine geringere Menge des öllöslichen Reaktionsprodukts (D) aus:
 - (A) einem hydrierten linearen Blockcopolymer mit einem Gehalt von nicht mehr als etwa 0,5% an verbliebener olefinischer Ungesättigtheit, bezogen auf die Gesamtzahl der kovalenten Kohlenstoff-Kohlenstoff-Bindungen, umfassend ein normales Blockcopolymer oder statistisches Blockcopolymer,

45 wobei das normale Blockcopolymer aus einem vinylsubstituierten Aromaten und einem aliphatischen konjugierten Dien hergestellt ist und zwei bis fünf Polymerblöcke mit mindestens einem Polymerblock aus dem vinylsubstituierten Aromaten und mindestens einem Polymerblock aus dem aliphatischen konjugierten Dien enthält, wobei das statistische Blockcopolymer aus vinylsubstituierten Aromaten und aliphatischen konjugierten Dienmonomeren hergestellt ist und die Gesamtmenge der vinylsubstituierten Aromatenblöcke im Blockcopolymer im Bereich von 20 bis 70 Gew.-% und die Gesamtmenge der Dienblöcke im Blockcopolymer im Bereich von 30 bis 80 Gew.-% liegt; wobei das Zahlenmittel des Molekulargewichts des normalen Blockcopolymers und des statistischen Blockcopolymers im Bereich von 10.000 bis 500.000 liegt;

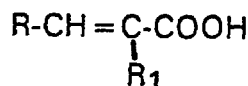
50 (B) einem alpha-beta olefinisch ungesättigten carboxylischen Reaktanden mit 2 bis 20 C-Atomen ausschließlich der Carboxylgruppen in einer Menge von 0,20 bis 20 Gew.-%, bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B); und 0,01 bis 5 Gew.-% eines freie Radikale bildenden Initiators (C), bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B);

55



wicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B);
als Schmiermitteladditiv-Konzentrat.

3. Verwendung einer Zusammensetzung nach Anspruch 1 oder 2, wobei das konjugierte Den 4 bis 10 C-Atome enthält, wobei der vinylsubstituierte Aromat 8 bis 12 C-Atome enthält und wobei der ungesättigte carboxylische Reaktand (B) ausgewählt ist aus Anhydriden, Estern, acylierten Stickstoff enthaltenden Verbindungen, Acylhalogeniden, Nitrilen und deren Metallsalzderivaten und einer Säure der allgemeinen Formel



- wobei der Rest R ein Wasserstoffatom oder ein gesättigter aliphatischer oder alicyclischer Rest, Aryl-, Alkylaryl- oder heterocyclischer Rest, der Rest R₁ ein Wasserstoffatom oder ein Alkylrest mit 1 bis 10 C-Atomen ist und die Gesamtzahl der C-Atome in den Resten R und R₁ 18 C-Atome nicht übersteigt.

4. Verwendung einer Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Blockcopolymer (A) 2 oder 3 Polymerblöcke enthält, wobei das Zahlenmittel des Molekulargewichts des Blockcopolymers 30.000 bis 200.000 beträgt und wobei die Gesamtmenge des konjugierten Diens im Blockcopolymer 40 bis 60 Gew.-% und die Gesamtmenge des vinylsubstituierten Aromaten 40 bis 60 Gew.-% beträgt.

5. Verwendung einer Zusammensetzung nach einem der vorstehenden Ansprüche, wobei der ungesättigte carboxylische Reaktand (B) ausgewählt ist aus Maleinsäureanhydrid, Citraconsäureanhydrid, Itaconsäureanhydrid, Glutaconsäureanhydrid, Chlormaleinsäureanhydrid, Methylmaleinsäureanhydrid, Acrylsäure, Methacrylsäure, C₁₋₁₀-Alkylestern dieser Säuren und Kombinationen davon und wobei die Menge des ungesättigten carboxylischen Reaktanden (B) 0,5 bis 5 Gew.-% beträgt.

6. Verwendung einer Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das konjugierte Den Isopren oder Butadien ist, wobei der vinylsubstituierte Aromat Styrol ist und wobei das Reaktionsprodukt eine Gesamtsäurezahl von 0,1 bis 60 hat.

7. Verwendung einer Zusammensetzung nach einem der Ansprüche 1 bis 4 oder 6, wobei das Reaktionsprodukt eine Gesamtsäurezahl von 0,5 bis 20 hat und wobei der ungesättigte carboxylische Reaktand (B) ausgewählt ist aus Fumarsäure, Maleinsäure und Maleinsäureanhydrid.

8. Verfahren zur Herstellung der nach Anspruch 1 verwendeten Zusammensetzung, umfassend die Schritte:

Vorlegen eines hydrierten linearen Blockcopolymers (A) mit einem Gehalt von nicht mehr als etwa 0,5% an verbliebener olefinischer Ungesättigtheit, bezogen auf die Gesamtzahl der kovalenten Kohlenstoff-Kohlenstoff-Bindungen, mit einem Zahlenmittel des Molekulargewichts von 10.000 bis 500.000, das aus einem vinylsubstituierten Aromaten und einem aliphatischen konjugierten Den hergestellt ist, wobei das Copolymer ein normales Blockcopolymer mit zwei bis fünf Polymerblöcken mit mindestens einem Polymerblock aus dem vinylsubstituierten Aromaten und mindestens einem Polymerblock aus dem aliphatischen konjugierten Den ist oder ein statistisches Blockcopolymer ist, hergestellt aus vinylsubstituierten Aromaten und aliphatischen konjugierten Dienmonomeren mit 20 bis 70 Gew.-% vinylsubstituierten Aromatenblöcken und 30 bis 80 Gew.-% aliphatischen konjugierten Dienblöcken, in einem Reaktor;

Zugabe von 0,20 bis 20 Gew.-% eines alpha-beta-ungesättigten carboxylischen Reaktanden (B) mit 2 bis 20 C-Atomen ausschließlich der Carboxylgruppen, bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B),

Zugabe von 0,01 bis 5 Gew.-% eines freie Radikale bildenden Initiators, bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B);

Umsetzung von Blockcopolymer (A) mit dem ungesättigten carboxylischen Reaktanden (B) und dem freie Radikale bildenden Initiator (C) in einem lösungsmittelfreien System zu einem öllöslichen



Reaktionsprodukt (D);

und Vermischen des Reaktionsprodukts mit einem Verdünnungsöl.

9. Verfahren zur Herstellung der nach Anspruch 2 verwendeten Zusammensetzung, umfassend die Schritte:

Vorlegen eines hydrierten linearen Blockcopolymers (A) mit einem Gehalt von nicht mehr als etwa 0,5% an verbliebener olefinischer Ungesättigtheit, bezogen auf die Gesamtzahl der kovalenten Kohlenstoff-Kohlenstoff-Bindungen, mit einem Zahlenmittel des Molekulargewichts von 10.000 bis 500.000, das aus einem vinylsubstituierten Aromaten und einem aliphatischen konjugierten Dien hergestellt ist, wobei das Copolymer ein normales Blockcopolymer mit zwei bis fünf Polymerblöcken mit mindestens einem Polymerblock aus dem vinylsubstituierten Aromaten und mindestens einem Polymerblock aus dem aliphatischen konjugierten Dien ist oder ein statistisches Blockcopolymer ist, hergestellt aus vinylsubstituierten Aromaten und aliphatischen konjugierten Dienmonomeren mit 20 bis 70 Gew.-% vinylsubstituierten Aromatenblöcken und 30 bis 80 Gew.-% aliphatischen konjugierten Dienblöcken, in einem Reaktor;

Zugabe von 0,20 bis 20 Gew.-% eines alpha-beta-ungesättigten carboxylischen Reaktanden (B) mit 2 bis 20 C-Atomen ausschließlich der Carboxylgruppen, bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B), Zugabe von 0,01 bis 5 Gew.-% eines freie Radikale bildenden Initiators, bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B);

Umsetzung von Blockcopolymer (A) mit dem ungesättigten carboxylischen Reaktanden (B) und dem freie Radikale bildenden Initiator (C) in einem lösungsmittelfreien System zu einem öllöslichen Reaktionsprodukt (D);

und Vermischen des Reaktionsprodukts mit einem Öl mit Schmierviskosität.

10. Verfahren nach Anspruch 8 oder 9, wobei die Blockcopolymere (A) und der ungesättigte carboxylische Reaktand (B) und der freie Radikale bildende Initiator (C) bei Temperaturen von 100°C bis 300°C umgesetzt werden, wobei das Zahlenmittel des Molekulargewichts des normalen Blockcopolymers und des statistischen Blockcopolymers (A) 30.000 bis 200.000 beträgt, wobei im Blockcopolymer die Gesamtmenge des konjugierten Diens von 40 bis 60 Gew.-% beträgt und wobei die Gesamtmenge des vinylsubstituierten Aromaten von 40 bis 60 Gew.-% beträgt.

11. Verfahren nach einem der Ansprüche 8 bis 10, wobei das normale Blockcopolymer 2 oder 3 Polymerblöcke enthält und wobei die Gesamtsäurezahl des Reaktionsprodukts 0,1 bis 60 beträgt.

12. Verfahren nach einem der Ansprüche 8 bis 11, wobei der ungesättigte carboxylische Reaktand (B) ausgewählt ist aus Acrylsäure, Methacrylsäure, Fumarsäure, Maleinsäure, C₁₋₁₀-Alkylestern dieser Säuren, Maleinsäureanhydrid, Maleinsäureimid, Maleinsäuremonoamid und Gemischen zweier oder mehrerer davon und wobei der freie Radikale bildende Initiator ein organisches Peroxid oder ein organischer Azoinitiator ist.

13. Verfahren nach einem der Ansprüche 8 bis 12, wobei der ungesättigte carboxylische Reaktand (B) Maleinsäureanhydrid ist, wobei das konjugierte Dien Isopren oder Butadien ist, wobei der vinylsubstituierte Aromat Styrol ist und wobei der freie Radikale bildende Initiator Benzoylperoxid oder tert.-Butylperbenzoat ist.

14. Verfahren nach einem der Ansprüche 8 bis 13, das die Spaltung des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B) in einer Vorrichtung zur Übertragung hoher mechanischer Energie einschließt.

15. Reaktionsprodukt aus einer Komponente (D) mit einer Komponente (E) zur Verwendung in einer Additiv-Zusammensetzung,

wobei das Reaktionsprodukt (D) das lösungsmittelfreie Reaktionsprodukt ist aus

einem hydrierten linearen Blockcopolymer (A) mit einem Gehalt von nicht mehr als etwa 0,5% an verbliebener olefinischer Ungesättigtheit, bezogen auf die Gesamtzahl der kovalenten Kohlenstoff-Kohlenstoff-Bindungen, umfassend ein normales Blockcopolymer oder statistisches Blockcopolymer, wobei das normale Blockcopolymer aus einem vinylsubstituierten Aromaten und einem aliphatischen konjugierten Dien hergestellt ist und zwei bis fünf Polymerblöcke mit mindestens einem Polymerblock



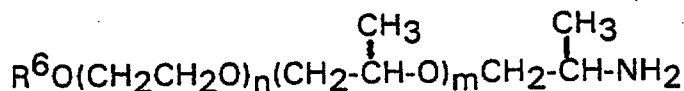
aus dem vinylsubstituierten Aromaten und mindestens einem Polymerblock aus dem aliphatischen konjugierten Dien enthält, wobei das statistische Blockcopolymer aus vinylsubstituierten Aromaten und aliphatischen konjugierten Dienmonomeren hergestellt ist und die Gesamtmenge der vinylsubstituierten Aromatenblöcke im Blockcopolymer im Bereich von 20 bis 70 Gew.-% und die Gesamtmenge der Dienblöcke im Blockcopolymer im Bereich von 30 bis 80 Gew.-% liegt; wobei das Zahlenmittel des Molekulargewichts des normalen Blockcopolymers und des statistischen Blockcopolymers im Bereich von 10.000 bis 500.000 liegt;

einem alpha-beta olefinisch ungesättigten carboxylischen Reaktanden (B) mit 2 bis 20 C-Atomen ausschließlich der Carboxylgruppen in einer Menge von 0,20 bis 20 Gew.-% bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B);

und 0,01 bis 5 Gew.-% eines freie Radikale bildenden Initiators (C), bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B);

und wobei die Komponente (E) eine ein primäres Amin enthaltende Verbindung ist, wobei die das primäre Amin enthaltende Verbindung Ammoniak oder eine Verbindung mit nur einer darin enthaltene-
nen primären Aminogruppe ist.

16. Reaktionsprodukt nach Anspruch 15, wobei die ein primäres Amin enthaltende Verbindung die allgemeine Formel R^4-NH_2 hat oder ein mit einem Amin terminierter Polyether ist, wobei der Rest R^4 ein Wasserstoffatom, ein Alkyl-, ein Cycloalkyl- oder ein aromatischer Rest oder eine Kombination daraus ist mit von 1 bis 25 C-Atomen; oder der Alkyl-, der Cycloalkyl- oder der aromatische Rest oder eine Kombination daraus ist mit mindestens einer sekundären oder tertiären Aminogruppe; oder der Alkyl-, der Cycloalkyl- oder der aromatische Rest oder eine Kombination daraus ist mit mindestens einem Heteroatomrest; oder der Alkyl-, der Cycloalkyl- oder der aromatische Rest oder eine Kombination daraus ist mit mindestens einer Sulfid- oder mindestens einer Oxybindung, wobei der mit einem Amin terminierte Polyether die allgemeine Formel



hat, wobei n eine Zahl von 0 bis 50, m eine Zahl von 0 bis 35 und der Rest R^6 ein Alkylrest mit 1 bis 18 C-Atomen ist.

17. Reaktionsprodukt nach Anspruch 16, wobei der Rest R^4 in der allgemeinen Formel R^4-NH_2 1 bis 7 C-Atome hat und wobei die Menge der ein primäres Amin enthaltenden Verbindung (E) so gewählt ist, daß für jeweils zwei Carbonylgruppen und für jede Anhydridgruppe des lösungsmittelfreien Reaktionsproduktes (D) 0,1 bis 3,0 primäre Aminogruppen vorliegen.
18. Reaktionsprodukt nach Anspruch 16, wobei die ein primäres Amin enthaltende Verbindung (E) ausgewählt ist aus Ammoniak, Methylamin, Ethylamin, Butylamin, 2-Methoxyethylamin, 3-Methylethylaminopropylamin, 3-(N,N-Dimethylamino)-propylamin, N-(3-Aminopropyl)-morpholin, 3-Alkoxypropylamin mit der allgemeinen Formel $R^5-O-CH_2CH_2CH_2-NH_2$, wobei der Rest R^5 1 bis 18 C-Atome hat, und dem mit einem Amin terminierten Polyether, wobei n eine Zahl von 5 bis 25 und m eine Zahl von 2 bis 15 ist.
19. Reaktionsprodukt nach einem der Ansprüche 16 oder 17, wobei die Menge der ein primäres Amin enthaltenden Verbindung (E) so gewählt ist, daß für jeweils zwei Carbonylgruppen und für jede Anhydridgruppe des lösungsmittelfreien Reaktionsproduktes (D) 0,1 bis 1,5 primäre Aminogruppen vorliegen und wobei die ein primäres Amin enthaltende Verbindung (E) ausgewählt ist aus N,N-Dimethyl-1,3-propandiamin, N-(3-Aminopropyl)-morpholin und N-Ethyl-N-methyl-1,3-propandiamin.

Patentansprüche für folgenden Vertragsstaat : AT

1. Verfahren zur Herstellung eines öllöslichen Reaktionsproduktes (D), umfassend die Schritte:
Vorlegen eines hydrierten linearen Blockcopolymers (A) mit einem Gehalt von nicht mehr als etwa 0,5% an verbliebener olefinischer Ungesättigtheit, bezogen auf die Gesamtzahl der kovalenten Kohlenstoff-Kohlenstoff-Bindungen, mit einem Zahlenmittel des Molekulargewichts von 10.000 bis 500.000,



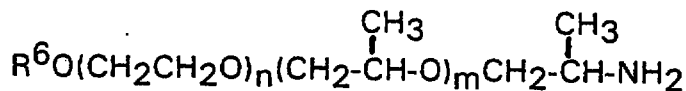
das aus einem vinylsubstituierten Aromaten und einem aliphatischen konjugierten Dien hergestellt ist, wobei das Copolymer ein normales Blockcopolymer mit zwei bis fünf Polymerblöcken mit mindestens einem Polymerblock aus dem vinylsubstituierten Aromaten und mindestens einem Polymerblock aus dem aliphatischen konjugierten Dien ist oder ein statistisches Blockcopolymer ist, hergestellt aus vinylsubstituierten aromatischen Monomeren und aliphatischen konjugierten Dienmonomeren mit 20 bis 70 Gew.-% vinylsubstituierten Aromatenblöcken und 30 bis 80 Gew.-% aliphatischen konjugierten Dienblöcken, in einem Reaktor;

Zugabe von 0,20 bis 20 Gew.-% eines alpha-beta-ungesättigten carboxylischen Reaktanden (B) mit 2 bis 20 C-Atomen ausschließlich der Carboxylgruppen, bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B),

Zugabe von 0,01 bis 5 Gew.-% eines freie Radikale bildenden Initiators, bezogen auf das Gesamtgewicht des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B);

Umsetzung von Blockcopolymer (A) mit dem ungesättigten carboxylischen Reaktanden (B) und dem freien Radikalinitiator (C) in einem lösungsmittelfreien System zum öllöslichen Reaktionsprodukt (D).

2. Verfahren nach Anspruch 1, wobei die Blockcopolymere (A) und der ungesättigte carboxylische Reaktand (B) und der freie Radikale bildende Initiator (C) bei Temperaturen von 100°C bis 300°C umgesetzt werden, wobei das Zahlenmittel des Molekulargewichts des normalen Blockcopolymers und des statistischen Blockcopolymers (A) 30.000 bis 200.000 beträgt, wobei im Blockcopolymer die Gesamtmenge des konjugierten Diens von 40 bis 60 Gew.-% beträgt und wobei die Gesamtmenge des vinylsubstituierten Aromaten von 40 bis 60 Gew.-% beträgt.
3. Verfahren nach einem der Ansprüche 1 und 2, wobei das normale Blockcopolymer 2 oder 3 Polymerblöcke enthält und wobei die Gesamtsäurezahl des Reaktionsprodukts 0,1 bis 60 beträgt.
4. Verfahren nach einem der vorstehenden Ansprüche, wobei der ungesättigte carboxylische Reaktand ausgewählt ist aus Acrylsäure, Methacrylsäure, Fumarsäure, Maleinsäure, C₁₋₁₀-Alkylestern dieser Säuren, Maleinsäureanhydrid, Maleinsäureimid, Maleinsäuremonoamid und Gemischen zweier oder mehrerer davon und wobei der freie Radikale bildende Initiator ein organisches Peroxid oder ein organischer Azoinitiator ist.
5. Verfahren nach einem der vorstehenden Ansprüche, wobei der ungesättigte carboxylische Reaktand (B) Maleinsäureanhydrid ist, wobei das konjugierte Dien Isopren oder Butadien ist, wobei der vinylsubstituierte Aromat Styrol ist und wobei der freie Radikalinitiator Benzoylperoxid oder t-Butylperbenzoat ist.
6. Verfahren nach einem der vorstehenden Ansprüche, das die Spaltung des Blockcopolymers (A) und des ungesättigten carboxylischen Reaktanden (B) in einer Vorrichtung zur Übertragung hoher mechanischer Energie einschließt.
7. Verfahren zur Herstellung eines Reaktionsprodukts zur Verwendung in einer Additiv-Zusammensetzung, umfassend:
Vermischen des lösungsmittelfreien Reaktionsprodukts (D) aus einem der Ansprüche 1 bis 6 und der ein primäres Amin enthaltenden Verbindung (E), wobei die das primäre Amin enthaltende Verbindung Ammoniak oder eine Verbindung mit nur einer darin enthaltenen primären Aminogruppe ist.
8. Verfahren nach Anspruch 7, wobei die ein primäres Amin enthaltende Verbindung die allgemeine Formel R⁴-NH₂ hat oder ein mit einem Amin terminierter Polyether ist, wobei der Rest R⁴ ein Wasserstoffatom, ein Alkyl-, ein Cycloalkyl- oder ein aromatischer Rest oder eine Kombination daraus ist mit von 1 bis 25 C-Atomen; oder der Alkyl-, der Cycloalkyl- oder der aromatische Rest oder eine Kombination daraus ist mit mindestens einer sekundären oder tertiären Aminogruppe; oder der Alkyl-, der Cycloalkyl- oder der aromatische Rest oder eine Kombination daraus ist mit mindestens einem Heteroatomrest; oder der Alkyl-, der Cycloalkyl- oder der aromatische Rest oder eine Kombination daraus ist mit mindestens einer Sulfid- oder mindestens einer Oxybindung, wobei der mit einem Amin terminierte Polyether die allgemeine Formel



5

hat, wobei n eine Zahl von 0 bis 50, m eine Zahl von 0 bis 35 und der Rest R^6 ein Alkylrest mit 1 bis 18 C-Atomen ist.

- 10 9. Verfahren nach Anspruch 8, wobei der Rest R^4 in der allgemeinen Formel $\text{R}^4\text{-NH}_2$ 1 bis 7 C-Atome hat und wobei die Menge der ein primäres Amin enthaltenden Verbindung (E) so gewählt ist, daß für jeweils zwei Carbonylgruppen und für jede Anhydridgruppe des lösungsmittelfreien Reaktionsproduktes (D) 0,1 bis 3,0 primäre Aminogruppen vorliegen.
- 15 10. Verfahren nach Anspruch 8, wobei die ein primäres Amin enthaltende Verbindung (E) ausgewählt ist aus Ammoniak, Methylamin, Ethylamin, Butylamin, 2-Methoxyethylamin, 3-Methylethylaminopropylamin, 3-(N,N-Dimethylamino)-propylamin, N-(3-Aminopropyl)-morpholin, 3-Alkoxypropylamin mit der allgemeinen Formel $\text{R}^5\text{-O-CH}_2\text{CH}_2\text{CH}_2\text{-NH}_2$, wobei der Rest R^5 1 bis 18 C-Atome hat, und dem mit einem Amin terminierten Polyether, wobei n eine Zahl von 5 bis 25 und m eine Zahl von 2 bis 15 ist.
- 20 11. Verfahren nach einem der Ansprüche 7 bis 9, wobei die Menge der ein primäres Amin enthaltenden Verbindung (E) so gewählt ist, daß für jeweils zwei Carbonylgruppen und für jede Anhydridgruppe des lösungsmittelfreien Reaktionsproduktes (D) 0,1 bis 1,5 primäre Aminogruppen vorliegen und wobei die ein primäres Amin enthaltende Verbindung (E) ausgewählt ist aus N,N-Dimethyl-1,3-propandiamin,
- 25 N-(3-Aminopropyl)-morpholin und N-Ethyl-N-methyl-1,3-propandiamin.
12. Verfahren zur Herstellung eines Schmiermitteladditiv-Konzentrats, umfassend das Vermischen von 1 bis 40 Gew.-% des Reaktionsproduktes des Verfahrens nach einem der Ansprüche 1 bis 11 mit einem Verdünnungsöl.
- 30 13. Verfahren zur Herstellung einer Schmiermittelzusammensetzung, umfassend das Vermischen einer geringeren Menge des Reaktionsproduktes des Verfahrens nach einem der Ansprüche 1 bis 11 mit einem Hauptbestandteil eines Öls mit Schmierviskosität.

35 Revendications

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

1. Utilisation d'une composition comportant une huile diluante et de 1% à 40% d'un produit de réaction (D) soluble dans l'huile de :
- 40 (A) un copolymère séquencé linéaire hydrogéné ne renfermant pas plus d'environ 0,5% en poids d'insaturation oléfinique résiduelle, en se basant sur le nombre total de liaisons covalentes carbone-carbone que comporte un copolymère séquencé normal ou un copolymère séquencé statistique, ledit copolymère séquencé normal étant constitué d'un monomère aromatique à substitution vinylique et d'un diène aliphatique conjugué, ledit copolymère séquencé normal ayant de deux à cinq
- 45 séquences polymères avec au moins une séquence polymère dudit composé à substitution vinylique et au moins une séquence polymère dudit diène conjugué aliphatique, ledit copolymère séquencé statistique étant réalisé à partir de monomères aromatiques à substitution vinylique et de monomères aliphatiques diéniques conjugués, la quantité totale desdites séquences aromatiques à substitution vinylique dans ledit copolymère séquencé se situant dans la gamme de 20% à 70% en poids, tandis que la quantité totale desdites séquences diène dans ledit copolymère séquencé se situe dans la gamme de 30% à 80% en poids, le poids moléculaire moyen en nombre dudit copolymère séquencé normal et dudit copolymère séquencé statistique se situant dans la gamme de 10 000 à 500 000 ;
- 50 (B) un réactif carboxylique à insaturation oléfinique alpha-béta renfermant de 2 à 20 atomes de carbone à l'exclusion des groupes carboxy en une quantité de 0,20 % à 20% en poids en se basant sur le poids total dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B) ; et de 0,01 à 5% en poids d'un initiateur de radicaux libres (C) en basant sur le poids dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B);
- 55



en tant que concentré d'addition pour lubrifiant.

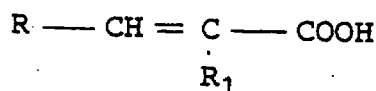
2. Utilisation d'une composition comportant une quantité prépondérante d'une huile de viscosité lubrifiante et une quantité plus faible du produit de la réaction (D), soluble dans l'huile, de :

5 (A) un copolymère séquencé linéaire hydrogéné ne renfermant pas plus d'environ 0,5% en poids d'insaturation oléfinique résiduelle, en se basant sur le nombre total de liaisons covalentes carbone-carbone que comporte un copolymère séquencé normal ou un copolymère séquencé statistique, ledit copolymère séquencé normal étant constitué d'un monomère aromatique à substitution vinylique et d'un diène aliphatique conjugué, ledit copolymère séquencé normal ayant de deux à cinq
10 séquences polymères avec au moins une séquence polymère dudit composé à substitution vinylique et au moins une séquence polymère dudit diène conjugué aliphatique, ledit copolymère séquencé statistique étant réalisé à partir de monomères aromatiques à substitution vinylique et de monomères aliphatiques diéniques conjugués, la quantité totale desdites séquences aromatiques à substitution vinylique dans ledit copolymère séquencé se situant dans la gamme de 20% à 70% en poids, tandis que la quantité totale desdites séquences diène dans ledit copolymère séquencé se situe dans la gamme de 30% à 80% en poids, le poids moléculaire moyen en nombre dudit copolymère séquencé normal et dudit copolymère séquencé statistique se situant dans la gamme de 10 000 à 500 000 ;

20 (B) un réactif carboxylique à insaturation oléfinique alpha-béta renfermant de 2 à 20 atomes de carbone à l'exclusion des groupes carboxy en une quantité de 0,20 % à 20% en poids en se basant sur le poids total dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B) ; et

de 0,01 à 5% en poids d'un initiateur de radicaux libres (C) en basant sur le poids dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B);
25 en tant que concentré d'addition pour lubrifiant.

3. Utilisation d'une composition selon l'une quelconque des revendications 1 et 2, dans laquelle ledit diène conjugué possède de 4 à 10 atomes de carbone et dans lequel ledit monomère aromatique à substitution mono-vinylique présente de 8 à 12 atomes de carbone, et dans lequel ledit réactif carboxylique insaturé (B) est choisi parmi un anhydride, un ester, un azote acylé, un halogénure
30 d'acyle, un nitrile et des dérivés de sel métallique de ceux-ci, et un acide ayant la formule



35 dans laquelle R est de l'hydrogène ou un groupe aliphatique ou alicyclique saturé, aryle, alkylaryle ou hétérocyclique, R₁ est de l'hydrogène ou un groupe alkyle renfermant de 1 à 10 atomes de carbone et le nombre total d'atomes de carbone dans R et R₁ ne dépasse pas 18 atomes de carbone.
40

4. Utilisation d'une composition selon l'une quelconque des revendications précédentes, dans laquelle ledit copolymère séquencé (A) comporte un total de deux ou trois séquences polymères, le poids moléculaire moyen en nombre dudit copolymère séquencé étant de 30 000 à 200 000, tandis que,
45 dans ledit copolymère séquencé, la quantité totale dudit diène conjugué est de 40% à 60% et la quantité totale dudit monomère aromatique à substitution vinylique est de 40% à 60% en poids.

5. Utilisation d'une composition selon l'une des revendications précédentes, dans laquelle ledit réactif carboxylique insaturé (B) est choisi parmi l'anhydride maléique, l'anhydride citraconique, l'anhydride itaconique, l'anhydride glutaconique, l'anhydride chloromaléique, l'anhydride méthyl-maléique, l'acide acrylique, l'acide méthacrylique, des esters alkylés en C₁ à C₁₀ de ces acides, et une combinaison de ceux-ci, tandis que la quantité dudit réactif carboxylique insaturé (B) est de 0,5 à 5% en poids.
50

6. Utilisation d'une composition selon l'une des revendications précédentes, dans laquelle ledit diène conjugué est de l'isoprène ou du butadiène, ledit monomère aromatique à substitution vinylique étant du styrène, tandis que ledit produit de réaction présente un indice d'acide total de 0,1 à 60.
55

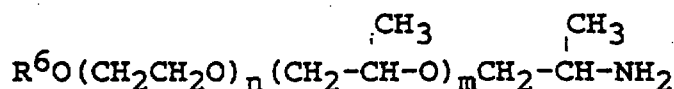


7. Utilisation d'une composition selon l'une quelconque des revendications 1 à 4 ou 6, dans laquelle le produit de réaction présente un indice d'acide total de 0,5 à 20 et dans laquelle ledit réactif carboxylique insaturé (B) est choisi parmi l'acide fumarique, l'acide maléique et l'anhydride maléique.
- 5 8. Un procédé pour la préparation de la composition utilisée selon la revendication 1, comportant les étapes de :
- 10 disposer dans un réacteur (A) un copolymère séquencé linéaire hydrogéné, ne renfermant pas plus qu'environ 0,5% d'insaturation oléfinique résiduelle, en se basant sur le nombre total de liaisons covalentes carbone-carbone, ayant un poids moléculaire moyen en nombre de 10 000 à 500 000 qui est réalisé à partir d'un monomère aromatique à substitution vinylique et d'un diène aliphatique conjugué, ce copolymère étant un copolymère séquencé normal ayant de 2 à 5 séquences polymères avec au moins une séquence de monomère aromatique à substitution vinylique et au moins une séquence de diène conjugué aliphatique, ou bien étant un copolymère séquencé statistique, réalisé à partir d'un monomère aromatique à substitution vinylique et de monomères diéniques aliphatiques conjugués, ayant de 20 à 70% en poids de séquences aromatiques à substitution vinylique et de 30 à 80% en poids de séquences diène conjugué aliphatique.
- 15 ajouter de 0,20% à 20% en poids d'un réactif carboxylique à insaturation oléfinique alpha-béta (B) renfermant de 2 à 20 atomes de carbone à l'exclusion des groupes carboxy, en se basant sur le poids total dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B), en ajoutant de 0,01 à 5% en poids d'un initiateur de radicaux libres, en se basant sur le poids dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B) ;
- 20 et faire réagir ledit copolymère séquencé (A) avec ledit réactif carboxylique insaturé (B) et ledit initiateur de radicaux libres (C) dans un système dépourvu de solvant afin de former un produit de réaction (D), soluble dans l'huile ;
- 25 et mélanger le produit de la réaction avec une huile diluante.
9. Un procédé pour la préparation de la composition utilisée selon la revendication 2, comportant les étapes de :
- 30 disposer dans un réacteur (A) un copolymère séquencé linéaire hydrogéné, ne renfermant pas plus qu'environ 0,5% d'insaturation oléfinique résiduelle, en se basant sur le nombre total de liaisons covalentes carbone-carbone, ayant un poids moléculaire moyen en nombre de 10 000 à 500 000 qui est réalisé à partir d'un monomère aromatique à substitution vinylique et d'un diène aliphatique conjugué, ce copolymère étant un copolymère séquencé normal ayant de 2 à 5 séquences polymères avec au moins une séquence de monomère aromatique à substitution vinylique et au moins une séquence de diène conjugué aliphatique, ou bien étant un copolymère séquencé statistique, réalisé à partir d'un monomère aromatique à substitution vinylique et de monomères diéniques aliphatiques conjugués, ayant de 20 à 70% en poids de séquences aromatiques à substitution vinylique et de 30 à 80% en poids de séquences diène conjugué aliphatique.
- 35 ajouter de 0,20% à 20% en poids d'un réactif carboxylique à insaturation oléfinique alpha-béta (B) renfermant de 2 à 20 atomes de carbone à l'exclusion des groupes carboxy, en se basant sur le poids total dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B), en ajoutant de 0,01 à 5% en poids d'un initiateur de radicaux libres, en se basant sur le poids dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B) ;
- 40 et faire réagir ledit copolymère séquencé (A) avec ledit réactif carboxylique insaturé (B) et ledit initiateur de radicaux libres (C) dans un système dépourvu de solvant afin de former un produit de réaction (D), soluble dans l'huile ;
- 45 et mélanger le produit de la réaction avec une huile diluante.
10. Le procédé selon l'une quelconque des revendications 8 et 9, dans lequel lesdits copolymères séquencés (A) et ledit réactif carboxylique insaturé (B) ainsi que ledit initiateur de radicaux libres (C) sont mis à réagir à des températures entre 100 °C et 300 °C, (A) comporte un total de deux ou trois séquences polymères, le poids moléculaire moyen en nombre dudit copolymère séquencé étant de 30 000 à 200 000, tandis que, dans ledit copolymère séquencé, la quantité totale dudit diène conjugué est de 40% à 60% et la quantité totale dudit monomère aromatique à substitution vinylique est de 40% à 60% en poids.
- 50
- 55
11. Le procédé selon l'une quelconque des revendications 8 à 10, dans lequel ledit copolymère séquencé normal possède deux ou trois séquences polymères et dans lequel l'indice d'acide dudit produit de



réaction est de 0,1 à 60.

12. Le procédé selon l'une quelconque des revendications 8 à 11, dans lequel ledit réactif carboxylique insaturé (B) est choisi parmi l'acide acrylique, l'acide méthacrylique, l'acide fumarique, l'acide maléique, des esters alkylés en C₁ à C₁₀ de ces acides, l'anhydride maléique, le maléimide, l'acide maléamique et les mélanges de deux ou de plus de deux d'un quelconque de ceux-ci et dans lequel ledit initiateur de radicaux libres est un peroxyde organique ou un initiateur azo organique.
13. Le procédé selon l'une quelconque des revendications 8 à 12, dans lequel ledit réactif carboxylique insaturé (B) est l'anhydride maléique, dans lequel ledit diène conjugué est l'isoprène ou le butadiène, dans lequel ledit monomère aromatique à substitution mono-butylique est le styrène et dans lequel ledit initiateur de radicaux libres est le peroxyde de benzoyle ou le perbenzoate de t-butyle.
14. Le procédé selon l'une quelconque des revendications 8 à 13, dans lequel on provoque la scission desdits copolymères séquencés (A) et dudit réactif carboxylique insaturé (B) dans un dispositif conférant une énergie mécanique élevée.
15. Un produit de réaction destiné à être utilisé dans une composition d'addition d'un composant (D) avec un composant (E), le produit de la réaction (D) étant le produit de la réaction, est pourvu de solvant de :
 (A) un copolymère séquencé linéaire hydrogéné ne renfermant pas plus d'environ 0,5% en poids d'insaturation oléfinique résiduelle, en se basant sur le nombre total de liaisons covalentes carbone-carbone que comporte un copolymère séquencé normal ou un copolymère séquencé statistique, ledit copolymère séquencé normal étant constitué d'un monomère aromatique à substitution vinylique et d'un diène aliphatique conjugué, ledit copolymère séquencé normal ayant de deux à cinq séquences polymères avec au moins une séquence polymère dudit monomère à substitution vinylique et au moins une séquence polymère dudit diène conjugué aliphatique, ledit copolymère séquencé statistique étant réalisé à partir d'un monomère aromatique à substitution vinylique et de monomères aliphatiques diéniques conjugués, la quantité totale desdites séquences aromatiques à substitution vinylique dans ledit copolymère séquencé se situant dans la gamme de 20% à 70% en poids, tandis que la quantité totale desdites séquences diène dans ledit copolymère séquencé se situe dans la gamme de 30% à 80% en poids, le poids moléculaire moyen en nombre dudit copolymère séquencé normal et dudit copolymère séquencé statistique se situant dans la gamme de 10 000 à 500 000 ;
 (B) un réactif carboxylique à insaturation oléfinique alpha-béta renfermant de 2 à 20 atomes de carbone à l'exclusion des groupes carboxy en une quantité de 0,20 % à 20% en poids en se basant sur le poids total dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B) ; et
 de 0,01 à 5% en poids d'un initiateur de radicaux libres (C) en se basant sur le poids dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B) ;
 tandis que le composant (E) est un composé renfermant une amine primaire, ce composé renfermant une amine primaire étant de l'ammoniac ou un composé possédant uniquement un groupe amine primaire.
16. Un produit de réaction selon la revendication 15, dans lequel ledit composé renfermant une amine primaire est un composé ayant la formule R⁴-NH₂ ou un polyéther se terminant par une amine, dans laquelle R⁴ est de l'hydrogène, ou bien un composé alkyle, cycloalkyle, aromatique ou bien une combinaison de ceux-ci ayant de 1 à 25 atomes de carbone, ou bien lesdits composés alkyle, cycloalkyle, aromatique, ou bien des combinaisons de ceux-ci renfermant au moins un groupe amino secondaire ou tertiaire ; ou bien lesdits composés alkyle, cycloalkyle, aromatique, ou bien des combinaisons de ceux-ci, renfermant au moins une partie hétéroatome, ou bien lesdits composés alkyle, cycloalkyle, aromatique ou des combinaisons de ceux-ci renfermant au moins du soufre ou bien au moins une liaison oxy, et dans lequel ledit polyéther se terminant par une amine possède la formule.





dans laquelle n est de 0 à 50, dans laquelle m est de 0 à 35 et dans laquelle R⁶ est un alkyle renfermant de 1 à 18 atomes de carbone.

17. Un produit de réaction selon la revendication 16, dans lequel R⁴ dans ledit R⁴-NH₂ a de 1 à 7 atomes de carbone et dans lequel la quantité dudit composé renfermant une amine primaire (E) est telle que de 0,1 à 3,0 groupes aminés primaires existent pour à chaque fois deux groupes carbonyle et pour chaque groupe anhydride dudit produit de réaction dépourvu de solvant (D).
18. Un produit de la réaction selon la revendication 16, dans lequel ledit composé renfermant une amine primaire est choisi parmi l'ammoniac, la méthylamine, l'éthylamine, la butylamine, la 2-méthoxyéthylamine, la 3-méthyléthylaminopropylamine, la 3-(N,N-diméthylamino)-propylamine, la N-(3-aminopropyl)morpholine, une 3-alkoxy-propylamine ayant la formule R⁵-O-CH₂CH₂CH₂-NH₂ dans laquelle R⁵ a de 1 à 18 atomes de carbone, et ledit polyéther terminé par une amine dans lequel ledit n est de 5 à 25, et dans lequel ledit m est de 2 à 15.
19. Un produit de réaction selon l'une quelconque des revendications 16 à 17, dans lequel la quantité dudit composé renfermant une amine primaire (E) est telle que de 0,5 à 1,5 groupes amine primaire existent pour à chaque fois deux groupes carbonyle et pour chaque groupe anhydride dudit produit de réaction (D) dépourvu de solvant et dans lequel ladite amine primaire (E) est choisie parmi la N-N-diméthyl-1,3-propanediamine, la N-(3-aminopropyl)morpholine, et la N-éthyl-N-méthyl-1,3-propanediamine.

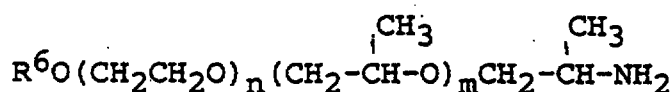
Revendications pour l'Etat contractant suivant : AT

1. Un procédé pour la préparation d'un produit de réaction (D), soluble dans l'huile comportant les étapes de :
disposer dans un réacteur (A) un copolymère séquencé linéaire hydrogéné, ne renfermant pas plus qu'environ 0,5% d'insaturation oléfinique résiduelle, en se basant sur le nombre total de liaisons covalentes carbone-carbone, ayant un poids moléculaire moyen en nombre de 10 000 à 500 000 qui est réalisé à partir d'un monomère aromatique à substitution vinylique et d'un diène aliphatique conjugué, ce copolymère étant un copolymère séquencé normal ayant de 2 à 5 séquences polymères avec au moins une séquence de monomère aromatique à substitution vinylique et au moins une séquence de diène conjugué aliphatique, ou bien étant un copolymère séquencé statistique, réalisé à partir d'un monomère aromatique à substitution vinylique et de monomères diéniques aliphatiques conjugués, ayant de 20 à 70% en poids de séquences aromatiques à substitution vinylique et de 30 à 80% en poids de séquences diène conjugué aliphatique;
ajouter de 0,20% à 20% en poids d'un réactif carboxylique à insaturation oléfinique alpha-béta (B) renfermant de 2 à 20 atomes de carbone à l'exclusion des groupes carboxy, en se basant sur le poids total dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B),
ajouter de 0,01 à 5% en poids d'un initiateur de radicaux libres, en se basant sur le poids dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B) ;
et faire réagir ledit copolymère séquencé (A) avec ledit réactif carboxylique insaturé (B) et ledit initiateur de radicaux libres (C) dans un système dépourvu de solvant afin de former un produit de réaction (D), soluble dans l'huile.
2. Le procédé selon la revendication 1, dans lequel lesdits copolymères séquencés (A) et ledit réactif carboxylique insaturé (B) ainsi que ledit initiateur de radicaux libres (C) sont mis à réagir à des températures entre 100°C et 300°C, (A) comporte un total de deux ou trois séquences polymères, le poids moléculaire moyen en nombre dudit copolymère séquencé étant de 30 000 à 200 000, tandis que, dans ledit copolymère séquencé, la quantité totale dudit diène conjugué est de 40% à 60% et la quantité totale dudit monomère aromatique à substitution vinylique est de 40% à 60% en poids.
3. Le procédé selon l'une quelconque des revendications 1 et 2, dans lequel ledit copolymère séquencé normal possède deux ou trois séquences polymère et dans lequel l'indice d'acide dudit produit de réaction est de 0,1 à 60.
4. Le procédé selon l'une des revendications précédentes, dans lequel ledit réactif carboxylique insaturé (B) est choisi parmi l'acide acrylique, l'acide méthacrylique, l'acide fumarique, l'acide maléique, des esters alkylés en C₁ à C₁₀ de ces acides, l'anhydride maléique, le maléimide, l'acide maléamique et



les mélanges de deux ou de plus de deux d'un quelconque de ceux-ci et dans lequel ledit initiateur de radicaux libres est un peroxyde organique ou un initiateur azo organique.

5. Le procédé selon l'une quelconque des revendications précédentes, dans lequel ledit réactif carboxylique insaturé (B) est l'anhydride maléique, dans lequel ledit diène conjugué est l'isoprène ou le butadiène, dans lequel ledit monomère aromatique à substitution mono-butylique est le styrène et dans lequel ledit initiateur de radicaux libres est le peroxyde de benzoyle ou le perbenzoate de t-butyle.
6. Le procédé selon l'une quelconque des revendications précédentes, dans lequel on provoque la scission desdits copolymères séquencés (A) et dudit réactif carboxylique insaturé (B) dans un dispositif conférant une énergie mécanique élevée.
7. Un procédé pour la préparation d'un produit de réaction destiné à être utilisé dans une composition d'addition, comportant : le mélange du produit de la réaction du produit de réaction (D) dépourvu de solvant, selon l'une quelconque des revendications 1 à 6 et un composé renfermant une amine primaire (E), dans lequel ladite amine primaire renfermant le composé est de l'ammoniac ou un composé comportant uniquement un groupe amine primaire.
8. Le procédé selon la revendication 7, dans lequel ledit composé renfermant une amine primaire est un composé ayant la formule R^4-NH_2 ou un polyéther se terminant par une amine, dans laquelle R^4 est de l'hydrogène, ou bien un composé alkyle, cycloalkyle, aromatique ou bien une combinaison de ceux-ci ayant de 1 à 25 atomes de carbone, ou bien lesdits composés alkyle, cycloalkyle, aromatique, ou bien des combinaisons de ceux-ci renfermant au moins un groupe amino secondaire ou tertiaire ; ou bien lesdits composés alkyle, cycloalkyle, aromatique, ou bien des combinaisons de ceux-ci, renfermant au moins une partie hétéroatome, ou bien lesdits composés alkyle, cycloalkyle, aromatique ou des combinaisons de ceux-ci renfermant au moins du sulfure ou bien au moins une liaison oxy, et dans lequel ledit polyéther se terminant par une amine possède la formule:



dans laquelle n est de 0 à 50, dans laquelle m est de 0 à 35 et dans laquelle R^6 est un alkyle renfermant de 1 à 18 atomes de carbone.

9. Le procédé selon la revendication 8, dans lequel R^4 dans ledit R^4-NH_2 a de 1 à 7 atomes de carbone et dans lequel la quantité dudit composé renfermant une amine primaire (E) est telle que de 0,1 à 3,0 groupes aminés primaires existent pour à chaque fois deux groupes carbonyle et pour chaque groupe anhydride dudit produit de réaction dépourvu de solvant (D).
10. Le procédé selon la revendication 8, dans lequel ledit composé renfermant une amine primaire est choisi parmi l'ammoniac, la méthylamine, l'éthylamine, la butylamine, la 2-méthoxyéthylamine, la 3-méthyléthylaminopropylamine, la 3-(N,N-diméthylamino)-propylamine, la N-(3-aminopropyl)-morpholine, une 3-alkoxy-propylamine ayant la formule $R^5-O-CH_2CH_2CH_2-NH_2$ dans laquelle R^5 a de 1 à 18 atomes de carbone, et ledit polyéther terminé par une amine dans lequel ledit n est de 5 à 25, et dans lequel ledit m est de 2 à 15.
11. Le procédé selon l'une quelconque des revendications 7 à 9, dans lequel la quantité dudit composé renfermant une amine primaire (E) est telle que de 0,5 à 1,5 groupes amine primaire existent pour à chaque fois deux groupes carbonyle et pour chaque groupe anhydride dudit produit de réaction (D) dépourvu de solvant et dans lequel ladite amine primaire (E) est choisie parmi la N-N-diméthyl-1,3-propanediamine, la N-(3-aminopropyl)morpholine, et la N-éthyl-N-méthyl-1,3-propanediamine.
12. Un procédé pour la préparation d'un concentré d'addition pour lubrifiant, comportant le mélange de 1% à 4% en poids du produit de réaction du procédé de l'une quelconque des revendications 1 à 11, avec une huile diluante.



13. Un procédé pour la préparation d'une composition lubrifiante comportant le mélange d'une quantité prépondérante d'une huile de viscosité lubrifiante avec une quantité plus faible du produit de la réaction du procédé de l'une quelconque des revendications 1 à 11.

5

10

15

20

25

30

35

40

45

50

55