

Description

The present invention relates to reacting polyamines and mono-functional acids with an acylating block copolymer.

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

For example, U.S. Patent No. 2,524,424 to Buret relates to the treatment of rubberlike polymers from butadiene hydrocarbons with carboxylic acid anhydrides.

10 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.

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

15 U.S. Patent No. 3,365,411 to Mertzweiler et al 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 polycarboxylic acid anhydride or its amination product.

20 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 products of a synthetic diene rubber with maleic anhydride.

25 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 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.

35 U.S. Patent No. 3,952,023 to Kaiya relates to preparing an adduct of (A) a butadiene lower polymer or 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.

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

40 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. 4,073,737 to Elliott relates to hydrogenated copolymers of conjugated dienes and when desired, a vinyl aromatic monomer which are useful as oil additives.

45 U.S. Patent No. 4,410,656 to Coran et al relates to a method 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 elastomeric copolymer of an EPDM type copolymer. The reaction is carried out free of any free radical initiators.

50 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. 4,082,817 to Imaizumi et al relates to a process for producing a maleic anhydride adduct of high molecular weight 1,2-polybutadiene.

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

5 U.S. Patent No. 4,284,414 to Byrant 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.

10 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 No. 4,077,893 and 4,141,847 to Kiovsky 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.

15 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 20 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 or more high molecular weight olefin polymers having 1 to 20 carbon atoms.

25 U.S. Patent No. 4,033,888 to Kiovsky 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.

Furthermore U.S. Patent No. 4,160,739 and 4,161,452 to Stambaugh et al relate to polyolefinic 30 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.

However, these last two documents, in particular do not disclose the use of a carboxylic acid to further modify the additives.

U.S. Patent No. 4,137,185 to Gardner et al relates to a stabilized imide graft of ethylene copolymeric 35 additives for lubricants, and British Patent No. 2,097,800 relates to oil-soluble viscosity index improving ethylene copolymers, such as copolymers of ethylene and propylene. In both these Patents the copolymers are reacted or grafted with ethylenically unsaturated carboxylic acid moieties and further reacted. However, these Patents do not disclose a carboxylic acid in accordance with the present invention, in combination with the other components of the composition of the present invention.

40 Accordingly, it is an aim of the present invention to provide an oil-soluble composition which comprises polyamines reacted with an acylating hydrogenated block copolymer in the presence of a mono-functional acid.

It is a further aim of the present invention to provide an oil-soluble composition, as above, which is 45 useful as a dispersant as well as a viscosity improver and can be made in the presence of a solvent or in a solvent-free environment.

These and other aspects of the present invention will become apparent from the following specification which later describes in detail the preparation of the composition.

According to one aspect of the present invention there is provided an oil soluble reaction product of: an acylating reaction product (D); a polyamine (F); and a hydrocarbon based mono-carboxylic acid having 50 from 8 to 20 carbon atoms (G); wherein said acylating reaction product (D) is the reaction product of:

(A) a hydrogenated block copolymer containing no more than 0.5 percent residual olefinic unsaturation, based upon the total number of carbon-to-carbon covalent linkages, comprising a normal block copolymer or a random block copolymer, or a combination thereof, said normal block copolymer being 55 derived from a vinyl substituted aromatic monomer and an aliphatic conjugated diene, and having from two to five polymer blocks of which at least one polymer block is derived from said vinyl substituted aromatic monomer and at least one polymer block is derived from said aliphatic conjugated diene, and said random block copolymer being derived from a vinyl substituted aromatic monomer and an aliphatic conjugated diene; 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 block copolymer (normal or random) being in the range of 10,000 to 500,000;

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

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

10 According to another aspect of the present invention there is provided a lubricant composition comprising a major amount of a mineral oil and a minor amount of a composition according to the present invention.

According to yet another aspect of the present invention there is provided an additive concentrate including a diluent oil and from 1 to 40 percent by weight of the composition according to the present invention.

15 According to a further aspect of the present invention there is provided a process for making an oil soluble reaction product according to the present invention comprising:

reacting an acylating reaction product (D) with a polyamine (F) and an effective amount of a hydrocarbon based monocarboxylic acid (G) having from 8 to 20 carbon atoms to produce the oil soluble composition; 20 wherein said acylating reaction product (D) is as previously defined. The reaction product of (A), (B) and (C) is referred to as acylating reaction product (D). The manufacture of reaction product (D) may be carried out in a solvent such as mineral oil or in a solvent-free environment. The reaction of the acylating reaction product (D) with a polyamine (F) and a monocarboxylic acid (G) may be carried out in either a solvent or solvent-free environment. The acylating reaction product (D) may also be additionally reacted with a primary 25 amine containing compound (E), that is, ammonia or a compound which contains only one primary amino group therein.

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

30 Considering the (A) hydrogenated block copolymer, it comprises either a normal block copolymer, that is a true block copolymer or a random block copolymer or a combination thereof. 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.

35 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.

40 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 normal block copolymers can be linear block copolymers wherein 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) 45 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:

aaaa--aa—ddd--ddd—aaa--aa

50

Block I

Block II

Block III

55

Linear ABA 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 60 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.

30 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, or not at all, 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 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 by 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 below.

45 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 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
50 block polymer The amount of the vinyl substituted aromatic block content of the random block copolymer preferably should be in the range of 20 to 45, more preferably 25 to 40 weight percent.

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

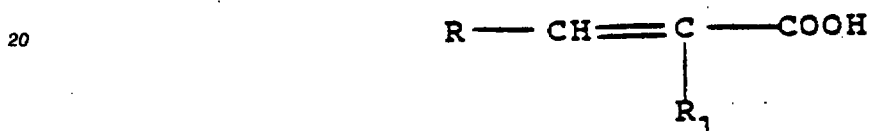
55 Regardless of whether a true or normal block copolymer or a random block copolymer, or combinations of both are utilized, they are hydrogenated before use in this invention so as to remove virtually all of their olefinic double bonds. Techniques for accomplishing this hydrogenation are well known to those of skill in the art and need not be described in detail at this point. Briefly, hydrogenation is accomplished by

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 percent 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 in the art, such as infrared, and 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 50,000 to 500,000, preferably 30,000 to 300,000.

The unsaturated carboxylic reagent (B) contains an alpha-beta olefinic unsaturation. By the term alpha-beta olefinic unsaturated carboxylic acid 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, and nitriles. These carboxylic acid reagents may be either monobasic or polybasic in nature. When they are polybasic they are preferably dicarboxylic acids, although tri- and tetracarboxylic acids can be used. Exemplary of the monobasic alpha-beta olefinic unsaturated carboxylic acid reagents are the carboxylic acids corresponding to the formula:



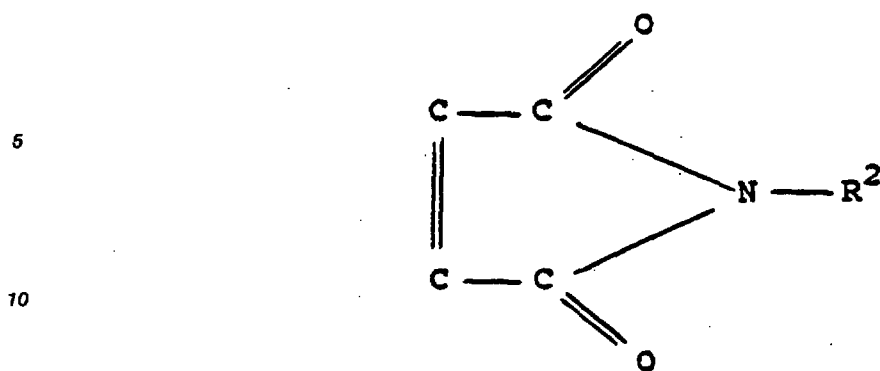
wherein R is hydrogen, or a saturated aliphatic or alicyclic, aryl, alkylaryl or heterocyclic group, preferably hydrogen or a lower alkyl group, and R₁ is hydrogen or a lower alkyl group. By lower alkyl it is meant from 1 to 10 carbon atoms. The total number of carbon atoms in R and R₁ should not exceed 18 carbon atoms. Specific examples of useful monobasic alpha-beta olefinic unsaturated carboxylic acids are acrylic acid, methacrylic acid, cinnamic acid, crotonic acid, and 2-phenylpropenoic acid. 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 halides, and nitriles and other nitrogen containing compounds of the aforescribed acids. A preferred alpha-beta olefinic unsaturated carboxylic acid reagent (B) is maleic anhydride.

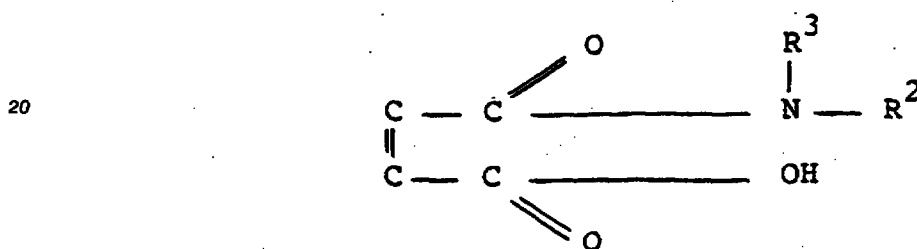
Especially preferred reagents (B) include maleic anhydride, citraconic anhydride, itaconic anhydride, glutaconic anhydride, chloromaleic anhydride, methyl maleic anhydride, acrylic acid, methacrylic acid, fumaric acid, maleic acid, maleimide, maleamic acid, C₁₋₁₀ alkyl esters of such acids, and combinations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

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 carboxylic acid to the corresponding nitrile by dehydration of the corresponding amide. 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

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



15 or



wherein R^2 and R^3 , 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 hetero 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. NH_4Cl , NH_4OH , $(NH_4)_2CO_3$) by conventional techniques well known to those of ordinary skill in the art.

The acid halide functional derivative of the aforescribed olefinic carboxylic acids (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, and 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. Often, 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 and 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, a 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 a 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 such 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 is utilized. Typical organic peroxides include benzoyl peroxide; *t*-butyl peroxyphthalate; 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-dihydroperoxyhexane; *t*-butyl hydroperoxide; lauroyl peroxide; *t*-amyl perbenzoate; or mixtures thereof. Preferred organic peroxides are benzoyl peroxide, *t*-butyl 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 as well as being useful as intermediates are also useful as viscosity improvers.

The intermediates of the present invention will be understood by reference to the following non-limiting examples.

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 insure 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:

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

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.

5

Example I

Maleinized Shellvis 40

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Extruder feed:	760 gm Shellvis 40 26 gm Maleic Anhydride 3 gm di- <u>tert</u> -Butyl Peroxide
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Extruder screw speed = 75 rpm

Residence time at temperature:

7 seconds at 160 °C (zone 1)

7 seconds at 240 °C (zone 2)

20 7 seconds at 240 °C (zone 3)

Approximate reaction time = 21 seconds TAN 10-15

Example II

25 Maleinized BASF Glissoviscal CE 5260

30

Extruder feed:	626 gm Glissoviscal CE 21 gm Maleic Anhydride 2 gm di- <u>tert</u> -Butyl Peroxide
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Extruder screw speed = 50 rpm

Residence time at temperature:

35 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

40 Example III

Maleinized Shellvis 50

45

Extruder feed:	626 gm Shellvis 50 21 gm Maleic Anhydride 2 gm di- <u>tert</u> -Butyl Peroxide
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50 Extruder screw speed = 50 rpm

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)

55 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. Desirably, any unreacted (B) carboxylic reagent such as maleic anhydride is removed in any conventional manner such as by stripping the same in a vacuum.

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 oils include mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of 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 about 200 Neutral mineral paraffinic and/or naphthenic oils, diphenyl-dodecanes, 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 70 percent to 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 carboxyl-base groups. The (C) initiators are also the same as set forth hereinabove with regard to the
25 solvent-free reaction and include the organic peroxides and the various organic azo compounds. The various reaction parameters, conditions, methods and the like 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 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
35 °C to 180°C with from 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 is subsequently added and the reaction conducted at a suitable temperature, as for example from 140 to 170°C. Desirably, the initiator is added in
40 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 invention will be better understood by reference to the following non-limiting examples.

45 EXAMPLE IV

A 1750g sample of a hydrogenated styrene/butadiene copolymer (BASF Glissoviscal CE5260) is changed to a 12-l flask containing 5250g Sun HPO 100N oil which has been heated to 150°C. During this
50 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 the flask and thoroughly dissolved while increasing the reaction temperature to 160°C. A dropwise addition of 14.1 g 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
55 (1.57x10⁻⁵ m³/s)) 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 NaOCH_3 , 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.

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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 hour. 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.

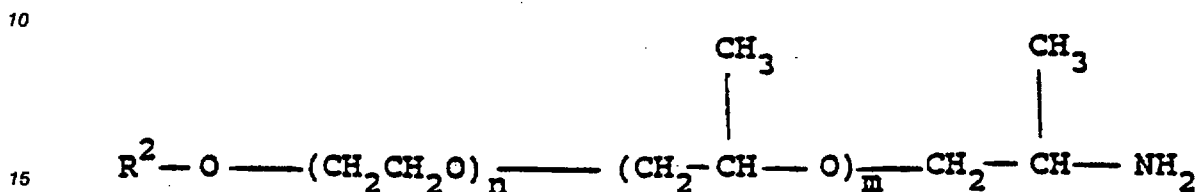
Regardless of whether a solvent-free process is utilized as carried out in an extruder or other apparatus or whether a solution process is utilized, it has been proposed that the (D) reaction product may also be further reacted with a (E) primary amine-containing compound. This reaction of (D) and (E) will be described by way of comparison. By "primary amine-containing compound" is meant ammonia or a compound which contains only one primary 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 R-NH_2 where R is hydrogen, an alkyl, a cycloalkyl, an aromatic, and combinations thereof, e.g. an alkyl substituted cycloalkyl. Furthermore, R can be an alkyl, an aromatic, a cycloalkyl group, or combination thereof containing one or more secondary or tertiary amine groups therein. R can also be an alkyl, a cycloalkyl, an aromatic group, or combinations thereof containing one or more heteroatoms (for example oxygen, nitrogen, and sulfur). R can further be an alkyl, a cycloalkyl, an aromatic, or combinations thereof containing sulfide or oxy linkages therein. Generally, R is hydrogen or said various R 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 R is as set forth immediately herein above: 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 has the formula $\text{R}^1\text{-O-CH}_2\text{CH}_2\text{CH}_2\text{-NH}_2$, such as 3-methoxypropylamine, 3-isobutoxypropylamine and 3-(alkoxypolyethoxy)-propylamines having the formula $\text{R}^1\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ wherein the alkoxy group is as immediately set forth above and where x is 1 to 50, 4,7-dioxaoctylamine, N-(3-aminopropyl)-N'-methylpiperazine, N-(2-

aminoethyl)piperazine, (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-methylpiperidine, 4-aminomethylpiperidine, N-(2-aminoethyl)morpholine, 1-ethyl-3-aminopiperidine, 1-aminopiperidine, and N-aminomorpholine.

5 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 R² is an alkyl having from 1 to 18 carbon atoms.

20 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 the reaction temperature, desired yield and the like. When a blending device such as an extruder is utilized having a relatively small amount reactants therein, the reaction time is generally quite short.

35 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.

40 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.

45 The reaction conditions of the (D) acylating reaction product with the (E) primary amine-containing compound 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 important that essentially only (E) primary amine-containing compounds be utilized, that is compounds which contain only one primary amine group therein as described hereinabove.

50 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 reaction of (D) and (E) will be illustrated by reference to the following comparative examples.

COMPARATIVE EXAMPLE VII

A 3000g sample of the 24.9% polymer solution prepared in Example IV is charged to a 12-l 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 hrs.). 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 ($7.86 \times 10^{-6} \text{ m}^3/\text{s}$)) 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 ($2.4 \times 10^{-4} \text{ m}^2/\text{s}$).

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 co-polymer. 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.

COMPARATIVE EXAMPLE VIII

In a manner similar to Example VII, 5500g of the 10% w 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 byproduct 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 4353 cSt ($4.353 \times 10^{-3} \text{ m}^2/\text{s}$). The product is clear.

An API SF/CC, SAE 10W30 oil is prepared by blending 9.5%W 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 = 6.22, TBN = 115.9, %Na = 1.56

COMPARATIVE EXAMPLE IX

7000g of the 14.9% 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 byproduct 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.

COMPARATIVE 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 160°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 Alkylate. 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. However, it is possible that polyamines, containing two or more primary amino groups can be utilized to manufacture an oil soluble effective VI improver/dispersant product. This depends upon the functionality of the polyamine and the (D) acylating reaction product.

The gel formation point is theoretically predicted by mathematical formulas as set forth in Prof. George Odian's textbook, "Principles of Polymerization. 2nd Edition," pp. 96-107, 1970, McGraw Hill Book Co., New York, N.Y.

Accordingly, assume that diethylene triamine (DETA) is used as a polyamine to react with the (D) acylating reaction product. DETA has the functionality of two because it contains two primary amino groups per molecule. If the number average functionality of the (D) acylating reaction products is two or less, the theory predicts that no gel, a crosslinked product, would be formed. If said functionality, however, is greater than two, a gel is predicted to form. The theories teach that the greater the functionality, the greater the gelation. Even if the functionality is two or less, the oil-soluble product can be undesirable because the viscosity will be increased excessively in many cases.

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.

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TOTAL ACID NUMBER (TAN) OF (D)						
Number average mol. wt. of (A)	Total Acid Number (TAN) of (D)		of (D)			
	$f_d = 1$	$f_d = 1.5$	$f_d = 2$	$f_d = 5$	$f_d = 10$	$f_d = 20$ a)
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

a) f_d = Number average functionality of (D): the average number of anhydride groups attached to each polymer molecule

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50 The compound (E), containing only one primary amine group as set forth above, will form an intermediate 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 illustrated of this fact, examples are presented showing the criticality of utilizing essentially
55 only compounds containing one primary amine group therein.

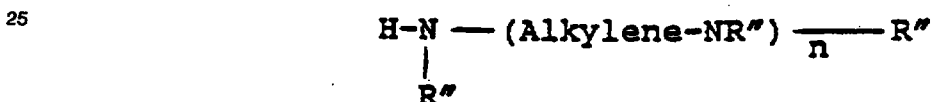
As previously indicated, the products of the present invention are suitable as VI improvers/ dispersants. Accordingly, the composition of the present invention can be effectively employed in a variety of lubricating compositions formulated for a variety of uses. These lubricating compositions are based 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 present invention relates to the utilization of a (F) polyamine in association with a (G) mono-functional acid to further extend the (D) acylating reaction product and to produce an oil soluble product. As noted above, the reaction product (D) can be made either by a solvent process, a desired route, or in a solvent-free environment. Similarly, the reaction with the polyamine and the mono-functional acid can desirably be carried out in a solvent medium or in a solvent-free environment. It is an important aspect of the present invention to utilize an effective amount of the mono-functional acid in association with the polyamines to manufacture desirable gel-free oil soluble products. The reaction with polyamines imparts dispersant properties to the compound and when such a compound is added to a hydrocarbon oil, aid in controlling the thickening of the oil. In addition to the (F) polyamine and the (G) mono-functional acid, (E) primary amine containing compounds as hereinbefore described can also be utilized.

By the term "polyamine", it is meant an amine compound having at least two amino groups therein with each said group having at least one active hydrogen thereon. Thus, the polyamine can contain two or more primary amino or one or more secondary amino groups therein.

A suitable (F) polyamine compound which can be utilized are the alkylene polyamines including polyalkylene polyamines. The alkylene polyamines include those conforming to the formula



wherein n is 1 to 10; each R'' is independently a hydrogen atom, or a hydrocarbyl group having up to 30 atoms, and the "Alkylene" group has from 1 to 10 carbon atoms but the preferred alkylene is ethylene or propylene. Especially desirable are the alkylene polyamines where each R'' is hydrogen with the ethylene polyamines and mixtures of ethylene polyamines being the most desirable. Usually n will have an average value of from 2 to 7. Such alkylene polyamines include methylene polyamine, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, hexylene polyamines, and heptylene polyamines. The high homologs of such amines and related aminoalkyl-substituted piperazines are also included.

Alkylene polyamines useful in preparing the dispersant-viscosity modifier compositions of the present invention include ethylene diamine, triethylene tetramine, propylene diamine, trimethylene diamine, hexamethylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene)triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene)triamine, N-(2-aminoethyl)piperazine, and 1,4-bis(2-aminoethyl)piperazine. Higher homologs as are obtained by condensing two or more of the above-illustrated alkylene amines are useful as (a) as are mixtures of two or more of any of the aforescribed polyamines.

Ethylene polyamines, such as those mentioned above, are especially useful for reasons of cost and effectiveness. Such polyamines are described in detail under the heading "Diamines and Higher Amines" in The Encyclopedia of Chemical Technology, Second Edition, Kirk and Othmer, Volume 7, pages 27-39, Interscience Publishers, Division of John Wiley and Sons, 1965.

Such compounds are prepared most conveniently by the reaction of an alkylene chloride with ammonia or by reaction of an ethylene imine with a ring-opening reagent such as ammonia, etc. These reactions result in the production of the somewhat complex mixtures of alkylene polyamines, including cyclic condensation products such as piperazines. Quite satisfactory products can also be obtained by the use of pure alkylene polyamines.

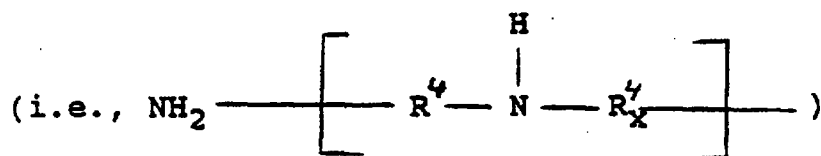
Other useful types of polyamine mixtures are those resulting from stripping of the above-described polyamine mixtures. In this instance, lower molecular weight polyamines and volatile contaminants are removed from an alkylene polyamine mixture to leave a residue what is often termed "polyamine bottoms". In general, alkylene polyamine bottoms can be characterized as having less than two, usually less than one percent (by weight) material boiling below about 200°C. In the instance of ethylene polyamine bottoms,

which are readily available and found to be quite useful, the bottoms contain less than about two percent (by weight) total diethylene triamine (DETA) or triethylene tetramine (TETA). A typical sample of such ethylene polyamine bottoms obtained from the Dow Chemical Company of Freeport, Texas designated "E-100" showed a specific gravity at 15.6°C of 1.0168, a percent nitrogen by weight of 33.15 and a viscosity at 40°C of 121 centistokes ($1.21 \times 10^{-4} \text{ m}^2/\text{s}$). Gas chromatography analysis of such a sample showed it to contain about 0.93 percent "Light Ends" (DETA), 0.72 percent TETA, 21.74 percent tetraethylene pentamine and 76.61 percent pentaethylene hexamine and higher (by weight). These alkylene polyamine bottoms include cyclic condensation products such as piperazine and higher analogs of diethylene triamine, triethylene tetramine and the like.

When reacted with the aforescribed (D) acylating reaction products, these polyamine bottoms often provide carboxylic derivative compositions which impart improved viscosity modifying properties to lubricants containing them. While not being bound to any particular theory or concept, it is believed that these improved viscosity properties are due to coupling of the (D) acylating reaction products through the polyamine bottoms which contain both longer molecules and an excess of reactive amino groups when compared to their lower molecular weight analogs such as triethylene tetramine.

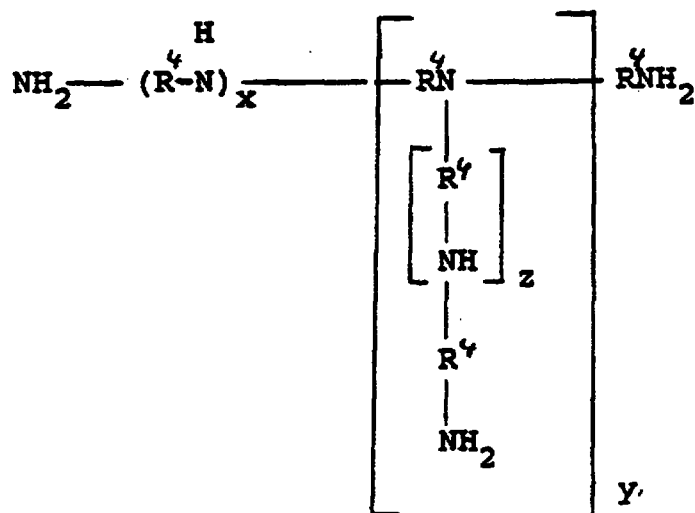
These alkylene polyamine bottoms can be reacted solely with the (D) acylating reaction products in the presence of said (G) monofunctional acid in which case the amino reactant consists essentially of alkylene polyamine bottoms, or they can be used with other amines and polyamines. In these latter cases, at least one amino reactant comprises alkylene polyamine bottoms.

Another group of (F) polyamine compounds which can be utilized for reaction with the (G) monofunctional acids and the (D) acylating reaction product are the branched polyalkylene polyamines. The branched polyalkylene polyamines are polyalkylene polyamines wherein the branched group is a side chain containing on the average at least one nitrogen-bonded aminoalkylene



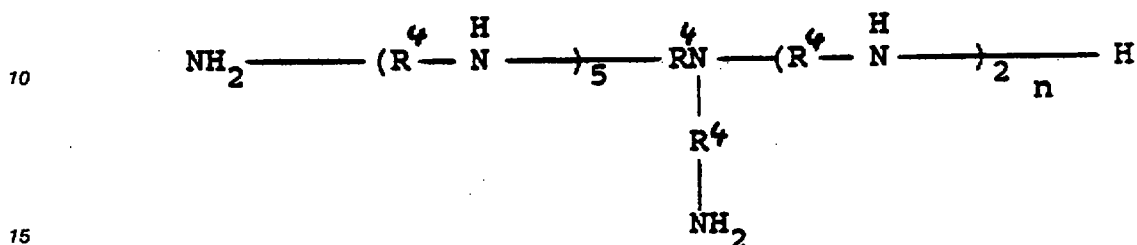
group per nine amino units present on the main chain, for examples, 1-4 of such branched chains per nine units on the main chain, but preferably one side chain unit per nine main chain units. Thus, these polyamines contain at least three primary amino groups and at least one tertiary amino group.

These reagents may be expressed by the formula:



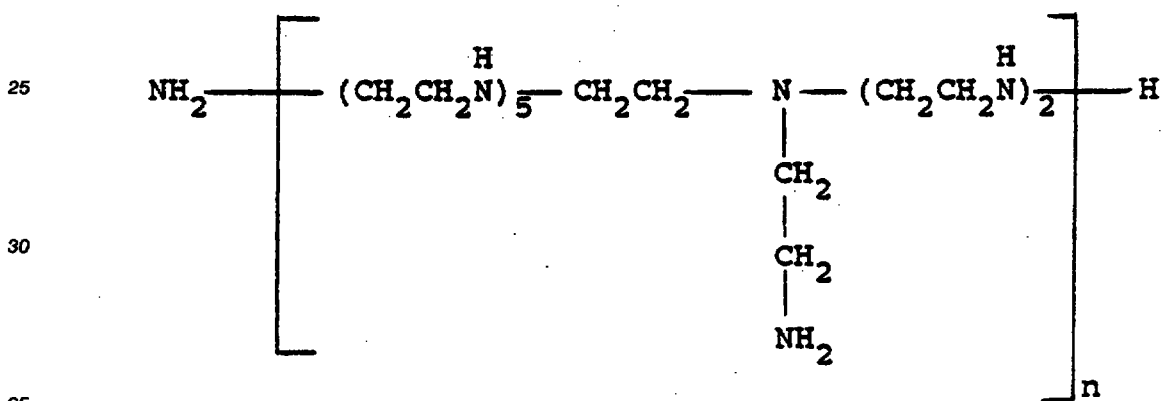
wherein R^4 is an alkylene group having from 2 to 20 carbon atoms, such as ethylene, propylene, butylene and other homologues (both straight chained and branched), etc., but preferably ethylene; and x, y and z are integers, x being for example, from 4 to 24 or more but preferably 6 to 18, y being for example 1 to 6 or more but preferably 1 to 3, and z being for example 0-6, preferably 0-1. The x and y units may be sequential, alternative, orderly or randomly distributed.

The preferred class of such polyamines includes those of the formula



wherein n is an integer, for example, 1-20 or more but preferably 1-3, wherein R^4 is preferably ethylene, but may be e.g. propylene or butylene (straight chained or branched).

The preferred embodiments are presented by the following formula:

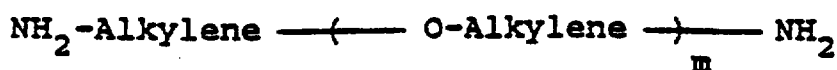


where $n = 1-3$.

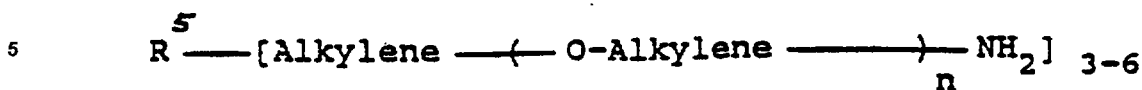
The radicals in the brackets may be joined in a head-to-head or a head-to-tail fashion. Compounds described by this formula wherein $n = 1-3$ are manufactured and sold as Polyamines N-400, N-800, N-1200 etc. Polyamine N-400 has the above formula wherein an average number of $n = 1$.

U.S. Patents 3,200,106 and 3,259,578 disclose how to make such polyamines and processes for reacting them with carboxylic acid acylating agents and analogous processes can be used with the acylating reagents of this invention. reagents of this invention.

Still another class of suitable (F) polyamine compounds include the polyoxyalkylene polyamines, e.g., polyoxyalkylene diamines and polyoxyalkylene triamines, having average molecular weights ranging from 200 to 4000, preferably from 400 to 2000. Illustrative examples of these polyoxyalkylene polyamines may be characterized by the formula:



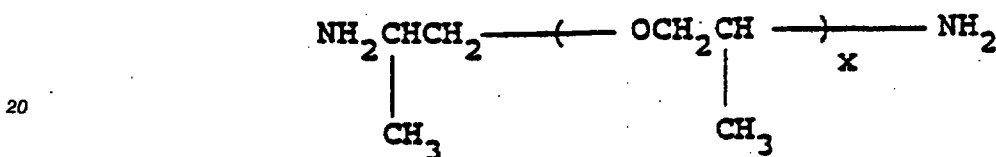
where m has a value of about 3 to 70 and preferably about 10 to 35.



where n is such that the total value is from 1 to 40 with the proviso that the sum of all of the n's is from 3 to 70 and generally from 6 to 35 and R⁵ is a polyvalent saturated hydrocarbon radical of up to 10 carbon atoms having a valence of 3 to 6. The alkylene groups may be straight or branched chains and contain from 1 to 7 carbon atoms, and usually from 1 to 4 carbon atoms. The various alkylene groups present within the two immediately preceding formulae may be the same or different.

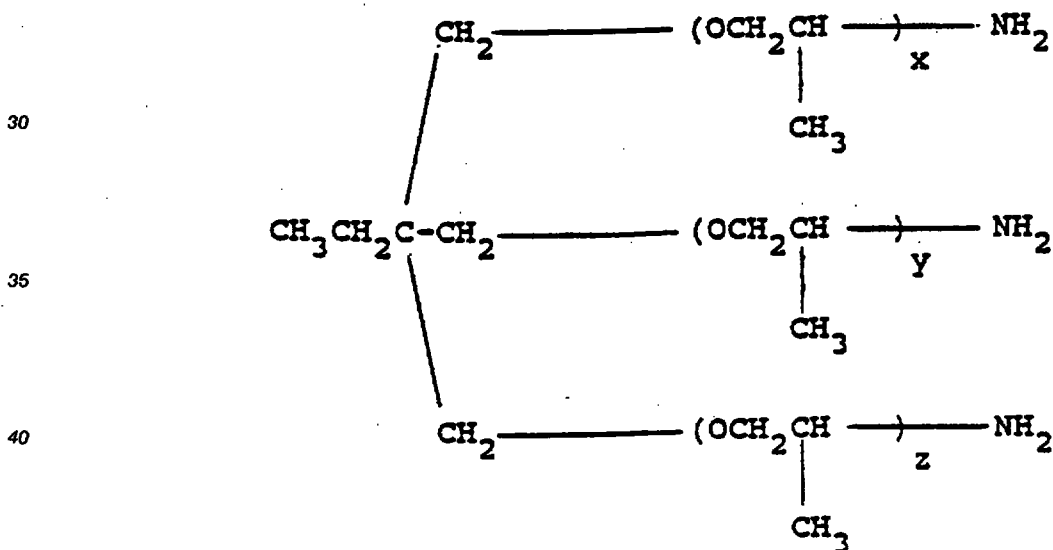
More specific examples of these polyamines include:

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wherein x has a value of from 3 to 70 and preferably from 10 to 35 and

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wherein x + y + z have a total value ranging from 3 to 30 and preferably from 5 to 10.

When used, desirable polyoxyalkylene polyamines for purposes of this invention include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having average molecular weights ranging from 200 to 2000. The polyoxyalkylene polyamines are commercially available and may be obtained, for example, from the Jefferson Chemical Company, Inc. under the trade name "JEFFAMINES D-230, D-400, D-1000, D-2000, T-403 etc." Moreover, U.S. Patent 3,804,763 and 3,948,800 disclose such polyoxyalkylene polyamines and processes for acylating them with carboxylic acid acylating agents which processes can be applied to their reaction with the acylating reagents of this invention.

Although the above noted polyamines are generally preferred, various other polyamine compounds can be utilized in the present invention. Such compounds and their preparation are set forth in U.S. Patent 4,234,435.

(G) is a hydrocarbon-based monocarboxylic acid wherein the definition of "hydrocarbon-based" is as set forth hereinbelow. Such monocarboxylic acids have from 8 to 20 carbon atoms. Desirably, the acids are

usually saturated. Examples of such specific acids include octanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid, and stearic acid.

As used herein, the terms "hydrocarbon-based", "hydrocarbon-based substituent" and the like denote a substituent having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbyl character within the context of this invention. Such substituents include the following:

- (1) hydrocarbon substituents, that is aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, aromatic-, aliphatic-, and alicyclic-substituted aromatic nuclei as well as cyclic substituents wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic radical);
- (2) substituted hydrocarbon substituents, that is, those substituents containing non-hydrocarbon radicals which, in the context of this invention, do not alter the predominantly hydrocarbyl substituent; those skilled in the art will be aware of such radical (e.g., halo(especially chloro and fluoro)), alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy.
- (3) hetero substituents, that is substituents which will, while having predominantly hydrocarbyl character within the context of this invention, contain other than carbon present in a ring or chain otherwise composed of carbon atoms. Suitable heteroatoms will be apparent to those of skill in the art and include, for example, sulfur, oxygen, nitrogen and such substituents as e.g., pyridyl, furanyl, thiophenyl, and imidazolyl, are exemplary of these hetero substituents.

The reaction of the (F) polyamine and the (G) monocarboxylic acid with the (D) acylating reaction product generally takes place by heating as from 50°C to 250°C and desirably from 140°C to 180°C. Optionally, the reaction can take place in an inert atmosphere such as nitrogen. The reaction time will naturally vary upon the reaction temperature, the desired yield and the like. Since water is generated during the reaction, it can be removed by any conventional manner.

The total amount of carbonyl groups including those in the (D) acylating reaction product and the (G) monocarboxylic acid for each primary amine group of the (F) polyamine is such that an undue viscosity increase is not produced. For comparison, generally, when succinic acid type compounds are utilized, the ratio of the total number of carbonyl groups for each primary amine group is from 0.5 to 8, desirably from 1 to 4, preferably from 1.8 to 2.2 with a highly preferred amount being about 2. When (G) is a monocarboxylic acid in accordance with the present invention the above ratios are reduced by a factor of one half; that is, the preferred ration of monocarboxylic acids for each amine group is 1.0 since each amine group can react with each monofunctional acid. Moreover, unlike succinic acid, the monocarboxylic acid can react with both primary and secondary amines. Although higher or lower amounts of acid can be utilized, they tend to be inefficient and/or costly. The amount of the (G) mono-functional carboxylic acid to the amount of carbonyl groups derived from (D) alpha-beta olefinic unsaturated carboxylic reagents on the polymer backbone is such that upon reaction with the (F) polyamine, gel-free products or products essentially gel-free, that is products not containing an excessively high viscosity are produced. That is, while some gel or viscosity increase is produced, the reaction product is substantially free from gel. A desirable ratio of (D) to (G) depends upon such factors as the number of acylating chemical functions attached to (D), the number of primary amino groups attached to (F) and the amount of (G) added to reaction mixture, as discussed hereinbelow.

When the (D) acylating reaction product reacts with the (F) polyamine in the absence of the (G) monofunctional acid, hereinafter (D), (F) and (G), respectively, the reaction proceeds forming branches and, in many cases, a three dimensional network or structure because of the multi-functional nature of the two reactants. This results in an excessive increase in the oil thickening property of the product and, in the latter case, formation of an oil insoluble gel. When (D) reacts with (F) in the presence of (G), undesirable gel formation is avoided which creates a desirable additional dispersant in the product. The gel formation can be theoretically predicted by mathematical formulas as set forth in Prof. George Odian's textbook, Principles of Polymerization, 2nd Edition, pp. 96-107, McGraw Hill Book Co., New York, N.Y.

An example of a theoretical aspect of a gelation reaction will be discussed. Assume that the number average molecular weights of (D) and (G) substrate polymers are 200,000 and 1,000, respectively; the acylating chemical function is the succinic group for both (D) and (G); (F) is a polyamine containing two primary amino groups such as diethylenetriamine (DETA), triethylenetetramine or tetraethylenepentamine; the ratio of the succinic acid group to primary amine is one to one or two carbonyls to one primary amino group; and the number of the succinic anhydride group attached to (D) is variable. The critical extent of reaction (Pc) at the gel point is calculated by

$$P_c = \frac{2}{f_{avg}}$$

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where f_{avg} is the number average functionality of a reaction mixture of (D), (G) and (F). The f_{avg} can be calculated by

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$$f_{avg} = \frac{n_d f_d + n_g f_g + n_f f_f}{n_d + n_g + n_f}$$

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where the n_d , n_g , and n_f are the numbers of molecules of (D), (G) and (F), respectively; f_d is the number average functionality of (D) which is variable; f_g is unity, the functionality of (F) a mono-functional acid; and f_f is two, the functionality of (F) a polyamine containing two primary amino groups. The Table below is the result of % P_c calculation against two variables, the weight ratio of (D) to (G), and the number average functionality, f_d , of (D) acylating product.

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Weight Ratio of (D) to (G)	CALCULATION ^{a)} OF CRITICAL EXTENT (% PC) OF REACTION AT THE GEL POINT						
	$f_d = 1$	$f_d = 2$	$f_d = 2.1$	$f_d = 5$	$f_d = 10$	$f_d = 20$	$f_d = 30$
100/0	No Gel	No Gel	98	70	65	55	53
99/1	No Gel	No Gel	No Gel	93	75	64	60
98/2	No Gel	No Gel	No Gel	No Gel	86	71	65
95/5	No Gel	No Gel	No Gel	No Gel	No Gel	88	79
90/10	No Gel	No Gel	No Gel	No Gel	No Gel	No Gel	95
80/20	No Gel	No Gel	No Gel	No Gel	No Gel	No Gel	No Gel
70/30	No Gel	No Gel	No Gel	No Gel	No Gel	No Gel	No Gel

a) Assumption: Number average molecular weight of (D) and (G) are 200,000 and 1,000, respectively. The acid function is the succinic anhydride group for both (D) and (G), and (F) is DETA. The ratio of the succinic anhydride group to primary amine is one to one, i.e., two carbonyls to one primary amino groups.

b) f_d = number average functionality of (D)

It is apparent from the Table that

- 55 (i) no gelation takes place when the functionality of (D), f_d , is two or less regardless of whether or not (G) is present.
- (ii) gelation occurs when f_d is greater than two, and the greater the f_d value is, the quicker gelation occurs.

(iii) the addition of (G) either delays the gelation or eliminates it depending upon the relative amount of (G) added to (D).

From this example, it is obvious to understand the function of (G) in this invention such as:

1. Elimination of undesirable oil-insoluble gel formation;
2. Increase in oil thickening characteristics of the product to any defined extend;
3. Allows an increased amount of (F) in the reaction. This results in an improved dispersancy in the product; and
4. Allows the use of a wide variety of more cost/performance effective amines.

Thus, various factors influence the avoidance of excessive viscosity or gel but such can be readily determined with regard to any given system, as noted above.

An alternative reaction route of the present invention, although not desired, is to initially react the (F) polyamine with the (G) monocarboxylic acid. The reaction conditions are generally the same as set forth above except that the reaction temperature can be much lower, for example ambient. That is, the reaction temperature can be from about ambient, that is from 20 °C to 250 °C and optionally can be carried out in the presence of an inert atmosphere. Generally, at lower temperatures water need not be removed but at higher temperatures it is generally removed as by stripping with a vacuum. The reaction is generally carried out in the presence of a solvent such as mineral oil, neutral oil or the like. When the prereacted amine-acid component has been formed, the amount thereof can readily be calculated based upon the above-noted overall ratio of the number of carbonyl groups for each primary amine group, or for each primary and secondary amine group.

The reaction of the (F) polyamines and the (G) monofunctional acids with the acylating reaction product (D) can take place in a solvent medium or in a solvent-free environment, as noted above. Typical solvents are known to the art and to the literature and include various oils which are lubricant base stock such as natural and/or synthetic lubricating oils such as the following: natural oils, for example mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of paraffinic, naphthenic or mixed paraffinic-naphthenic types. Alternatively, animal and vegetable oils can also be used. Synthetic lubricating oils include alkylated aromatics, poly-alpha-olefins, alkyl phosphates, and esters derived from polybasic acids, polyols and fatty acids. Specific examples of such solvents include refined 100 to about 200 neutral mineral, paraffinic and/or naphthenic oils, diphenyldodecanes, didodecylbenzenes, hydrogenated dodecene, oligomers, and mixtures of the above. The amount of oil is generally adjusted such that viscosity of the reaction mixture is suitable for mixing. Typically the amount of oil is from 50 to 99 % by weight and more desirably from 70% to 95% by weight based upon the weight of the total reaction mixture.

When the reaction is carried out in a solvent-free process, the various reactants can be added to any suitable vessel, device or apparatus in the absence of a solvent. Desirably, the various steps in the reaction sequence occur in a blending device such as an extruder, a Banbury or a 2-roll mill. Inasmuch as the reaction mixture is often very viscous, high torque blending devices are desired. The temperature of the solvent free process is similar to that set forth above with regard to the solvent process except that a higher preferred temperature, that is from 140 °C to 200 °C is desired. Preferred types of high torque blending devices include a twin screw extruder, and the like.

Regardless of whether the reaction is carried out in a solvent medium or in a solvent-free environment, care should be taken to remove any unreacted (B) alpha-beta carboxylic acid as by stripping. Otherwise, the unreacted acid will react with the polyamine.

In the above ratios, with regard to the various amounts of carbonyl compounds based upon the number of available primary amine groups from the (F) polyamines, it is to be noted that various amounts of (E) primary amine compounds can also be utilized. The amount of such (E) primary amine compounds is such that the above indicated ratios are satisfied. That is, the amount of (E) primary amine compounds can virtually be substituted for up to 99% by weight of the total amount of (F) polyamine compounds.

The final or oil soluble composition which is the reaction product of the (D) acylating reaction product, the (F) polyamine and the (G) mono-functional acid can be utilized in various types of lubricating oils derived not only from petroleum but also includes synthetic lubricating oils, as set forth herein below. The amount of said reaction product (D) + (F) + (G) in such lubricating oils is generally from 0.1% to 30% by weight and preferably from 0.5% to 6% by weight based upon a total weight of said lubricating oil composition which can contain various additives therein. Moreover, the said reaction product (D) + (F) + (G) of the present invention may be utilized in a concentrate form, as from 1% to 40% by weight and preferably from 5% to 25% by weight based upon the total weight of the concentrate including lubricating oil and various additives therein. The lubricating oil compositions or concentrates can contain additives such as antiwear agents, antioxidants, viscosity-index improvers, dispersants, pour point depressants and dyes.

COMPARATIVE EXAMPLE XI

A 3505g sample of the 24.9% polymer solution prepared in Example IV is charged to a 12-l flask equipped with a mechanical stirrer, thermometer, N₂ inlet, additional funnel, Dean-Stark trap, condenser, and heating mantle. Wibarco Heavy Alkylate (Wibarco GmbH; 3561.7 g) is charged along with 195.0 g polyisobutynyl succinic anhydride (TAN = 98), and the mixture is stirred and heated to 150°C under a N₂ blanket to obtain a homogeneous solution (approximately 2 hrs.). When this solution has been obtained, 23.6g DETA (diethylenetriamine) is added dropwise to the mixture from the addition funnel for over 1 hr. When all the amine has been charged, the reaction mixture is heated to 170°C and held 4.0 hrs. while subsurface N₂ purging ($1.0 \text{ SCFH} (7.8 \times 10^{-6} \text{ m}^3/\text{s})$) to remove byproduct water. This 12% polymer solution is the final product. Analytical assay of the final product gives an ANA nitrogen content of 0.13% Infrared analysis of the product confirms imide formation with no residual anhydride absorption. The kinematic viscosity at 100°C of this dispersant-viscosity modifier is 460.0 cSt ($4.6 \times 10^{-4} \text{ m}^2/\text{s}$).

An API SF/CC, SAE 10W30 oil was prepared by blending 9.0% of the final product from Example XI, 8.13%W of performance additive d^d, 0.2%W Acr 156, in a lubricating base stock. This oil thereby contains 1.08%W of the product copolymer. When evaluated in the Ford Sequence VD engine test, a merit rating of 9.51 sludge, 6.64 varnish and 6.88 piston skirt varnish is achieved after 192 test hours.

d) Performance Additive D: %SA = 12.9; %Zn = 1.56; P = 1.41; %Ca = 1.23; %Mg = 1.16; %N = 0.52; %S = 4.27 TBN = 85.8

COMPARATIVE EXAMPLE XII

700 g of the 14.9%W polymer solution prepared in Example VI is charged to a flask equipped in a manner as set forth in Example XI. 321.2 g Wibarco Heavy Alkylate (Wibarco GmbH) is added along with 24.8 g polyisobutenyl succinic anhydride (TAN = 98) and heated to 150°C under a N₂ blanket. Once a homogenous solution is obtained, 3.0g of DETA is added dropwise over 1 hr. After all the amine is charged, the reaction mixture is heated to 175°C and held 4.0 hrs with subsurface N₂ purge ($110 \text{ SCFH} (8.6 \times 10^{-4} \text{ m}^3/\text{s})$) to remove byproduct water. This 10%W polymer solution gives the final product. Analytical assay of the final product gives an ANA nitrogen content of 0.12% (0.12% theoretical). Infrared analysis of the product confirms imide formation with no residual anhydride absorptions. the appearance of the concentrate is clear.

The following description with regard to natural and synthetic lubricating oils in which the VI improver/dispersant of the present invention is applicable with regard to the reaction of said (D) acylating reaction product with said (F) polyamine and said (G) mono-functional acid including any reaction with the (E) primary amine containing compound. Accordingly, the following list not only serves as lubricating oils to which the compositions of the present invention can be added but also compositions which can serve as a suitable solvent. Suitable lubricating oils include natural oils, animal oils, and vegetable oils as well as mineral lubricating oils such as liquid petroleum oils, solvent-treated or acid-treated mineral lubricating oils of 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 interpolymerized olefins (e.g., oligobutylenes, oligopropylenes, and propylene-ethylene oligomers, chlorinated polybutylenes,); oligo(1-hexenes), oligo (1-octenes), oligo(1-decenes), and mixtures thereof; alkyl-benzenes (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 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., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a 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 acids, alkenylsuccinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenylmalonic acids, etc.) 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.

- 5 Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, and 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, 10 tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-hexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxy)-disiloxane, poly(methyl) siloxanes, poly(methylphenyl)siloxanes).

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 15 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 in 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, 20 acid or base extraction, filtration, and percolation. Re-refined oils are obtained by processes similar to those used to obtain refined oils applied 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.

The invention also contemplates the use of other additives in combination with the viscosity improver 25 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, antiwear 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 30 direct carbon-to-phosphorus linkage such as those prepared by the treatment of an olefin polymer (e.g., polyisobutene having a 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.

35 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 40 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-phenyl-betanaphthylamine, and dodecylamine. A particularly effective 45 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 $60\text{--}200^\circ\text{C}$.

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; 50 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 about 34 and preferably at least about 54 carbon atoms with nitrogen containing compounds such as amine, organic 55 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 about 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 or 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

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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 antiwear agents. Zinc dialkylphosphorodithioates are well known example.

Pour point depressants are a particularly useful type of additive often included in the lubricating oils described herein. The use of such pour point depressants in oil-based compositions to improve low temperature properties of 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 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.

Claims

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1. An oil soluble reaction product of:

an acylating reaction product (D); a polyamine (F); and a hydrocarbon-based monocarboxylic acid having from 8 to 20 carbon atoms (G); wherein said acylating reaction product (D) is the reaction product of:

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(A) a hydrogenated block copolymer containing no more than 0.5 percent residual olefinic unsaturation, based upon the total number of carbon-to-carbon covalent linkages, comprising a normal block copolymer, a random block copolymer, or a combination thereof, said normal block copolymer being derived from a vinyl substituted aromatic monomer and an aliphatic conjugated diene, and having from two to five polymer blocks of which at least one polymer block is derived from said vinyl substituted aromatic monomer and at least one polymer block is derived from an aliphatic conjugated diene, and said random block copolymer being derived from a vinyl substituted aromatic monomer and an aliphatic conjugated diene; 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 block copolymer (normal or random) being in the range of 10,000 to 500,000.

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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



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

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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 antiwear agents. Zinc dialkylphosphorodithioates are well known example.

Pour point depressants are a particularly useful type of additive often included in the lubricating oils described herein. The use of such pour point depressants in oil-based compositions to improve low temperature properties of 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 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.

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1. An oil soluble reaction product of:

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(A) a hydrogenated block copolymer containing no more than 0.5 percent residual olefinic unsaturation, based upon the total number of carbon-to-carbon covalent linkages, comprising a normal block copolymer, a random block copolymer, or a combination thereof, said normal block copolymer being derived from a vinyl substituted aromatic monomer and an aliphatic conjugated diene, and having from two to five polymer blocks of which at least one polymer block is derived from said vinyl substituted aromatic monomer and at least one polymer block is derived from an aliphatic conjugated diene, and said random block copolymer being derived from a vinyl substituted aromatic monomer and an aliphatic conjugated diene; 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 block copolymer (normal or random) being in the range of 10,000 to 500,000.

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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 block copolymer (A) and said unsaturated carboxylic reagent (B);

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

- 5 2. An oil soluble reaction product according to claim 1 wherein said polyamine (F) is an amine compound having at least two amino groups with each said amino group having at least one active hydrogen thereon.
3. An oil soluble reaction product according to either of claims 1 and 2, wherein said polyamine (F) is an
10 alkylene polyamine, a polyamine bottom, a branched polyalkylene polyamine, or a polyoxyalkylene polyamine.
4. An oil soluble reaction product according to any preceding claim, wherein the amount of said monocarboxylic acid (G) is an effective amount to substantially produce a substantially gel-free product.
- 15 5. An oil soluble reaction product according to any preceding claim, wherein said (A) normal block copolymer has a total of 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 by weight and the total amount of said mono-
20 vinyl substituted aromatic is from 40 percent to 60 percent by weight, wherein said unsaturated carboxylic reagent (B) is selected from maleic anhydride, citraconic anhydride, itaconic anhydride, glutaric anhydride, chloromaleic anhydride, methyl maleic anhydride, acrylic acid, methacrylic acid, fumaric acid, maleic acid, maleimide, maleamic acid, C₁₋₁₀ alkyl esters of such acids, and combinations thereof, and wherein the amount of said unsaturated carboxylic reagent (B) is from 0.5 to 5.0
25 percent by weight.
6. An oil soluble reaction product according to any preceding claim, wherein said monocarboxylic acid (G) comprises octanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid and stearic acid.
- 30 7. An oil soluble reaction product according to any preceding claim wherein said conjugated diene is isoprene or butadiene, and wherein said vinyl substituted aromatic monomer is styrene.
8. An oil soluble reaction product according to any preceding claim wherein said reaction product (D) has a total acid number of from 0.1 to 60, wherein said polyamine (F) is an alkylene polyamine of formula:



wherein n is from 1 to 10, and each R'', independently, is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, and wherein said alkylene group has from 1 to 10 carbon atoms.

- 45 9. An oil soluble reaction product according to any preceding claim, wherein said free radical initiator (C) is an organic peroxide or an organic azo initiator.
10. An oil soluble reaction product according to any preceding claim, wherein said reaction product (D) has a total acid number of from 0.5 to 20 and wherein said unsaturated carboxylic reagent (B) is selected
50 from fumaric acid, maleic acid, and maleic anhydride.
11. An oil soluble reaction product according to any of claims 8 - 10, wherein n of said alkylene polyamine is from 2 to 7, and wherein each R'' is hydrogen.
- 55 12. A lubricant composition comprising a major amount of a mineral oil and a minor amount of the reaction product of any of claims 1 - 11.



13. An additive concentrate including a diluent oil and from 1 percent to 40 percent by weight of the reaction product of any of claims 1 - 11.
14. A process for making an oil soluble reaction product according to any one of claims 1 - 11 comprising:
 5 reacting an acylating reaction product (D) as defined in claim 1 with a polyamine (F) and an effective amount of a hydrocarbon-based monocarboxylic acid having from 8 to 20 carbon atoms (G) to produce the oil soluble reaction product.
15. A process according to claim 14, wherein said polyamine (F) is an amine compound having at least two
 10 amino groups with each said amino group having at least one active hydrogen thereon.
16. A process according to claim 14, wherein said polyamine (F) is an alkylene polyamine, a polyamine bottom, a branched polyalkylene polyamine, or a polyoxyalkylene polyamine.
17. A process according to any one of claims 14 to 16, wherein said monocarboxylic acid (G) comprises
 15 octanoic acid, decanoic acid, lauric acid, myristic acid, palmitic acid and stearic acid.
18. A process according to any one of claims 14 to 17, wherein said conjugated diene is isoprene or butadiene, wherein vinyl substituted aromatic monomer is styrene, and wherein said reaction product
 20 (D) has a total acid number of from 0.1 to 60, wherein said polyamine is an alkylene polyamine of the formula:



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wherein n is from 1 to 10, and each R'', independently, is hydrogen or a hydrocarbyl group having from 1 to 30 carbon atoms, and wherein said alkylene group has from 1 to 10 carbon atoms.

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19. A process according to any one of claims 14 to 18, wherein said reaction product (D) has a total acid number of from 0.5 to 20 and wherein said unsaturated carboxylic reagent (B) is selected from fumaric acid, maleic acid, and maleic anhydride.
20. A process according to any of claims 14 to 19, wherein said reaction is carried out in a solvent.
21. A process according to any of claims 14 to 19, wherein said reaction is carried out in a solvent-free environment.
22. A process according to any of claims 14 to 21, wherein said reaction is carried out at a temperature of
 40 from 50 °C to 250 °C.
23. A process according to claim 14, wherein the acylating reaction product (D) formation temperature is from 100 °C to 300 °C, and wherein the reaction temperature of said acylating reaction product (D) with
 45 said polyamine (F) and said monocarboxylic acid (G) is from 50 °C to 250 °C.
24. A process according to claim 14 wherein said acylating reaction product (D) is made in the presence of a solvent.
25. A process according to claim 14 wherein said acylating reaction product (D) is made in a solvent-free environment.

Patentansprüche

1. Öllösliches Reaktionsprodukt aus:
 55 einem Acylierungsreaktionsprodukt (D), einem Polyamin (F) und einer Monocarbonsäure auf Kohlenwasserstoffbasis (G) mit 8 bis 20 C-Atomen, wobei das Acylierungsreaktionsprodukt das Reaktionsprodukt ist aus:



- (A) einem hydrierten Blockcopolymer, das nicht mehr als 0.5 % olefinische Doppelbindungen enthält, bezogen auf die Gesamtzahl der kovalenten Kohlenstoff-Kohlenstoff-Bindungen, umfassend ein normales Blockcopolymer und/oder ein statistisches Blockcopolymer, wobei das normale Blockcopolymer sich von einem Vinyl-substituierten aromatischen Monomer und einem aliphatischen konjugierten Dien ableitet und 2 bis 5 Polymerblöcke besitzt, wobei sich mindestens ein Polymerblock von dem Vinyl-substituierten aromatischen Monomer ableitet, und mindestens ein Blockcopolymer sich von einem aliphatischen, konjugierten Dien ableitet, und das statistische Blockcopolymer sich von einem Vinyl-substituierten aromatischen Monomer und einem aliphatischen, konjugierten Dien ableitet, wobei die Gesamtmenge der Vinyl-substituierten aromatischen Blöcke in dem Blockcopolymer im Bereich von 20 bis 70 Gew.-% und die Gesamtmenge der Dienblöcke in dem Blockcopolymer im Bereich von 30 bis 80 Gew.-% liegt und das Molekulargewicht-Zahlenmittel des normalen oder statistischen Blockcopolymers im Bereich von 10 000 bis 500 000 liegt,
- (B) 0.20 bis 20 Gew.-% einer alpha-beta-olefinisch ungesättigten Carbonsäureverbindung mit 2 bis 20 C-Atomen, ausgenommen die Carboxylgruppen, bezogen auf das Gesamtgewicht des Blockcopolymers (A) und der ungesättigten Carbonsäureverbindung (B),
- und 0.01 bis 5 Gew.-% eines freie Radikale bildenden Initiators (C), bezogen auf das Gewicht des Blockcopolymers (A) und der ungesättigten Carbonsäureverbindung (B).
2. Öllösliches Reaktionsprodukt nach Anspruch 1, wobei das Polyamin (F) eine Aminverbindung mit mindestens 2 Aminogruppen ist, wobei jede Aminogruppe mindestens ein aktives Wasserstoffatom trägt.
 3. Öllösliches Reaktionsprodukt nach Anspruch 1 oder 2, wobei das Polyamin (F) ein Alkylpolyamin, ein Polyaminsumpf, ein verzweigtes Polyalkylpolyamin oder ein Polyoxyalkylpolyamin ist.
 4. Öllösliches Reaktionsprodukt nach einem der vorstehenden Ansprüche, wobei die Menge an Monocarbonsäure (G) eine zur Herstellung eines im wesentlichen Gel-freien Produkts wirksame Menge ist.
 5. Öllösliches Reaktionsprodukt nach einem der vorstehenden Ansprüche, wobei das normale Blockcopolymer (A) insgesamt 2 oder 3 Polymerblöcke besitzt, das Molekulargewicht-Zahlenmittel des Blockcopolymers bei 30 000 bis 200 000 liegt, wobei in diesem Blockcopolymer die Gesamtmenge des konjugierten Diens 40 bis 60 Gew.-% und die Gesamtmenge der Monovinyl-substituierten aromatischen Verbindung 40 bis 60 Gew.-% ist, die ungesättigte Carbonsäureverbindung (B) ausgewählt ist aus Maleinsäureanhydrid, Citraconsäureanhydrid, Itaconsäureanhydrid, Glutaconsäureanhydrid, Chlormaleinsäureanhydrid, Methylmaleinsäureanhydrid, Acrylsäure, Methacrylsäure, Fumarsäure, Maleinsäure, Maleinimid, Maleaminsäure, C₁₋₁₀-Alkylester derartiger Säuren und deren Kombinationen, und die Menge der ungesättigten Carbonsäureverbindung (B) 0.5 bis 5.0 Gew.-% beträgt.
 6. Öllösliches Reaktionsprodukt nach einem der vorstehenden Ansprüche, wobei die Monocarbonsäure (G) Octansäure, Decansäure, Laurinsäure, Myristinsäure, Palmitinsäure und Stearinsäure umfaßt.
 7. Öllösliches Reaktionsprodukt nach einem der vorstehenden Ansprüche, wobei das konjugierte Dien Isopren oder Butadien ist und das Vinyl-substituierte aromatische Monomer Styrol ist.
 8. Öllösliches Reaktionsprodukt nach einem der vorstehenden Ansprüche, wobei das Reaktionsprodukt (D) eine Gesamtsäurezahl von 0.1 bis 60 hat und das Polyamin (F) ein Alkylpolyamin der allgemeinen Formel (I) ist,

$$\text{HR}^n\text{N}(\text{Alkyl-NR}^n)_n\text{-R}^n \quad (\text{I})$$
 in der n einen Wert von 1 bis 10 hat, jeder Rest Rⁿ unabhängig voneinander ein Wasserstoffatom oder ein Hydrocarbylrest mit 1 bis 30 C-Atomen ist und der Alkylrest 1 bis 10 C-Atome hat.
 9. Öllösliches Reaktionsprodukt nach einem der vorstehenden Ansprüche, wobei der freie Radikale bildende Initiator (C) ein organisches Peroxid oder ein organischer Azo-Initiator ist.
 10. Öllösliches Reaktionsprodukt nach einem der vorstehenden Ansprüche, wobei das Reaktionsprodukt (D) eine Gesamtsäurezahl von 0.5 bis 20 hat und die ungesättigte Carbonsäureverbindung (B)



ausgewählt ist aus Fumarsäure, Maleinsäure und Maleinsäureanhydrid.

11. Öllösliches Reaktionsprodukt nach einem der Ansprüche 8 bis 10, wobei n des Alkylenpolyamins einen Wert von 2 bis 7 hat und jeder Rest R" ein Wasserstoffatom ist.
 12. Schmiermittelzusammensetzung, umfassend als Hauptbestandteil ein Mineralöl und eine geringere Menge des Reaktionsprodukts nach einem der Ansprüche 1 bis 11.
 13. Additivkonzentrat, das ein Verdünnungsöl und 1 bis 40 Gew.-% des Reaktionsprodukts nach einem der Ansprüche 1 bis 11 einschließt.
 14. Verfahren zur Herstellung eines öllöslichen Reaktionsprodukts nach einem der Ansprüche 1 bis 11, umfassend: Umsetzung eines Acylierungsreaktionsprodukts (D) nach Anspruch 1 mit einem Polyamin (F) und einer wirksamen Menge einer Monocarbonsäure auf Kohlenwasserstoffbasis mit 8 bis 20 C-Atomen (G) zur Herstellung des öllöslichen Reaktionsprodukts.
 15. Verfahren nach Anspruch 14, wobei das Polyamin (F) eine Aminverbindung mit mindestens 2 Aminogruppen ist, wobei jede Aminogruppe mindestens ein aktives Wasserstoffatom trägt.
 16. Verfahren nach Anspruch 14, wobei das Polyamin (F) ein Alkylenpolyamin, ein Polyaminsumpf, ein verzweigtes Polyalkylenpolyamin oder ein Polyoxyalkylenpolyamin ist.
 17. Verfahren nach einem der Ansprüche 14 bis 16, wobei die Monocarbonsäure (G) Octansäure, Decansäure, Laurinsäure, Myristinsäure, Palmitinsäure und Stearinsäure umfaßt.
 18. Verfahren nach einem der Ansprüche 14 bis 17, wobei das konjugierte Dien Isopren oder Butadien ist, das Vinyl-substituierte aromatische Monomer Styrol ist, das Reaktionsprodukt (D) eine Gesamtsäurezahl von 0.1 bis 60 hat und das Polyamin ein Alkylenpolyamin der allgemeinen Formel (I) ist.
- $$\text{HR}''\text{N}-(\text{Alkylen-NR}'')_n-\text{R}'' \quad (\text{I})$$
- in der n einen Wert von 1 bis 10 hat, jeder Rest R'' unabhängig voneinander ein Wasserstoffatom oder ein Hydrocarbylrest mit 1 bis 30 C-Atomen ist und der Alkylenrest 1 bis 10 C-Atome besitzt.
19. Verfahren nach einem der Ansprüche 14 bis 18, wobei das Reaktionsprodukt (D) eine Gesamtsäurezahl von 0.5 bis 20 hat und die ungesättigte Carbonsäureverbindung (B) ausgewählt ist aus Fumarsäure, Maleinsäure und Maleinsäureanhydrid.
 20. Verfahren nach einem der Ansprüche 14 bis 19, wobei die Umsetzung in einem Lösungsmittel durchgeführt wird.
 21. Verfahren nach einem der Ansprüche 14 bis 19, wobei die Umsetzung in Abwesenheit eines Lösungsmittels durchgeführt wird.
 22. Verfahren nach einem der Ansprüche 14 bis 21, wobei die Umsetzung bei einer Temperatur von 50 °C bis 250 °C durchgeführt wird.
 23. Verfahren nach Anspruch 14, wobei die Temperatur bei der Bildung des Acylierungsreaktionsprodukts (D) 100 °C bis 300 °C und die Reaktionstemperatur des Acylierungsreaktionsprodukts (D) mit dem Polyamin (F) und der Monocarbonsäure (G) 50 °C bis 250 °C beträgt.
 24. Verfahren nach Anspruch 14, wobei das Acylierungsreaktionsprodukt (D) in Anwesenheit eines Lösungsmittels hergestellt wird.
 25. Verfahren nach Anspruch 14, wobei das Acylierungsreaktionsprodukt in Abwesenheit eines Lösungsmittels hergestellt wird.



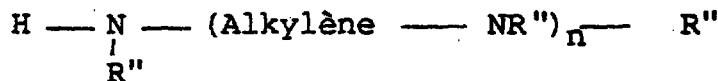
Revendications

1. Un produit de réaction soluble dans l'huile de :
 un produit de réaction acylé (D) ; une polyamine (F) ; et un acide monocarboxylique à base
 5 d'hydrocarbure présentant de 8 à 20 atomes de carbone (G) ; dans lequel ledit produit de réaction
 acylé (D) est le produit de réaction de :
 (A) un copolymère séquencé hydrogéné renfermant au maximum 0,5 pour cent d'insaturation
 oléfinique résiduelle, en se basant sur le nombre total des liaisons covalentes carbone-carbone,
 comportant un polymère séquencé normal, un copolymère séquencé statistique, ou une combinai-
 10 son de ceux-ci, ledit copolymère séquencé normal étant dérivé d'un monomère aromatique à
 substitution vinylique et d'un diène aliphatique conjugué, et ayant de 2 à 5 séquences polymères dont
 au moins une séquence polymère est dérivée dudit monomère aromatique à substitution vinylique et
 au moins une séquence polymère est dérivée d'un diène conjugué aliphatique, et ledit copolymère
 15 séquencé statistique étant dérivé d'un monomère aromatique à substitution vinylique et d'un diène
 conjugué aliphatique ; la quantité totale desdites séquences aromatiques à substitution vinylique dans
 ledit copolymère séquencé étant dans la gamme de 20 à 70 pour cents en poids que la quantité
 totale desdites séquences diènes dans ledit copolymère séquencé se situe dans la gamme de 30
 pour cents à 80 pour cents en poids ; le poids moléculaire moyen en nombre dudit copolymère
 20 séquencé (normal ou statistique) se situant dans la gamme de 10 000 à 500 000 ;
 0,20 pour cent à 20 pour cents en poids de (B) un réactif carboxylique à insaturation oléfinique
 alpha-bêta, 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) ;
 et de 0,01 à 5 pour cents en poids d'un initiateur de radicaux libres (C), en se basant sur le
 25 poids dudit copolymère séquencé (A) et dudit réactif carboxylique insaturé (B).
2. Un produit de réaction soluble dans l'huile selon la revendication 1, dans lequel ledit polyamine (F) est
 un composé aminé ayant au moins deux groupes amino, chacun desdits groupes amino possédant au
 moins un hydrogène actif.
- 30 3. Un produit de réaction soluble dans l'huile selon l'une quelconque des revendications 1 et 2, dans
 lequel ladite polyamine (F) est une alcylène polyamine, une polyamine de fond, une polyalcylène
 polyamine ramifié ou une polyoxyalkylène polyamine.
4. Un produit de réaction soluble dans l'huile selon l'une quelconque des revendications précédentes
 35 dans lequel la quantité dudit acide monocarboxylique (G) est une quantité efficace pour préparer, en
 pratique, un produit essentiellement dépourvu de gel.
5. Un produit de réaction soluble dans l'huile selon l'une quelconque des revendications précédentes,
 dans lequel ledit copolymère séquencé normal (A) présente un total de deux ou de trois séquences
 40 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 pour cents en poids et la quantité totale du composé aromatique à substitution mono-vinylique est
 de 40 à 60 pour cents en poids, ledit réactif carboxylique insaturé (B) étant choisi parmi l'anhydride
 45 maléique, l'anhydride citraconique, l'anhydride itaconique, l'anhydride glutaconique, l'anhydride chloro-
 maléique, l'anhydride méthyl-maléique, l'acide acrylique, l'acide méthacrylique, l'acide fumarique,
 l'acide maléique, le maléimide, l'acide maléique, les esters alkylés en C₁ à C₁₀ de ces acides, ainsi
 que des combinaisons de ceux-ci, tandis que la quantité du réactif carboxylique insaturé (B) est de 0,5
 à 5,0 pour cents en poids.
- 50 6. Un produit de réaction soluble dans l'huile selon l'une quelconque des revendications précédentes,
 dans lequel ledit acide monocarboxylique (G) comporte de l'acide octanoïque, de l'acide décanoïque,
 de l'acide laurique, de l'acide myristique, de l'acide palmitique et de l'acide stéarique.
7. Un produit de réaction soluble dans l'huile selon l'une quelconque des revendications précédentes,
 55 dans lequel ledit diène conjugué est l'isoprène ou le butadiène, et dans lequel ledit monomère
 aromatique à substitution vinylique est le styrène.



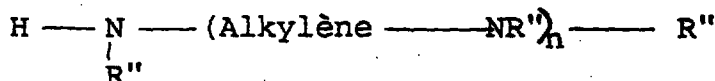
8. Un produit de réaction soluble dans l'huile selon l'une quelconque des revendications précédentes, dans lequel ledit produit de réaction (D) présente un indice d'acide total de 0,1 à 60, dans lequel ladite polyamine (F) est une alkylène polyamine de formule :

5



- 10 dans laquelle n est de 1 à 10, et chaque R'', représente, indépendamment, de l'hydrogène ou un groupe hydrocarbyle ayant de 1 à 30 atomes de carbone, et dans lequel ledit groupe alcyène possède de 1 à 10 atomes de carbone.
- 15 9. Un produit de réaction soluble dans l'huile selon l'une quelconque des revendications précédentes, dans lequel ledit initiateur de radicaux libres (C) est un peroxyde organique ou un initiateur azo-organique.
- 20 10. Un produit de réaction soluble dans l'huile selon l'une quelconque des revendications précédentes, dans lequel ledit produit de réaction (D) possède un indice d'acide total de 0,5 à 20 et dans lequel ledit réactif carboxylique insaturé (B) est choisi parmi l'acide fumarique, l'acide maléique et l'anhydride maléique.
- 25 11. Un produit de réaction soluble dans l'huile selon l'une quelconque des revendications 8 à 10, dans lequel n dans ladite alkylène polyamine est de 2 à 7, et dans lequel chaque R'' est de l'hydrogène.
- 30 12. Une composition lubrifiante comportant une quantité prépondérante d'une huile minérale et une quantité plus faible du produit de réaction de l'une quelconque des revendications 1 à 11.
- 35 13. Un concentré d'addition comportant une huile diluante et de 1 à 40%, en poids du produit de réaction de l'une des revendications 1 à 11.
- 40 14. Un procédé pour réaliser un produit de réaction soluble dans l'huile selon l'une quelconque des revendications 1 à 11, comportant : la réaction d'un produit de réaction alkylé (D) tel que défini dans la revendication 1 avec une polyamine (F) et une quantité efficace d'un acide monocarboxylique à base d'hydrocarbure, ayant de 8 à 20 atomes de carbone (G) afin d'obtenir le produit de réaction soluble dans l'huile.
- 45 15. Un procédé selon la revendication 14, dans lequel ladite polyamine (F) est un composé aminé ayant au moins deux groupes amino, chacun desdits groupes amino ayant au moins un hydrogène actif.
- 50 16. Un procédé selon la revendication 14, dans lequel ladite polyamine (F) est une alkylène polyamine, une polyamine de fond, une polyalkylène polyamine ramifiée ou bien une polyalkylène polyamine.
17. Un procédé selon l'une quelconque des revendications 14 à 16, dans lequel ledit acide monocarboxylique (G) comporte de l'acide octanoïque, de l'acide décanoïque, de l'acide laurique, de l'acide myristique, de l'acide palmitique et de l'acide stéarique.
18. Un procédé selon l'une quelconque des revendications 14 à 17, dans lequel le diène conjugué est l'isoprène ou le butadiène, dans lequel le monomère aromatique substitué est le styrène et dans lequel ledit produit de réaction (D) possède un indice d'acide total de 0,1 à 60, dans lequel ladite polyamine est une alkylène polyamine de la formule :

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dans laquelle n est de 1 à 10, et chaque R'', est, indépendamment de l'hydrogène ou un groupe



hydrocarbyle ayant de 1 à 30 atomes de carbone, et dans lequel ledit groupe alkylène présente de 1 à 10 atomes de carbone.

- 5 19. Un procédé selon l'une quelconque des revendications 14 à 18, dans lequel ledit produit de réaction (D) a un indice d'acide total de 0,5 à 20 et dans lequel ledit réactif carboxylique insaturé (B) est choisi parmi l'acide fumarique, l'acide maléique, l'anhydride maléique.
- 10 20. Un procédé selon l'une quelconque des revendications 14 à 19, dans lequel ladite réaction est mise en oeuvre dans un solvant.
- 15 21. Un procédé selon l'une quelconque des revendications 14 à 19, dans lequel la réaction est mise en oeuvre dans un environnement dépourvu de solvant.
- 20 22. Un procédé selon l'une quelconque des revendications 14 à 21, dans lequel ladite réaction est mise en oeuvre à une température de 50 °C à 250 °C.
- 25 23. Un procédé selon la revendication 14, dans lequel le produit de réaction alcylé (D) est réalisé à une température de 100 à 300 °C, et dans lequel la température de réaction dudit produit de réaction alcylé (D) avec ladite polyamine (F) et ledit acide monocarboxylique (G) est de 50 à 250 °C.
24. Un procédé selon la revendication 14, dans lequel ledit produit de réaction alcylé (D) est réalisé en présence d'un solvant,
- 25 25. Un procédé selon la revendication 14, dans lequel ledit produit de réaction alcylé (D) est réalisé dans un environnement dépourvu de solvant.

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