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<p>(54) Title: GEL-FREE ETHYLENE INTERPOLYMER DISPERSANT ADDITIVES USEFUL IN OLEAGINOUS COMPOSITIONS</p>		
<p>(57) Abstract</p>		
<p>Gel-free dispersant additives for lubricating and fuel oil compositions comprise at least one adduct of (A) α-olefin homopolymer or interpolymer of 700 to 10,000 M_n, free radically grafted with an average of from about 0.5 to about 5 carboxylic acid producing moieties per polymer chain, and (B) at least one non-aromatic nucleophilic post-treating reactant selected from (i) amine compounds containing only a single reactive amino group per molecule, (ii) alcohol compounds containing only a single hydroxy group per molecule, (iii) polyamine compounds containing at least two reactive amino groups per molecule, (iv) polyol compounds containing at least two reactive hydroxy groups per molecule, (v) aminoalcohol compounds containing at least one reactive amino group and at least one reactive hydroxy group per molecule, and (vi) mixtures of (i) to (v); provided that when said post-treating reactant includes one or more of (iii), (iv) or (v), the reaction between (A) and (B) is conducted in the presence of sufficient chain-stopping or end-capping co-reactant (C) to ensure that the grafted and post-reacted product mixture is gel-free.</p>		

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GEL-FREE ETHYLENE INTERPOLYMER DISPERSANT
ADDITIVES USEFUL IN OLEAGINOUS COMPOSITIONS

5 This invention relates to improved oil soluble polymeric dispersant
additives useful in oleaginous compositions, particularly oleaginous lubricating oil
compositions. The additives, which are gel-free and substantially free from haze and
cross-linking, comprise unsaturated homopolymers or interpolymers functionalized at
unsaturated sites on the polymer chains and free-radically grafted with acid-
10 producing moieties, which may then be reacted with a nucleophilic post-treating
reactant, where appropriate with a chain-stopping or end-capping co-reactant to
ensure that the grafted and post-reacted product mixture is gel-free.

 Ashless ester and nitrogen containing lubricating oil dispersants have
been widely used by the industry. Typically, these dispersants are prepared from a
15 long chain hydrocarbon polymer by reacting the polymer with maleic anhydride to
form the corresponding polymer which is substituted with succinic anhydride groups.
Polyisobutylene has been widely used as the polymer of choice, chiefly because it is
readily available by cationic polymerization from butene streams (e.g., using $AlCl_3$
catalysts). Such polyisobutylenes generally contain residual unsaturation in amounts
20 of about one ethylenic double bond per polymer chain, positioned along the chain.

 The polyisobutylene polymers (PIB) employed in most conventional
dispersants are based on a hydrocarbon chain of a \bar{M}_n of from about 900 to 2500.
PIB having a M_n of less than about 300 gives rather poor performance results when
employed in dispersants because the molecular weight is insufficient to keep the
25 dispersant molecule fully solubilized in lubricating oils. On the other hand, high
molecular weight PIB ($M_n > 3000$) becomes so viscous that conventional industrial
practices are incapable of handling this product in many operations. This problem
becomes much more severe as the PIB molecular weight increases to 5,000 to
10,000.

30 Increased amounts of terminal ethylenic unsaturation in polyisobutylene
(so-called "reactive polyisobutylene") has been achieved by BF_3 catalyzed
polymerization of isobutylene. However, such reactive polyisobutylene materials can
still contain substantial amounts of unsaturation elsewhere along the chain. Further,
it is difficult to produce such reactive polyisobutylene polymers at molecular weights
35 of greater than about 2,000, and, even so, the reactive polyisobutylenes themselves
still suffer the above-noted viscosity increase disadvantages as molecular weights
are increased.

Other polymers, such as ethylene-alpha-olefin interpolymers, (e.g., ethylene-propylene copolymers and terpolymers containing non-conjugated dienes), have been disclosed as suitable polymers for the preparation of ashless dispersants. However, ethylene-alpha-olefin interpolymers of the above molecular weights could
5 be produced using Ziegler-Natta catalysts only in combination with H₂ as molecular weight control in order to terminate the growing copolymer chains within this molecular weight range. Without use of H₂ or other conventional, so-called "chain-stoppers", the interpolymers produced with Ziegler-Natta catalysts would tend to have molecular weights greatly in excess of the above range. (Such higher copolymers, for
10 example, are widely employed in ungrafted form as viscosity index improvers, and when grafted with nitrogen-containing groups, as described below, are conventionally employed as dispersant-viscosity index improver polymers.) The use of H₂ as a chain stopper has the disadvantage of causing the saturation of the olefinic double bond content of the copolymer. Thus, while lower molecular weight copolymers were
15 theoretically possible to prepare, their low unsaturation content (and the accompanying low graft copolymer yields) would have made their further functionalization by a thermal "ene" reaction, e.g., with dicarboxylic acid moieties in preparing dispersants, highly unattractive.

High molecular weight ethylene-propylene copolymer and ethylene-propylene-diene terpolymers, having viscosity average molecular weights of from
20 20,000 to 300,000, are generally produced employing Ziegler catalysts, generally VCl₄ or VOCl₃ with a halide source, such as organoaluminum halides and/or hydrogen halides. Such high molecular weight EP and EPDM polymers find use as viscosity index improvers.

25 EP-A-171167 discloses a process for grafting oil soluble hydrocarbon polymers or copolymers of M_n from 5,000 to 500,000 with an ethylenically unsaturated C₃-C₁₀ carboxylic acid having 1 to 2 carboxylic acid groups or an anhydride group in the presence of a free radical initiator and a chain stopping agent.

30 US-A- 4557847 teaches polymeric viscosity index improver-dispersant additives for lubricating oils produced by reacting an ethylene-alpha-olefin copolymer grafted with an ethylenically unsaturated carboxylic material having 1 or 2 carboxylic acid groups or anhydride groups, preferably maleic anhydride, with an alkylene or oxyalkylene amine having at least two primary amine groups and a branched chain acid. The ethylene-alpha-olefin copolymer has a M_n of from 5,000 to 500,000.

35 The present invention provides an oil-soluble functionalized and grafted alpha-olefin polymer composition prepared by grafting onto a functionalized polymer mono- or dicarboxylic acid-producing moieties having 1 to 2 carboxylic acid producing groups per moiety such that the functionalized and grafted polymer contains an

average of 0.5 to 5 grafted acid-producing moieties per polymer chain, wherein at least 75% of the functionalized polymer chains of the functionalized starting polymer are monofunctional prior to being free radically grafted, and wherein said functionalized polymer is prepared by functionalizing an unsaturated α -olefin starting polymer having a number average molecular weight of 700 to 10,000 and a polydispersity of 1 to 5.

The functionalized and grafted polymers may be further reacted with at least one nucleophilic post-treating reactant selected from (i) amines containing only a single reactive amino group per molecule, (ii) alcohols containing only a single hydroxy group per molecule, (iii) polyamines containing at least two reactive amino groups per molecule, (iv) polyols containing at least two reactive hydroxy groups per molecule, (v) aminoalcohols containing at least one reactive amino group and at least one reactive hydroxy group per molecule, and (vi) mixtures of (i) to (v); provided that when said post-treating reactant includes one or more of (iii), (iv) or (v), the reaction between the functionalized and grafted polymer and the post-treating reactant is conducted in the presence of sufficient chain-stopping or end-capping co-reactant to ensure that the functionalized, grafted and post-reacted product mixture is gel-free.

In one preferred aspect of the invention, the unsaturated α -olefin polymer comprises interpolymers of ethylene with at least one C_3 - C_{28} α -olefin having a \bar{M}_n of from 700 to 10,000, preferably from 800 to 5,500, e.g., 1,000 to 3,000. In another preferred aspect of the invention, the unsaturated α -olefin polymers are characterized in that at least about 30 percent of the polymer chains, preferably at least 60 percent, and even more preferably at least 75 % (e.g., 75-98 %) possess terminal ethenylidene, i.e., vinylidene, unsaturation.

In still other preferred aspects, the unsaturated α -olefin polymer is functionalized, either before or after or while simultaneously being free-radically grafted, under thermal "ene" reaction conditions, under neo-acid or ester producing reaction conditions, or under still other reaction conditions effective to functionalize the polymer chains selectively at olefinically unsaturated sites. The present invention, for the first time, makes it possible to ensure a higher conversion of the starting polymer material to active dispersant without simultaneously increasing the risk of gelation and other adverse effects, such as viscosity growth, which often accompany the addition of sufficient free radically grafted acid moieties to raise the level of active dispersant in the product mixture to a commercially acceptable level.

The dispersant materials of the invention are different from the prior art because they contain a relatively higher level of active ingredient with a reduced level of cross-linking than would be expected from free radically grafted, post-reacted alpha-olefin dispersant additives. The dispersant additives of the present invention

also differ from those of the prior art in that the present dispersant additives optimize the distribution of carboxylic acid producing moieties on the alpha-olefin polymer backbone so as to minimize the amount of unreacted polymer, so as to minimize any tendency toward gelation and cross-linking, and so as to maximize the dispersant properties of the product mixture relative to the cost of its production. In fuels, the additives serve to minimize the degree of carburetor and fuel injector fouling from deposits. In addition, the additives of this invention possess superior viscometric properties.

The process of this invention permits the preparation of lubricating oil and fuel dispersant additives which are simultaneously characterized by a high active ingredient content (usually at least 60 wt. %, and up to 95 wt. %) and by advantageous viscosity properties which permit the additives to be readily handled. In addition, the process of the present invention can produce such dispersant additives in a highly concentrated form as substantially halogen free materials, thereby reducing the corrosivity, processing difficulties and environmental concerns which are associated with halogen-containing lubricating oil additives.

Alpha-Olefin Polymer

The polymers employed in this invention are homopolymers or interpolymers of at least one C₃ to C₂₈ alpha-olefin having the formula H₂C=CHR¹ wherein R¹ is straight or branched chain alkyl radical comprising 1 to 26 carbon atoms and wherein the polymer contains carbon-to-carbon unsaturation, preferably a high degree of terminal ethenylidene unsaturation. Preferably, the polymers employed in this invention comprise interpolymers of ethylene and at least one alpha-olefin of the above formula, wherein R¹ is alkyl of from 1 to 18 carbon atoms, and more preferably is alkyl of from 1 to 8 carbon atoms, and still 1 to 2 carbon atoms. Therefore, useful alpha-olefin monomers and comonomers include, for example, propylene, butene-1, hexene-1, octene-1, 4-methylpentene-1, decene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1, heptadecene-1, octadecene-1, nonadecene-1, and mixtures thereof (e.g., mixtures of propylene and butene-1, and the like). Exemplary of such polymers are propylene homopolymers, butene-1 homopolymers, ethylene-propylene copolymers, ethylene-butene-1 copolymers and the like, wherein the polymer contains at least some terminal and/or internal unsaturation. Preferred polymers are unsaturated copolymers of ethylene and propylene and ethylene and butene-1. The interpolymers of this invention may contain a minor amount, e.g. 0.5 to 5 mole percent of a C₄ to C₁₈ non-conjugated diolefin comonomer. However, it is preferred that the polymers of this invention comprise only alpha-olefin homopolymers, interpolymers of alpha-olefin comonomers

and interpolymers of ethylene and alpha-olefin comonomers. The molar ethylene content of the polymers employed in this invention is preferably in the range of 20 to 80 percent, and more preferably 30 to 70 percent. When propylene and/or butene-1 are employed as comonomer(s) with ethylene, the ethylene content of such copolymers is most preferably between 45 and 65 percent, although higher or lower ethylene contents may be present.

The polymers employed in this invention generally possess a Mn of 700 to 10,000 (e.g., 1,000 to 8,000), preferably 800 to 5,500; more preferably 1,000 to 3,000 (e.g., 1,500 to 2,500). Polymers having a Mn weight of 700 to 5,000 (e.g., 1,000 to 3,000) are particularly useful in the present invention. The Mn for such polymers can be determined by several known techniques such as size exclusion chromatography (also known as gel permeation chromatography (GPC)) which also provides molecular weight distribution information.

Suitable polymers will typically have a narrow molecular weight distribution (MWD) also referred to as polydispersity, as determined by the ratio of weight average molecular weight (Mw) to (Mn). Polymers having a Mw/Mn of less than 5, preferably less than 4, are most desirable. Suitable polymers have a polydispersity of, for example, 1 to 5. Consequently, such polymers generally possess an intrinsic viscosity (as measured in tetralin at 135°C) of 0.025 to 0.9 dl/g, preferably 0.05 to 0.5 dl/g, most preferably 0.075 to 0.4 dl/g. The polymers employed in this invention preferably exhibit a degree of crystallinity such that, when grafted, they are essentially amorphous.

The polymers employed in this invention, which preferably are further characterized in that up to 95 % and more of the polymer chains possess terminal ethenylidene-type unsaturation, may be prepared by polymerizing alpha-olefin monomer, or mixtures of alpha-olefin monomers, or mixtures comprising ethylene and at least one C₃ to C₂₈ alpha-olefin monomer, in the presence of a catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and an alumoxane compound. Interpolymers of this latter type, which are preferred interpolymers for use in the invention, may be characterized by the formula POLY-C(R¹)=CH₂ wherein R¹ is C₁ to C₂₆ alkyl, preferably C₁ to C₁₈ alkyl, more preferably C₁ to C₈ alkyl, and most preferably C₁ to C₂ alkyl, (e.g., methyl or ethyl) and wherein POLY represents the polymer chain. The chain length of the R¹ alkyl group will vary depending on the comonomer(s) selected for use in the polymerization. A minor amount of the polymer chains can contain terminal ethenyl, i.e., vinyl, unsaturation, i.e. POLY-CH=CH₂, and a portion of the polymers can contain internal monounsaturations, e.g. POLY-CH=CH(R¹), wherein R¹ is as defined above.

In the preferred polymers contemplated for use in this invention, at least about 30 percent of the polymer chains possess terminal ethenylidene unsaturation. Preferably at least 50 percent, more preferably at least 60 percent, and most preferably at least 75 percent (e.g. 75-98 %), of such polymer chains exhibit terminal ethenylidene unsaturation. The percentage of polymer chains exhibiting terminal ethenylidene unsaturation may be determined by FTIR spectroscopic analysis, titration, or C¹³NMR.

The preferred terminally unsaturated interpolymer to be used in this invention may be prepared by known metallocene chemistry. Preferred polymers to be used in this invention also may be prepared as described in USSN's 992871; 992690; and 992192, all filed December 17, 1992.

The preferred interpolymers can be prepared by polymerizing monomer mixtures comprising ethylene in combination with other monomers such as alpha-olefins having from 3 to 28 carbon atoms (and preferably from 3 to 4 carbon atoms, i.e., propylene, butene-1, and mixtures thereof) in the presence of a catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and an alumoxane compound. The comonomer content can be controlled through the selection of the metallocene catalyst component and by controlling the partial pressure of the various monomers. Most preferably, the polymers used in this invention are substantially free of ethylene homopolymer. The catalysts employed in the production of the preferred polymers are organometallic coordination compounds which are cyclopentadienyl derivatives of a Group 4b metal of the Periodic Table of the Elements (56th Edition of Handbook of Chemistry and Physics, CRC Press [1975]) and include mono, di and tricyclopentadienyls and their derivatives of the transition metals. Particularly desirable are the metallocene of a Group 4b metal such as titanium, zirconium, and hafnium. The alumoxanes employed in forming the reaction product with the metallocenes are themselves the reaction products of an aluminum trialkyl with water.

In general, at least one metallocene compound is employed in the formation of the catalyst. The metal is most preferably hafnium and zirconium. The cyclopentadienyl ring can be unsubstituted or contain one or more substituents (e.g., 1 to 5 substituents) such as, for example, a hydrocarbyl substituent (e.g., up to 5 C₁ to C₅ hydrocarbyl substituents) or other substituents, e.g. such as, for example, a trialkyl silyl substituent. The metallocene can contain one, two, or three cyclopentadienyl rings; however, two rings are preferred.

Useful metallocenes can be represented by the general formulas:



wherein Cp is a cyclopentadienyl ring, M is a Group 4b transition metal, R is a hydrocarbyl group or hydrocarboxy group having from 1 to 20 carbon atoms, X is a halogen, and m is a whole number from 1 to 3, n is a whole number from 0 to 3, and q is a whole number from 0 to 3;

II. $(C_5R'_k)_gR''_s(C_5R'_k)MQ_{3-g}$; and

III. $R''_s(C_5R'_k)_2MQ'$

wherein $(C_5R'_k)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' is the same or different and is hydrogen or a hydrocarbyl radical such as alkyl, alkenyl, aryl, alkylaryl, or arylalkyl radical containing from 1 to 20 carbon atoms, a silicon containing hydrocarbyl radical, or hydrocarbyl radicals wherein two carbon atoms are joined together to form a C₄-C₆ ring, R'' is a C₁-C₄ alkylene radical, a dialkyl germanium or silicon, or an alkyl phosphine or amine radical bridging two $(C_5R'_k)$ rings, Q is a hydrocarbyl radical such as aryl, alkyl, alkenyl, alkylaryl, or aryl alkyl radical having from 1-20 carbon atoms, hydrocarboxy radical having from 1-20 carbon atoms or halogen and can be the same or different from each other, Q' is an alkylidene radical having from 1 to about 20 carbon atoms, s is 0 or 1, g is 0, 1 or 2, s is 0 when g is 0, k is 4 when s is 1, and k is 5 when s is 0, and M is as defined above. Exemplary hydrocarbyl radicals are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, phenyl and the like. Exemplary silicon containing hydrocarbyl radicals are trimethylsilyl, triethylsilyl and triphenylsilyl. Exemplary halogen atoms include chlorine, bromine, fluorine and iodine and of these halogen atoms, chlorine is preferred. Exemplary hydrocarboxy radicals are methoxy ethoxy, butoxy, amyloxy and the like. Exemplary of the alkylidene radicals is methylidene, ethylidene and propylidene.

Illustrative examples of the metallocenes represented by formula I are dialkyl metallocenes such as bis(cyclopentadienyl)titanium di-methyl, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)zirconium di-neopentyl, etc. Illustrative examples of II and III metallocenes which can be usefully employed are monocyclopentadienyl titanocenes such as, pentamethyl-cyclopentadienyl titanium trichloride, substituted bis(Cp)Ti(IV) compounds such as bis(indenyl) titanium diphenyl etc. Illustrative examples of the zirconocenes of Formula II and III which can be usefully employed are, pentamethylcyclopentadienyl zirconium tri-chloride, etc. Mixed cyclopentadienyl metallocene compounds such as cyclopentadienyl (pentamethyl cyclopentadienyl)-zirconium dichloride, can be employed. Bis(cyclopentadienyl)hafnium dichloride, is illustrative of other metallocenes. Some

preferred metallocenes are bis(cyclopentadienyl)zirconium dimethyl; and the racemic and/or meso isomer of 1, 2-ethylene-bridged bis-(4, 5, 6, 7 -tetra-hydroindenyl) zirconium dichloride.

The alumoxane compounds useful in the polymerization process may be cyclic or linear. Cyclic alumoxanes may be represented by the general formula $(R-Al-O)_n$ while linear alumoxanes may be represented by the general formula $R(R-Al-O)_n'AlR_2$. In the general formula R is a C₁-C₅ alkyl group such as, for example, methyl, ethyl, propyl, butyl and pentyl, n is an integer of from 3 to 20, and n' is an integer from 1 to 20. Preferably, R is methyl and n and n' are 4-18. Generally, in the preparation of alumoxanes from, for example, aluminum trimethyl and water, a mixture of the linear and cyclic compounds is obtained. Preferably, they are prepared by contacting water with a solution of aluminum trialkyl, such as aluminum trimethyl in a suitable organic solvent such as toluene or an aliphatic hydrocarbon. The mole ratio of aluminum in the alumoxane to total metal in the metallocenes which can be usefully employed can be in the range of 0,5:1 to 1000:1, and desirably 1:1 to 100:1. Preferably, the mole ratio will be in the range of 50:1 to about 5:1 and most preferably 20:1 to 5:1. The solvents used in the preparation of the catalyst system are inert hydrocarbons, in particular a hydrocarbon that is inert with respect to the catalyst system. Such solvents include isobutane, butane, pentane, etc.

Polymerization is generally conducted at temperatures ranging between 20° and 300°C, preferably between 30° and 200°C. Reaction time is not critical and may vary from several hours or more to several minutes or less, depending upon factors such as reaction temperature, the monomers to be copolymerized, and the like. The skilled artisan may readily obtain the optimum reaction time for a given set of reaction parameters by routine experimentation. The catalyst systems described herein are suitable for the polymerization of olefins in solution over a wide range of pressures. Preferably, the polymerization will be completed at a pressure of 10 to 3,000 bar, and generally at a pressure within the range of 40 bar to 2,000 bar, and most preferably, the polymerization will be completed at a pressure within the range from 50 bar to 1,500 bar. After polymerization and, optionally, deactivation of the catalyst (e.g., by conventional techniques such as contacting the polymerization reaction medium with water or an alcohol, such as methanol, propanol, isopropanol, etc., or cooling or flashing the medium to terminate the polymerization reaction), the product polymer can be recovered by known processes. Excess reactants may be flashed off. The polymerization may be conducted employing liquid monomer, such as liquid propylene or mixtures of liquid monomers (such as mixtures of liquid propylene and 1-butene as the reaction medium. Alternatively, polymerization may be accomplished in the presence of a hydrocarbon inert to the polymerization such as

butane, pentane, isopentane, hexane, isooctane, decane, toluene, xylene, and the like. In those situations wherein the molecular weight of the polymer product that would be produced at a given set of operating conditions is higher than desired, any of the techniques known in the art for control of molecular weight, such as the use of hydrogen and/or polymerization temperature control, may be used in the process of this invention. If so desired, the polymerization may be carried out in the presence of hydrogen to lower the polymer molecular weight. Care should be taken, however, to assure that terminal ethenylidene unsaturation is not reduced below the preferred level of at least 30 percent of the polymer chains.

However, since the preferred polymers are reactive polymers possessing ethenylidene-type terminal unsaturation, it is preferred to prepare the polymers in the substantial absence of added H₂ gas, that is, the absence of H₂ gas added in amounts effective to substantially reduce the polymer molecular weight. More preferably, the polymerizations will be conducted employing less than 5 wppm, and more preferably less than 1 wppm, of added H₂ gas, based on the moles of the ethylene monomer charged to the polymerization zone.

When carrying out the polymerization in a batch-type fashion, the reaction diluent (if any), ethylene and alpha-olefin comonomer(s) are charged at appropriate ratios to a suitable reactor.

The polymerization may be conducted in a continuous manner by simultaneously feeding the reaction diluent (if employed), monomers, catalyst and cocatalyst to a reactor and withdrawing solvent, unreacted monomer and polymer from the reactor so as to allow a residence time of ingredients long enough for forming polymer of the desired molecular weight and separating the polymer from the reaction mixture.

Preparation of Functionalized and Free-Radically Grafted Alpha-Olefin Polymer

In accordance with this invention, the unsaturated alpha-olefin polymer is functionalized, e.g., with carboxylic acid producing moieties (preferably acid or anhydride moieties) selectively at sites of carbon-to-carbon unsaturation on the polymer chains, either before or after or while simultaneously reacting the polymer with monounsaturated carboxylic reactant, e.g., maleic anhydride, preferably in the presence of a free-radical initiator, to randomly attach carboxylic acid producing moieties, i.e., acid or anhydride or acid ester moieties, onto the polymer chains.

The unsaturated α -olefin polymer may be functionalized, for example, with carboxylic acid producing moieties (preferably acid or anhydride) by reacting the polymer under conditions that result in the addition of functional moieties, i.e., acid, anhydride, ester moieties, etc., onto the polymer chains primarily, and preferably only,

at sites of carbon-to-carbon unsaturation (also referred to as ethylenic or olefinic unsaturation). In one embodiment, this selective functionalization can be accomplished by halogenating, e.g., chlorinating or brominating the unsaturated α -olefin polymer to about 1 to 8 wt. %, preferably 3 to 7 wt. % chlorine, or bromine, based on the weight of polymer, by passing the chlorine or bromine through the polymer at a temperature of 60 to 250°C, preferably 110 to 160°C, e.g., 120 to 140°C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer is then reacted with sufficient monounsaturated reactant capable of adding functional moieties to the polymer, e.g., monounsaturated carboxylic reactant, at 100 to 250°C, usually about 180°C to 235°C, for about 0.5 to 10, e.g., 3 to 8 hours, such that the product obtained will contain the desired number of moles of the monounsaturated carboxylic reactant per mole of the halogenated polymer. Alternatively, the polymer and the monounsaturated carboxylic reactant are mixed and heated while adding chlorine to the hot material.

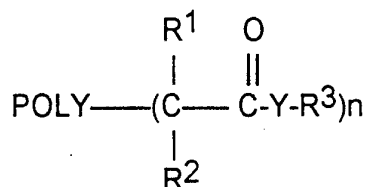
The preferred monounsaturated reactants that are used to functionalize the unsaturated α -olefin polymer comprise mono- and dicarboxylic acid material, i.e., acid, anhydride or acid ester material, including (i) monounsaturated C₄ to C₁₀ dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (i.e., located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; (ii) derivatives of (i) such as anhydrides or C₁ to C₅ alcohol derived mono- or diesters of (i); (iii) monounsaturated C₃ to C₁₀ monocarboxylic acid wherein the carbon-carbon double bond is conjugated with the carboxy group, i.e., of the structure -C=C-CO-; and (iv) derivatives of (iii) such as C₁ to C₅ alcohol derived mono- or diesters of (iii). Mixtures of monounsaturated carboxylic materials (i) - (iv) also may be used. Upon reaction with the polymer, the monounsaturation of the monounsaturated carboxylic reactant becomes saturated. Thus, for example, maleic anhydride becomes polymer substituted succinic anhydride, and acrylic acid becomes polymer substituted propionic acid. Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C₁ to C₄ alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate and methyl fumarate. The monounsaturated carboxylic reactant, preferably maleic anhydride, typically will be used in an amount ranging from about 0.01 percent to about 10 percent, preferably 0.1 to 2.0 percent, based on the weight of the polymer.

While chlorination normally helps increase the reactivity of starting olefin polymers with monounsaturated functionalizing reactant, it is not necessary with the unsaturated polymers contemplated for use in the present invention,

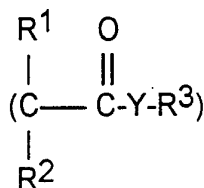
particularly those preferred polymers which possess a high terminal bond content and reactivity. Preferably, therefore, the unsaturated polymer and the monounsaturated functionality reactant, e.g., carboxylic reactant, are contacted at elevated temperature to cause an initial thermal "ene" reaction to take place, whereafter the partially "ene" reacted polymer is reacted further in the presence of a free-radical initiator. Ene reactions are known.

In an alternative embodiment, the unsaturated α -olefin polymer may be functionalized, selectively at the sites of olefinically unsaturated bonds in the polymer chains, with carboxylic acid, carboxylic ester or thiol ester functional groups via a Koch reaction. A Koch process comprises contacting a polymer composition comprising at least one polymer having at least one carbon-carbon double bond, with carbon monoxide and a Koch catalyst. The catalyst is preferably a classical Broensted acid or Lewis acid catalyst. These catalysts which are useful for Koch reactions, are distinguishable from transition metal catalysts of the type useful in hydroformylation reactions. The Koch reaction is conducted in a manner and under conditions sufficient to form, theoretically, a carbenium ion at the cite of said carbon-carbon double bond, which carbenium ion can be reacted with carbon monoxide to form theoretically, an acylium cation, which in turn is reacted with at least one nucleophilic trapping agent selected from the group consisting of water or at least one hydroxyl or one thiol group containing compound. The Koch reaction as applied to polymer has resulted in yields of Koch functionalized polymer of 95 mole % or more of the polymer reacting to form acylium cations which form functional groups, e.g. carbonyl functional groups.

Such Koch compositions comprise functionalized polymer of the formula:



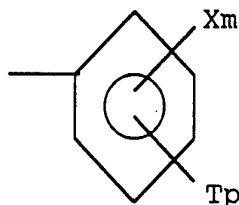
POLY is a polymer group having Mn of 700 to 10,000, and preferably 800 to 5,500, e.g., 1,000 to 3,000; n is the average value of functional groups, i.e.,



per polymer chain in the polymer composition and is greater than 0. Specific embodiments of n being $1 \geq n > 0$; $2 \geq n > 1$; and $n > 2$. n can be determined by C^{13} NMR. The amount of functional groups will typically increase with \bar{M}_n . Typically, the number of functional groups per M_n is about $n=1$ for each M_n of from about 5000 to 7000 for polymer used in oleaginous compositions. In effect, there should be a sufficient number of functional groups per total weight of polymer composition.

R^1 , R^2 and R^3 can be the same or different and are selected from -H, various hydrocarbyl groups and polymeric groups. Y is selected from O and S. In preferred embodiments, the "leaving group" ($-YR^3$) has a pKa of less or equal to 12, preferably less than 10, and more preferably less than 8 as determined by the pKa of $HY-R^3$. The Koch compositions are useful as "neo" functionalized polymer. By neo structure, it is meant that at least 50 mole percent of the functional groups have both R^1 and R^2 not H. In more specific embodiments, the polymer can be at least 60, 80, or 90 and even about 100 mole percent neo. POLY- is typically derived from unsaturated polymer. Preferred unsaturated polymers include those selected from the group consisting of polyalkenes derived from monoolefinic monomers, diolefinic monomers and copolymers thereof. In one preferred composition, Y is oxygen, at least 50 mole percent of the functional groups have both R^1 and R^2 as hydrocarbyl groups, and R^3 is H or a hydrocarbyl group. Where the leaving group is an acid or alkyl ester, the pKa of the leaving group is not critical. Typically, carboxylic acid and carboxylic esters have leaving groups greater than 12, e.g., 13 to 15. In some embodiments, the leaving group should have a pKa of less than 12, preferably less than 10 and more preferably 8 or less. The pKa of the leaving group indicates that the leaving group is relatively acidic and will readily react with derivatizing compounds for derivative compositions.

A particularly preferred composition has R^3 of the formula:



wherein X is an electron withdrawing substituent, T represents a non-electron withdrawing substituent, and m and p are from 0 to 5 with the sum of m and p being from 0 to 5. More preferably, X is an electron withdrawing substituent, m is from 1 to 5 and preferably 1 to 3, and T is a substituent which is selected such that its presence does not increase the pKa of the leaving group to greater than 12. In a

particularly preferred embodiment, X is selected from -Cl, -F, -CF₃, cyano groups, and nitro groups and p = 0. A preferred R³ is derived from 2,4-dichlorophenol. When m is greater p is greater than 1, each T may be the same or different.

The Koch reaction mechanism permits controlled functionalization of
5 unsaturated polymers. This makes possible the use of relatively inexpensive materials i.e., carbon monoxide at relatively low temperatures and pressures. The leaving group -YR³ can be removed and recycled upon derivatizing the Koch functionalized polymer. The polymers react with carbon monoxide in the presence of an acid catalyst or a catalyst complexed with a nucleophilic trapping agent. Preferred
10 nucleophilic trapping agents are selected from the group consisting of water, monohydric alcohols, polyhydric alcohols hydroxyl-containing aromatic compounds and hetero substituted phenolic compounds. The catalyst and nucleophilic trapping agent can be combined to form a catalytic complex.

The acid catalyst is preferably selected from the group consisting of HF,
15 BF₃, BF₃, H₂O and H₂SO₄. The catalytic complex can be selected from the group consisting of BF₃.xH₂O, BF₃.(2,4-dichlorophenol), BF₃.xH₂O.y(n-heptanoic acid), BF₃.y(n-heptanoic acid), BF₃.xH₂O.zH₃PO₄, and BF₃.wCH₃SO₃H, wherein x is from 0.5 to 1.5; y is from 0.5 to 2.0, z is from 0.5 to 1.5 and w is from 0.5 to 5.0. The acid catalyst or catalyst complexes preferably have a Hammet acidity value of from -8.0 to
20 -11.5 and preferably from -10.0 to -11.5. Processes for functionalizing unsaturated polymers via a Koch reaction are described more fully in USSN 992403 filed December 17, 1992.

In still other preferred embodiments, the unsaturated α -olefin polymers of this invention may be functionalized with carboxylic acid or ester moieties by
25 reacting the starting polymers with carbon monoxide and an alcohol in the presence of a protonic acid and catalyst system comprising (a) at least one of the metals palladium, rhodium, ruthenium, iridium and cobalt in elemental or compound form and (b) a copper compound. In preferred embodiments, the functionalized olefin polymers are characterized by a high degree of monofunctionality, i.e., at least 65 % and
30 preferably at least 75 % of the polymer chains contain only one functional group (e.g., acid or anhydride group) at a point in the respective polymer chains where a carbon-carbon unsaturated bond was located prior to being functionalized. The α -olefin polymers may be functionalized in the manner described above either before, after, or while simultaneously subjecting the polymer to the attachment of functional moieties
35 randomly along the polymer chains (as opposed to selectively at sites of carbon-to-carbon unsaturation). However, in preferred aspects of this invention, it is preferred to functionalize the polymer selectively at sites of olefinic unsaturation prior to

functionalizing the polymers at random locations along their respective polymer chains.

Random attachment of functional moieties along the polymer chains may be accomplished by a variety of methods. For example, the polymer, in solution or in solid form, may be grafted with the monounsaturated carboxylic reactant, as described above, in the presence of a free-radical initiator. When performed in solution, the grafting takes place at an elevated temperature in the range of about 100°C to 260°C, preferably 120°C to 240°C. Preferably, free-radical initiated grafting would be accomplished in a mineral lubricating oil solution containing, e.g., 1 to 50, preferably 5 to 30 wt. % polymer based on the initial total oil solution.

The free-radical initiators which may be used are peroxides, hydroperoxides, and azo compounds, preferably those which have a boiling point greater than about 100°C and decompose thermally within the grafting temperature range to provide free-radicals. Representative of these free-radical initiators are azobutyronitrile, 2,5-dimethylhex-3-ene-2,5-bis-tertiary-butyl peroxide and dicumene peroxide. The initiator, when used, typically is used in an amount of between 0.005% and 1% by weight based on the weight of the reaction mixture solution. Typically, the aforesaid monounsaturated carboxylic reactant material and free-radical initiator are used in a weight ratio range of from about 1.0:1 to 30:1, preferably 3:1 to 6:1. The grafting is preferably carried out in an inert atmosphere, such as under nitrogen blanketing. The resulting grafted polymer is characterized by having carboxylic acid (or ester or anhydride) moieties randomly attached along the polymer chains; it being understood, of course, that some of the polymer chains remain ungrafted.

In the solid or melt process for forming a graft polymer, the unsaturated carboxylic acid with the optional use of a radical initiator is grafted on molten copolymer using masticating or shearing equipment. The temperature of the molten material in this process may range from about 150-400°C. Processes for free-radically grafting ethylene-alpha-olefin polymers are described, for example, in US-A-4505834; 4749504 and 4863623; and in GB-A- 2055852A.

Normally, not all of the polymer reacts with the monounsaturated carboxylic reactant and the reaction mixture will contain unreacted polymer. The unreacted polymer typically is not removed from the reaction mixture (because such removal is difficult and would be commercially infeasible) and the product mixture, stripped of any monounsaturated carboxylic reactant, is employed for further reaction with at least one nucleophilic reactant, i.e., amine, alcohol or aminoalcohol, and sometimes with end-capping reactant, as described more fully hereinafter, to make the dispersant additives of this invention.

Characterization of the average number of moles of monounsaturated carboxylic reactant which have reacted per mole of polymer charged to the reaction (whether it has undergone reaction or not) is defined herein as functionality, and such functionality is based upon (i) determination of the saponification number of the resulting product mixture using potassium hydroxide; and (ii) the \bar{M}_n of the polymer charged, using techniques well known in the art. Functionality is defined solely with reference to the resulting product mixture. Although the amount of said reacted polymer contained in the resulting product mixture can be subsequently modified, i.e. increased or decreased by techniques known in the art, such modifications do not alter functionality as defined above. The terms "grafted ethylene-alpha-olefin polymer", "functionalized and grafted olefin polymers", "grafted olefin polymers" or the like, are intended to refer to the product mixture whether it has undergone such modification or not.

Accordingly, the functionality of the alpha-olefin polymer, which has been functionalized (selectively at unsaturated sites) and graft reacted (at random sites) with the monounsaturated carboxylic reactant, will be typically at least 0.5, preferably at least 0.8, and most preferably at least 0.9, and will vary typically from 0.5 to 5 (e.g., 0.6 to 4), preferably from 0.9 to 3.

In the free-radical grafting processes contemplated for use in this invention, the selected polymer, monounsaturated carboxylic reactant, and free-radical initiator are contacted for a time and under conditions effective to form the desired randomly grafted (or selectively functionalized and randomly grafted) alpha-olefin polymer material. Generally, the polymer, monounsaturated carboxylic reactant, and free-radical initiator will be contacted in a polymer to unsaturated carboxylic reactant mole ratio usually from about 1:1 to 1:5, at an elevated temperature, generally from 100 to 260°C, preferably from about 120 to 240°C. The reaction will be generally carried out, with stirring for a time of from about 1 to 20 hours, preferably from about 2 to 6 hours. The reaction is preferably conducted in the substantial absence of O₂ and water (to avoid competing side reactions), and to this end can be conducted in an atmosphere of dry N₂ gas or other gas inert under the reaction conditions. The reactants can be charged separately or together as a mixture to the reaction zone, and the reaction can be carried out continuously, semi-continuously or batchwise. Although not generally necessary, the reaction can be carried out in the presence of a liquid diluent or solvent, e.g., a hydrocarbon diluent such as mineral lubricating oil, toluene, xylene, dichlorobenzene, etc. The randomly grafted (or selectively functionalized and randomly grafted) polymer material thus formed can be recovered from the liquid reaction mixture, e.g., after stripping the

reaction mixture, if desired, with an inert gas such as N₂ to remove unreacted unsaturated carboxylic reactant.

The reaction product mixture thereby obtained has been surprisingly found to have a substantially reduced content of sediment or other solid by-products as impurities and can be employed, without filtering, centrifuging, clarification, phase separation or other conventional product purification treatments, as intermediate in the preparation of dispersant additive products for use in lubricating oils. The preferred reaction product mixture is prepared by "ene" or "Koch" reacting the α -olefin polymer, and then free-radically grafting the resulting polymer material. Therefore, the preferred reaction product mixture is further improved by being substantially free of chlorine, that is, by having a chlorine content of less than about 25 ppm by weight, preferably less than 10 ppm by weight.

One aspect of this invention is the ability to control, or at least favorably alter, the statistical distribution of carboxylic acid (anhydride) substituents on the different polymer chains of the alpha-olefin polymer. For example, assuming a random free-radical grafting of maleic anhydride onto a copolymer of ethylene-butene-1 (having a number average degree of polymerization of 37.5, a \bar{M}_n of 1400, an ethylene content of 50 wt. %, and an average of at least 30 % of its polymer chains containing terminal ethenylidene unsaturation), the number fraction (P_n) and weight fraction (P_w) of chains with "n" grafted anhydride groups, given that there are average "m" anhydride groups per chain, are illustrated below in Tables I-V. Table VI (m=2) illustrates the results obtained using the thermal "ene" reaction to add one anhydride group to the end of each copolymer chain, followed by free-radical grafting.

25 TABLE I (m=1)

<u>n</u>	<u>P_n</u>	<u>P_w</u>
0	0.5000	0.2433
1	0.2500	0.2500
2	0.1250	0.1892
30 3	0.0625	0.1267
4	0.0313	0.0794
5	0.0156	0.0477
6	0.0078	0.0279
7	0.0039	0.0159
35 8	0.0020	0.0090

TABLE II (m=2)

<u>n</u>	<u>P_n</u>	<u>P_w</u>
0	0.3333	0.1052
1	0.2222	0.1462
2	0.1481	0.1481
3	0.0988	0.1326
4	0.0658	0.1109
5	0.0439	0.0890
6	0.0293	0.0693
7	0.0195	0.0529
8	0.0130	0.0397

TABLE III (m=3)

n	P_n	P_w
0	0.2500	0.0575
1	0.1875	0.0913
5 2	0.1406	0.1045
3	0.1055	0.1055
4	0.0791	0.0994
5	0.0593	0.0898
6	0.0445	0.0787
10 7	0.0334	0.0676
8	0.0250	0.0571

TABLE IV (m=4)

n	P_n	P_w
0	0.2	0.035733
1	0.16	0.06144
2	0.128	0.075435
3	0.1024	0.081374
4	0.08192	0.08192
5	0.065536	0.078993
6	0.052429	0.07396
7	0.041943	0.06778
8	0.033554	0.061114

TABLE V (m = 5)

n	P_n	P_w
15 0	0.166667	0.024074
1	0.138889	0.043827
2	0.115741	0.056327
3	0.096451	0.063443
4	0.080376	0.066622
20 5	0.06698	0.06698
6	0.055816	0.065367
7	0.046514	0.062432
8	0.038761	0.058659

TABLE VI (m=2 "ENE")

n	P_n	P_w
0	0	0
1	0.5	0.243333
2	0.25	0.25
3	0.125	0.189167
4	0.0625	0.126667
5	0.03125	0.079375
6	0.015625	0.047708
7	0.007813	0.027865
8	0.003906	0.015938
	~ 100%	~ 100%

25

Referring to Tables I - V, it can be seen that randomly grafting (by free-radical initiation) at a level below an average of 1 anhydride group per polymer chain ($m < 1$) would reduce the percent of polyfunctional gelable product, but it would also significantly increase the level of unreacted polymer. This, of course, would "waste" most of the starting polymer as diluent. Similarly, while grafting an average of more than 3 anhydride groups per polymer chain ($m > 3$) would greatly reduce the amount of "wasted" (unreacted) polymer, it would unduly increase the amount of gelable product. Referring to Table VI, it can be seen that when one anhydride group is added to the end of chain of the alpha-olefin polymer by first conducting the thermal "ene" reaction, and then additional anhydride groups are grafted randomly along the polymer chains by subjecting the polymer to free-radical grafting, there will be few, if any, unfunctionalized polymer chains, as well as fewer highly functionalized chains than when the polymer is subjected only to free-radical grafting. Thus, using a

35

combination of "ene" reaction and free radical grafting will result in less wasted polymer, while simultaneously reducing the likelihood of gel formation. It will be understood, of course, that results similar to those illustrated in Table VI would be achieved if the polymer were to be selectively functionalized, e.g., by using Koch chemistry or hydroformylation chemistry in place of the "ene" reaction, prior to, during, or after being the random free-radical grafting step.

Even with the increased yields of functionalized grafted alpha-olefin polymer contemplated herein, the reaction product mixture comprising the desired alpha-olefin polymer (e.g., ethylene-propylene polymer-substituted with succinic anhydride) formed by the process of this invention generally will contain some unreacted polymer, (that is, polymer which is unsubstituted by carboxylic acid producing moieties). Generally, the concentration of unreacted polymer will be less than 40 wt. % (e.g., from 5 to 35 wt. %), more preferably less than 30 wt. % (e.g. from 10 to 25 wt. %), and even more preferably less than 25 wt. %.

The alpha-olefin polymers of this invention which are charged to the reaction zone can be charged alone or together with (e.g., in admixture with) other polyalkenes derived from alkenes having from 1 to 20 carbon atoms (butene, pentene, octene, decene, dodecene, tetradodecene and the like) and homopolymers of C₃ to C₁₀, e.g., C₂ to C₅, monoolefins, and copolymers of C₂ to C₁₀, e.g., C₂ to C₅, monoolefins, said additional polymer having a \bar{M}_n of at least about 900, and a molecular weight distribution of less than about 4.0, preferably less than 3.0 (e.g., from 1.2 to 2.8). Preferred such additional olefin polymers comprise a major molar amount of C₂ to C₁₀, e.g. C₂ to C₅ monoolefin. Such olefins include ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene, etc. Exemplary of the additionally charged homopolymers is polypropylene, polyisobutylene, and poly-n-butene as well as interpolymers of two or more of such olefins such as copolymers of ethylene and propylene (prepared by conventional methods other than as described above for the preferred ethylene alpha-olefin copolymers employed in this invention, that is, ethenylene-propylene copolymers which are substantially saturated, wherein less than about 10 wt. % of the polymer chains contain ethylenic unsaturation); butylene and isobutylene; propylene and isobutylene; etc. Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is a C₄ to C₁₈ non-conjugated diolefin, e.g., a copolymer of isobutylene and butadiene; etc. The additional such olefin polymers charged to the reaction will usually have \bar{M}_n of at least about 700, more generally 1200-5,000, more usually 1500-4,000. Particularly useful such additional olefin polymers have \bar{M}_n 's of 1500 to 3,000 with approximately one double bond per chain. An especially useful additional such polymer is polyisobutylene. Preferred are mixtures of such polyisobutylene with

ethylene-propylene copolymers wherein at least 30 wt. % of the copolymers chains contain terminal ethenylidene monounsaturations as described above.

Nucleophilic Post-Treating Reactants

5 The alpha-olefin polymer substituted (i.e., selectively functionalized and randomly grafted) with carboxylic acid producing moieties, i.e., acid, anhydride or ester moieties, prepared as described above, can be contacted with a suitable nucleophilic post-treating reactant to form the novel dispersants of this invention. The post-treating reactants of group (i), i.e. the amines having a single reactive amino
10 group, generally comprise from 2 to 60, preferably 2 to 40 (e.g. 3 to 20), total carbon atoms and about 1 to 12, preferably 2 to 12, and most preferably 2 to 6 nitrogen atoms in the molecule. These amines may be hydrocarbyl amines or may include other groups, e.g., alkoxy groups, amide groups, nitrile, imidazoline groups, morpholine groups and the like. The amines of group (i) may contain only one
15 reactive (primary or secondary) amino group, and no other reactive groups may be present. As used in this disclosure, the term "reactive groups" is meant to describe nucleophilic groups, such as primary or secondary amino groups or hydroxy groups, which may react with the carboxylic acid producing moieties attached to the alpha-olefin polymer, e.g., to form ester, amide, imide, oxazoline, etc., linkages. By using an
20 amine having only a single reactive group as the nucleophilic reactant, cross-linking between the carboxylic acid (anhydride or ester) groups of the substituted alpha-olefin polymer will be avoided. Polyamines containing a single primary amino group and 1 or more tertiary amino groups, such as N-(3-aminopropyl)morpholine, are the preferred amines of group (i).

25 Examples of group (i) amine compounds include N-(2-aminoethyl)morpholine; N,N-dimethylethylenediamine; N,N-diethylethylenediamine; N,N-dimethyl-1,3-propanediamine; and N-(aminomethyl)-pyridine.

 The post-treating reactants in group (ii), i.e., alcohols having a single
30 reactive hydroxy group per molecule, generally comprise from 4 to about 8 carbon atoms and include, for example, C₄ - C₈ aliphatic alcohols such as butanol, pentanol and hexanol. The use of alcohols having less than 4 carbon atoms generally is to be avoided because of their low volatility. Alcohols having more than about 8 carbon atoms generally are to be avoided since it is difficult to remove unreacted higher
35 molecular weight alcohols from the post-reacted product and since the presence of unreacted higher molecular weight alcohols in the product mixture can result in dispersant additives having less favorable viscometric properties.

 The post-treating reactants of group (iii), i.e. polyamines containing at least two reactive amino groups per molecule, generally comprise from 2 to 60,

preferably 2 to 40 (e.g. 3 to 20), total carbon atoms and 2 to 12, preferably 2 to 9, and most preferably 3 to 9 nitrogen atoms per molecule. These amines may be hydrocarbyl amines or may be hydrocarbyl amines including other groups, e.g., alkoxy groups, amide groups, nitrile, imidazoline groups, morpholine groups and the like. Preferred amines of group (iii) are aliphatic saturated amines. The most preferred amines of the above type contain at least two primary amino groups and at least one, and preferably at least three, secondary amino groups.

Examples of suitable amines of group (iii) include: 1,2-diaminoethane; 1,3-diaminopropane; 1,4-diaminobutane; polyethylene amines such as diethylene triamine; poly-propylene amines such as 1,2-propylene diamine; triamine; N,N-di-(2-aminoethyl) ethylene diamine; di-, and tri-tallow amines and mixtures thereof. Other useful group (iii) amines include: alicyclic diamines such as 1,4-di(aminomethyl) cyclohexane, and heterocyclic nitrogen compounds such as imidazolines, and N-aminoalkyl piperazines. Non-limiting examples of such amines include 2-pentadecyl imidazoline; N-(2-aminoethyl) piperazine. Non-limiting examples of such amines include 2-pentadecyl imidazoline; N-(2-aminoethyl) piperazine; etc.

Commercial mixtures of amines may advantageously be used. Low cost poly(ethyleneamines) compounds averaging about 5 to 7 nitrogen atoms per molecule are available commercially under trade names such as "Polyamine H", "Polyamine 400", "Dow Polyamine E-100", etc.

Useful group (iii) amines also include polyoxyalkylene polyamines. The alkylene groups may be straight or branched chains containing 2 to 7, and preferably 2 to 4 carbon atoms.

The polyoxyalkylene polyamines above, preferably polyoxyalkylene diamines and polyoxyalkylene triamines, may have \bar{M}_n 's ranging from 200 to 4000 and preferably 400 to 2000. The preferred polyoxyalkylene polyamines include the polyoxyethylene and polyoxypropylene diamines and the polyoxypropylene triamines having \bar{M}_n 's 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.

A particularly useful class of group (iii) amines comprise bis(p-amino cyclohexyl)methane (PACM) and oligomers and mixtures of PACM with isomers and analogs thereof containing on average, from 2 to 6 or higher (usually 3 to 4) cyclohexyl rings per PACM oligomer molecule. The total nitrogen content of the PACM oligomers will comprise generally from 8 to 16 wt. %, and preferably from 10 to 14 wt.%. The PACM oligomers can be obtained, e.g., by fractionation, or distillation, as a heavies by-product or bottoms from the PACM-containing product produced by

high pressure catalytic hydrogenation of methylene-dianiline. The hydrogenation of methylene dianiline and the separation of PACM oligomers from the resulting hydrogenation product can be accomplished by known means.

Still another useful class of group (iii) amines are the polyamido and related amines, which comprise reaction products of a polyamine and an alpha, beta unsaturated compound. Any polyamine, whether aliphatic, cycloaliphatic, heterocyclic, etc., (but not aromatic) can be employed provided it is capable of adding across the acrylic double bond and amidifying with for example the carbonyl group of an acrylate-type compound or with a thiocarbonyl group of a thioacrylate-type compound.

The polyamido groups can comprise alkyl, cycloalkyl, or heterocyclic, which can be substituted with groups which are substantially inert to any component of the reaction mixture under conditions selected for preparation of the amido-amine. Such substituent groups include hydroxy, halide (e.g., Cl, F, I, Br), -SH and alkylthio. When one or more are alkyl, such alkyl groups can be straight or branched chain, and will generally contain from 1 to 20, more usually from 1 to 10, and preferably from 1 to 4, carbon atoms. Illustrative of such alkyl groups are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tridecyl, hexadecyl, octadecyl and the like. When one or more are cycloalkyl, the cycloalkyl group will generally contain from 3 to 12 carbon atoms, and preferably from 3 to 6 carbon atoms. Illustrative of such cycloalkyl groups are cyclopropyl, cyclobutyl, cyclohexyl, cyclooctyl, and cyclododecyl. When one or more are heterocyclic, the heterocyclic group generally consists of a compound having at least one ring of 6 to 12 members in which one or more ring carbon atoms is replaced by oxygen or nitrogen. Examples of such heterocyclic groups are furyl, pyranyl, pyridyl, piperidyl, dioxanyl, tetrahydrofuryl, pyrazinyl and 1,4-oxazinyl. Examples of the alpha, beta-ethylenically unsaturated carboxylate compounds are acrylic acid, methacrylic acid, the methyl, ethyl, isopropyl, n-butyl, and isobutyl esters of acrylic and methacrylic acids, 2-butenic acid, etc.

The alpha, beta ethylenically unsaturated carboxylate thioester compounds may be employed. Examples of such alpha, beta-ethylenically unsaturated carboxylate thioesters are methylmercapto 2-butenate, ethylmercapto 2-hexenoate, etc.

The alpha, beta ethylenically unsaturated carboxamide compounds may be employed. Examples are 2-butenamide, 2-hexenamide, etc.

The alpha, beta ethylenically unsaturated thiocarboxylate compounds may be employed. Examples are 2-butenethioic acid, 2-hexenthioic acid, etc.

The alpha, beta ethylenically unsaturated dithioic acid and acid ester compounds may be employed. Examples are 2-butendithioic acid, 2-hexendithioic acid, etc.

The alpha, beta ethylenically unsaturated thiocarboxamide compounds
5 may be employed. Examples are 2-butenthioamide, 2-hexenthioamide, 2-decenthio-
amide, 3-methyl-2-heptenthioamide, 3-methyl-2-butenthio-amide, 3-cyclohexyl-2-
butenthioamide, 2-methyl-2-buten-thioamide, 2-propyl-2-propenthioamide, 2-
isopropyl-2-hexenthioamide, 2,3-dimethyl-2-butenthio-amide, 3-cyclo-hexyl-2-methyl-
2-penththioamide, N-methyl 2-butenthio-amide, N,N-diethyl 2-hexenthioamide, N-
10 isopropyl 2-decenthioamide, N-tertiary butyl 2-propenthioamide, N-octadecyl 2-
propenthioamide, N-N-didodecyl 2-decen-thioamide, N-cyclopropyl 2,3-dimethyl-2-
butenthioamide, 2-propenthioamide, 2-methyl-2-propenthioamide, 2-ethyl-2-
propenthioamide and the like.

Preferred compounds for reaction with the polyamines in accordance
15 with this invention are lower alkyl esters of acrylic and (lower alkyl) substituted acrylic
acid. In the preferred embodiments these compounds are acrylic and methacrylic
esters such as methyl or ethyl acrylate, methyl or ethyl methacrylate. When the
selected alpha, beta-unsaturated compound contains oxygen, the resulting reaction
product with the polyamine contains at least one amido linkage (-C(O)N<) and such
20 materials are herein termed "amido-amines." Similarly, when the selected alpha, beta
unsaturated compound contains sulfur, the resulting reaction product with the
polyamine contains thioamide linkage (-C(S)N<) and these materials are herein
termed "thioamido-amines."

The post-treating reactants in group (iv), i.e. the polyols containing at
25 least two reactive hydroxy groups, generally comprise up to 100 carbon atoms and
from 2 to 10, and preferably 3 to 8 hydroxy groups per molecule. These polyols can
be quite diverse in structure and chemical composition. For example, they can be
substituted or unsubstituted, hindered or unhindered, branched chain or straight
chain, etc. as desired. Typical polyols are alkylene glycols such as ethylene glycol,
30 propylene glycol, and polyglycol such as diethylene glycol, triethylene glycol and
other alkylene glycols and polyalkylene glycols in which the alkylene radical contains
from two to about eight carbon atoms. Other useful polyhydric alcohols include
glycerol, monomethyl ether of glycerol, pentaerythritol, dipenta-erythritol, the ethyl
ester of 9,10-dihydroxystearic acid, 3-chloro-1, 2-propanediol, 1,2-butanediol,
35 pinacol, tetrahydroxy pentane, erythritol, 1,4-cyclohexanediol, the carbohydrates such
as glucose, etc.

Included among the polyols which may be employed are the cyclic
poly(methylol) compounds, such as 2,2,6,6-tetramethylol cyclohexanol, tetrahydro-

3,3,5,5-tetrakis-(hydroxymethyl)-4-pyranol and tetrahydro-3,3,5-tris-(hydroxymethyl)-5-methyl-4-pyranol; and heterocyclic polyols.

The post-treating reactants in group (v), i.e. aminoalcohols having at least one reactive amino group and at least one reactive hydroxy group per molecule, include aminoalcohols containing up to about 50 total carbon atoms, preferably up to 10 total carbon atoms, from about 1 to 5 nitrogen atoms, preferably from 1 to 3 nitrogen atoms, and from about 1 to 15 hydroxyl groups, preferably from 1 to 5 hydroxyl groups. Preferred aminoalcohol compounds include the 2,2-disubstituted-2-amino-1-alkanols having from two to three hydroxy groups and containing a total of 4 to 8 carbon atoms. Examples of such amino alcohols include: 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-propanediol, and 2-amino-2-(hydroxymethyl) 1,3-propanediol, the latter also being known as THAM or tris(hydroxymethyl)amino methane. THAM is particularly preferred because of its effectiveness, availability, and low cost.

The post-treating reactants (i) - (v) may be used alone or in admixture with one another. However, as will be discussed more fully hereinbelow, when the post-treating reactant comprises a polyfunctional compound, i.e. a compound containing more than one reactive group, regardless of whether such reactive group is an amino group or a hydroxy group, it is necessary to use sufficient chain-stopping or end-capping reactant in combination with the polyfunctional post-treating reactant to ensure that the grafted and post-reacted product mixture will be gel-free.

Chain-Stopping Reactant

The chain-stopping or end-capping reactants contemplated for use in this invention include monofunctional reactants which are capable of reacting with reactive amine groups or reactive hydroxy groups present in the polyfunctional post-treating reactants of groups (ii) - (v) or with the acid producing groups which are grafted or otherwise attached to the alpha-olefin polymer to inhibit cross linking and gelation and/or viscosity increase due to any further reaction of unreacted amino groups or hydroxy groups in the grafted and aminated or esterified alpha-olefin polymer. Preferred chain-stopping or end-capping reactants include, for example, hydrocarbyl substituted dicarboxylic anhydride or acid, preferably succinic anhydride or acid, having from about 12 to 400 carbons in the hydrocarbyl group; long chain monocarboxylic acid of the formula RCOOH where R is a hydrocarbyl group of 12 to 400 carbons in the hydrocarbyl group; alcohol compounds of the type described above in connection with the nucleophilic post-treating reactants of group (ii), i.e., alcohol compounds having only a single hydroxy group per molecule; and amine compounds of the type described above in connection with the post-treating reactants

of group (i), i.e., amine compounds having only a single reactive amine group per molecule. The hydrocarbonyl groups are essentially aliphatic and include alkenyl and alkyl groups. The longer chain acids and anhydrides are preferred, particularly when the grafting reaction is carried out in lubricating oil because of their ability to impart dispersancy to reacted oil molecules as well as their greater solubilizing effect. In one preferred embodiment, the chain-stopping or end-capping reactant comprises a C₁₂ to C₄₉ hydrocarbonyl substituted succinic anhydride, e.g. a C₁₂ to C₁₈ hydrocarbonyl substituted succinic anhydride. In other preferred embodiments, the hydrocarbonyl substituent contains from 50 to 400 carbon atoms.

Primarily because of its ready availability and low cost, the hydrocarbonyl portion, e.g. alkenyl groups, of the carboxylic acid or anhydride is preferably derived from a polymer of a C₂ to C₅ monoolefin, said polymer generally having a \bar{M}_n of about 140 to 6500, e.g. 700 to 5000, most preferably 700 to 3000. Particularly preferred polymer is polyisobutylene. Particularly preferred chain-stopping reactants include polyisobutylene succinic anhydride wherein the \bar{M}_n of the polyisobutylene portion is from 700 to 2500.

Pre-Reacted Post-Treating Reactant/Chain-Stopping Reactant

The aforesaid nucleophilic post-treating reactants (iii) - (v) having more than one reactive amino and/or hydroxy group and the chain-stopping or end-capping reactants may be pre-reacted with the chain-stopping or end-capping reactant generally being attached to the post-treating reactant through salt, imide, amide amidine, ester, or other linkages so that a single reactive group of the post-treating reactant is still available for reaction with the acid producing moieties of the grafted polymer. A convenient source of these prereacted materials are the well-known carboxylic acid derivatives such as succinimides used as lubricating oil dispersants, provided they retain reactive amine and/or hydroxy groups capable of further reaction with the grafted polymer.

Reaction of Polymer Substituted Mono- and Dicarboxylic Acid Material with Post-Treating Reactant

The selected polymer functionalized and grafted with acid producing moieties, e.g., ethylene-propylene copolymer substituted succinic anhydride, can be reacted with any individual post-treating reactant (or post-treating reactant and chain-stopping or end-capping reactant) or any combination of two or more of any of these reactants; that is, for example, one or more monoreactive amines, monoreactive alcohols, polyamines, polyols and/or aminoalcohols can be used, so long as sufficient

monoreactive reactant is used when a reactant having more than one reactive group is used, to ensure a gel-free reaction.

The reaction between the polymer functionalized and grafted with acid producing moieties and the nucleophilic post-treating and/or chain-stopping or end-capping reactants is readily accomplished, for example, by heating a solution
5 containing 5 to 95 wt. percent of the polymer in a substantially inert organic solvent or diluent at from 100 to 250°C, preferably 125 to 175°C, generally for 1 to 10, e.g., 2 to 6 hours until the desired amount of water is removed. Suitable diluents include, for example, aliphatic, cycloaliphatic, and aromatic hydrocarbons, as well as the
10 corresponding halogenated hydrocarbons, particularly chlorinated hydrocarbons. These diluents are exemplified by benzene, toluene, xylene, chlorobenzenes, hexane, heptane, or mixtures of these. Mineral oils particularly low viscosity mineral oils are very good diluents. Preferred diluents are mineral oils of lubricating viscosity.

Reaction ratios of polymer substituted with carboxylic acid material to
15 equivalents of amine reactant, as well as the other nucleophilic post-treating reactants and chain-stopping or end-capping reactants described herein, can vary considerably, depending, e.g., on the reactants and type of bonds formed. Generally, when an amine compound or other nucleophilic reactant, is reacted with a polymer substituted with carboxylic acid material; i.e., polymer containing carboxylic acid
20 producing moieties derived from any of the above monounsaturated carboxylic acids, or anhydride or ester derivatives thereof, from 0.05 to 4.0, preferably from 0.5 to 2.0, e.g., 0.6 to 1.5, moles of carboxylic acid moiety content (e.g., grafted maleic anhydride content) is used, per equivalent of nucleophilic reactant.

A preferred group of ashless dispersants, in accordance with the
25 present invention, are those derived from ethylene-propylene copolymer or ethylene-butene-1 copolymer substituted with succinic anhydride groups and reacted with polyethylene amines, e.g., tetraethylene pentamine, pentaethylene hexamine, polyoxyethylene or polyoxypropylene amines, e.g., polyoxypropylene diamine, and with polyisobutylene succinic anhydride chain-stopping reactant. Another preferred
30 group of ashless dispersants are those derived from ethylene-propylene or ethylene-butene-1 copolymer substituted with succinic anhydride groups and reacted with monofunctional heterocyclic amines, e.g., N-(3-aminopropyl)morpholine.

Oleaginous Compositions

35 The compositions of the present invention used as dispersants can be incorporated into a lubricating oil (or a fuel) in any convenient way. Thus, these dispersants can be added directly to the lubricating oil (or fuel) by dispersing or dissolving the same in the lubricating oil (or fuel) at the desired level of concentration

of the dispersant, typically in an amount of from 0.01 to 49 wt. % of the lubricating oil (or fuel). Such blending into the additional lubricating oil (or fuel) can occur at room temperature or elevated temperatures.

5 Dispersant concentrates will typically contain (on an active ingredient (A.I.) basis) from about 3 to 45 wt.%, and preferably from 10 to 35 wt.%, dispersant additive, and typically from 30 to 90 wt.%, preferably from 40 to 60 wt.%, base oil, based on the concentrate weight.

10 The dispersant products of the present invention possess very good dispersant properties as measured herein in a wide variety of environments. When the products of this invention are incorporated into crude oil refinery process streams and other hydrocarbon fluid process streams, where they function as antifoulants, they will be generally used, e.g., in amounts of up to 100 ppm, e.g., 5 to 50 ppm, of the treated stream.

15 When the dispersant products of this invention are used in normally liquid petroleum fuels such as middle distillates boiling from 65° to 430°C, including kerosene, diesel fuels, home heating fuel oil, jet fuels, etc., a concentration of the additives in the fuel in the range of typically from 0.001 to 0.5, and preferably 0.005 to 0.15 weight percent, based on the total weight of the composition, will usually be employed. The properties of such fuels are well known as illustrated, for example, by
20 ASTM Specifications D #396-73 (Fuel Oils) and D #439-73 (Gasolines) available from the American Society for Testing Materials ("ASTM"). The fuel compositions of this invention can also contain other additives. These can include anti-knock agents, lead scavengers, deposit preventers or modifiers, dyes, cetane improvers, antioxidants rust inhibitors, bacteriostatic agents, gum inhibitors, metal deactivators, upper
25 cylinder lubricants and the like.

The dispersant products of the present invention find their primary utility in lubricating oil compositions which employ a base oil in which the additives are dissolved or dispersed, often together with other conventional additives for such compositions. Such base oils may be natural or synthetic. Base oils suitable for use
30 in preparing the lubricating oil compositions of the present invention include those conventionally employed as crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Advantageous results are also achieved by employing the additive mixtures of the present invention in base oils
35 conventionally employed in and/or adapted for use as power transmitting fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Gear lubricants, industrial oils, pump oils and other

lubricating oil compositions can also benefit from the incorporation therein of the additive mixtures of the present invention.

The ashless dispersants of the present invention will be generally used in admixture with a lube oil basestock, comprising an oil of lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. Natural oils include animal oils and vegetable oils (e.g., castor, lard oil) liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils. Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids. Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, etc. Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils comprise another useful class of synthetic lubricants. Unrefined, refined and rerefined oils can be used in the lubricants of the present invention.

Metal-containing rust inhibitors and/or detergents are frequently used with ashless dispersants. Such detergents and rust inhibitors include the metal salts of sulphonic acids, alkyl phenols, sulphurized alkyl phenols, alkyl salicylates, naphthenates, and other oil soluble mono- and di-carboxylic acids. Highly basic, that is overbased metal salts which are frequently used as detergents appear particularly prone to interaction with the ashless dispersant. Highly basic alkaline earth metal sulfonates are frequently used as detergents. According to a preferred embodiment the invention therefore provides a crankcase lubricating composition also containing from 2 to 8000 parts per million of calcium or magnesium.

A particular advantage of the dispersants of the invention is use with V.I improvers to form multi-grade automobile engine lubricating oils. Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain relatively viscous at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Viscosity modifiers are generally high molecular weight hydrocarbon polymers including polyesters. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties. These oil soluble viscosity modifying polymers will generally have \overline{M}_n 's of from 10^3 to 10^6 , preferably 10^4 to 10^6 , e.g., 20,000 to 250,000, as determined by gel permeation chromatography or osmometry.

Examples of suitable hydrocarbon polymers include homopolymers and copolymers of two or more monomers of C₂ to C₃₀, e.g. C₂ to C₈ olefins, including both alpha olefins and internal olefins, which may be straight or branched, aliphatic, aromatic, alkyl-aromatic, cycloaliphatic, etc. Frequently they will be of ethylene with
5 C₃ to C₃₀ olefins, particularly preferred being the copolymers of ethylene and propylene. Other polymers can be used such as polyisobutylenes, homopolymers and copolymers of C₆ and higher alpha olefins. The preferred hydrocarbon polymers are ethylene copolymers containing from 15 to 90 wt.% ethylene, preferably 30 to 80 wt.% of ethylene and 10 to 85 wt.%, preferably 20 to 70 wt.% of one or more C₃ to
10 C₂₈, preferably C₃ to C₁₈, more preferably C₃ to C₈, alpha-olefins.

Dihydrocarbyl dithiophosphate metal salts are frequently used as anti-wear agents and also provide antioxidant activity. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10, preferably 0.2 to 2 wt. %, based upon the total weight of the lubricating oil composition. They may be prepared in
15 accordance with known techniques by first forming a dithiophosphoric acid, usually by reaction of an alcohol or a phenol with P₂S₅ and then neutralizing the dithiophosphoric acid with a suitable zinc compound. The antioxidants useful in this invention include oil soluble copper compounds. The copper may be blended into the oil as any suitable oil-soluble copper compound. By oil-soluble we mean the
20 compound is oil soluble under normal blending conditions in the oil or additive package.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition. Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the
25 products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide.

Oxidation inhibitors reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as
30 sludge and varnish-like deposits on the metal surfaces and by viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, barium t-octylphenyl sulfide, dioctylphenylamine, phenylaliphatic-phthylamine, phosphosulfurized or sulfurized hydro-carbons, etc.

Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such as automatic transmission fluids. Representative
35 examples of suitable friction modifiers are fatty acid esters, amides; and molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols.

Pour point depressants lower the temperature at which the lubricating oil will flow or can be poured. Foam control can be provided by an antifoamant of the polysiloxane type, e.g. silicone oil and polydimethyl siloxane. Organic, oil-soluble compounds useful as rust inhibitors in this invention comprise nonionic surfactants such as polyoxyalkylene polyols and esters thereof. Other suitable demulsifiers include esters. The liquid polyols available from Wyandotte Chemical Co. under the name Pluronic Polyols and other similar polyols are particularly well suited as rust inhibitors.

These compositions of our invention may also contain other additives and other metal containing additives, for example, those containing barium and sodium. The lubricating composition of the present invention may also include copper lead bearing corrosion inhibitors. Typically such compounds are the thiadiazole polysulphides containing from 5 to 50 carbon atoms, their derivatives and polymers thereof. Preferred materials are the derivatives of 1,3,4-thiadiazoles; especially preferred is the compound 2,5 bis (t-octadithio)-1,3,4-thiadiazole commercially available as Amoco 150. Other suitable additives are the thio and polythio sulphenamides of thiadiazoles such as those described in GB-A-1560830.

Some of these numerous additives can provide a multiplicity of effects, e.g., a dispersant-oxidation inhibitor. When these various additives are included in a lubricating composition, we prefer that they be present in a total amount from 0.01 to 10, preferably 0.1 to 5.0 weight percent based on the weight of the final composition.

When a number of additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the novel dispersants of this invention together with one or more of said other additives whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. It is common practice to introduce the additives in the form of 10 to 80 wt. %, e.g., 20 to 80 wt. % active ingredient concentrates in hydrocarbon oil, e.g. mineral lubricating oil, or other suitable solvent. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential.

All of said weight percents expressed herein (unless otherwise indicated) are based on active ingredient (A.I.) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the A.I. weight of each additive plus the weight of total oil or diluent.

In the following examples, which are provided by way of illustration only, all parts are by weight, unless otherwise noted, and wt.% ethylene in the polymers was determined by FTIR (ASTM Method D3900).

EXAMPLE 1: Free-radical grafting of an ethylene propylene copolymer reacted with maleic anhydride.

A 2 liter glass reactor is charged with 800 gm of an ethylene content of
5 50 wt. percent, a \overline{M}_n of 790 and a terminal vinylidene content greater than 90
percent. The reactor is purged with nitrogen for 2 hours and the temperature of the
flask and contents is increased to 150°C. Maleic anhydride (196 gms) is charged to
the flask and then 30 gms of di-tertiary butyl peroxide (DTBP) is added over the
course of 4 hours. The reaction is then continued for an additional 5 hours. The
10 temperature is then increased to 180°C, and unreacted maleic anhydride and catalyst
decomposition products are removed under a reduced pressure of 0.5 mm. The
resulting modified ethylene propylene copolymer is a grafted adduct with about 22
gms of maleic anhydride grafted per 100 gms of original polymer. This corresponds
roughly to about 2 molecules of maleic anhydride grafted per molecule of ethylene
15 propylene copolymer.

Example 2: Amination of the product in Example 1 with an amine which contains only 1 reactive nitrogen.

200 gms of the modified polymer of Example 1 are placed in a suitable
20 glass reactor. 72 grams of N-(3-aminopropyl) morpholine are added to the reactor
(corresponding approximately to stoichiometric equivalence to grafted maleic
anhydride) and the temperature increased to 160°C. Stirring the mixture is continued
for 3 hours, and then a stream of nitrogen is maintained through the reaction mixture
to remove unreacted N-(3-aminopropyl) morpholine and water of reaction. The
25 temperature is then raised to 180°C for 30 minutes to complete the removal. The
reaction product is a gel-free imide product which is effective as a dispersant.

Example 3: Amination of the product of Example 1 with a polyamine and a chain stopper (polyisobutenyl succinic anhydride).

30 200 gms of the modified polymer of Example 1 are placed in a suitable
glass reactor equipped with adequate stirring. The reactor is purged with nitrogen for
30 minutes and the contents are heated to about 100°C. About 350 gms of
polyisobutenyl succinic anhydride having an ASTM, D-64 Sap. No. 112 which are
diluted with 350 gms of solvent 100N diluent oil are added to the polymer with stirring
35 and the temperature is raised to about 190°C. The reaction mixture is held at that
temperature with nitrogen stripping for 3 hours, followed by cooling. The resulting
product is a viscous liquid substantially free of gel.

Example 4: Free-radical grafting of ethylene propylene copolymer reacted with maleic anhydride.

A 2 liter glass reactor is charged with 800 gm of an ethylene propylene random copolymer having an ethylene content of about 50%, a \bar{M}_n of about 1900 (0.42 moles) and a terminal vinylidene content of greater than 60%. The reactor is heated to 100°C and purged with nitrogen for 2 hours. The contents of the flask are heated to 150°C. Maleic anhydride (88 gm) is charged to the flask and 8 gms of DTBP is added over the course of 2 hours, and the reaction is continued for an additional 4 hours. The temperature is then increased to 180°C, and unreacted maleic anhydride and catalyst decomposition products are removed under a reduced pressure of 0.5 mm. The resulting adduct is a grafted ethylene propylene copolymer with about 10 gms of maleic anhydride grafted per 100 gms of polymer, or roughly 2 molecules of maleic anhydride per molecule of copolymer on the average.

Example 5: Esterification of the product of Example 4 in presence of chain-stopper.

About 200 gms of the product of Example 4 (about 0.105 moles of anhydride) is mixed with 100 gms of mineral oil (solvent 150N) and 15 gms of pentaerythritol in the presence of 0.2 gms of stannous octanoate as an esterification catalyst. 4 gms of normal hexanol (about .04 moles) is added as a chain stopper and the mixture is heated to 175°C with reflux for about 3 hours. The reaction mixture is nitrogen stripped for one-half hour. The reaction mixture is filtered, collected and demonstrated to be substantially gel-free. The resulting material is an effective dispersant and viscosity modifier.

Example 6: Esterification of product of Example 4 in presence of chain-stopper.

The reaction protocol of Example 2 is followed, except that 5 gms of N-(3-amino propyl morpholine) is employed as a monoreactive amine chain stopper. The reaction is run under similar conditions as Example 2 with reflux for 5 hours and the resultant mixture is nitrogen stripped for one-half hour at reaction temperature. The resulting material is substantially gel-free and is an effective dispersant and viscosity modifier.

CLAIMS:

1. An oil-soluble functionalized and grafted α -olefin polymer
5 composition prepared by grafting onto a functionalized polymer mono- or dicarboxylic acid producing moieties having 1 to 2 carboxylic acid-producing groups per moiety such that the functionalized and grafted polymer contains an average of 0.5 to 5 grafted acid producing moieties per polymer chain, wherein at least 75% of the functionalized polymer chains of the functionalized starting polymer are
10 monofunctional prior to being free radically grafted, and wherein said functionalized polymer is prepared by functionalizing an unsaturated α -olefin starting polymer having a \overline{M}_n of 700 to 10,000 and a polydispersity of 1 to 5.
2. The polymer composition of claim 1 wherein said starting polymer
15 comprises α -olefin homopolymer or interpolymer of α -olefins.
3. The polymer composition of claim 2 wherein the starting polymer is an ethylene/ α -olefin interpolymer having 20 to 80 wt. % of units derived from ethylene and 20 to 80 wt. % of units derived from at least one C₃ to C₂₈ α -olefin.
20
4. The composition of claim 3 wherein the α -olefin is propylene or butene-1.
5. The composition of any of claims 1 to 4 wherein the starting
25 polymer has a Mn of 800 to 5,500 prior to being functionalized and grafted.
6. The composition of any of claims 1 to 5 wherein at least about 30 wt. % of the polymer chains of the starting polymer possess terminal ethenylidene unsaturation prior to being functionalized.
30
7. The polymer composition of any of claims 1 to 6 wherein said functionalized polymer is prepared by contacting said starting polymer under "ene" reaction conditions with monounsaturated carboxylic reactant comprising at least one of (i) monounsaturated C₄ to C₁₀ dicarboxylic acid wherein (a) the carboxyl groups are located on adjacent carbon atoms and (b) at least one of said adjacent carbon atoms is part of said mono unsaturation; (ii) derivatives of (i); (iii) monounsaturated C₃ to C₁₀ monocarboxylic acid wherein the carbon-carbon double bond is conjugated with the carboxy group; and (iv) derivatives of (iii).
35

8. The polymer composition of any of claims 1 to 7 wherein said functionalized starting polymer is a neo-acid or ester.

5 9. A gel-free composition useful as a dispersant additive for oleaginous compositions comprising the reaction product of:

(a) a polymer composition of any of claims 1 to 8 and

(b) at least one nucleophilic post-treating reactant of: (i)

10 amines containing only a single reactive amino group per molecule, (ii) alcohols containing only a single hydroxy group per molecule, (iii) polyamines containing at least two reactive amino groups per molecule, (iv) polyols containing at least two reactive hydroxy groups per molecule, (v) aminoalcohols containing at least one reactive amino group and at least one reactive hydroxy group per molecule, and (vi)
15 mixtures of (i) to (v); provided that when said nucleophilic post-treating reactant includes one or more of (iii), (iv) or (v), the reaction between (a) and (b) is conducted in the presence of a monofunctional chain-stopping or end-capping co-reactant to ensure that the grafted and post-reacted product mixture is gel-free.

20 10. The composition of claim 9 wherein said monofunctional chain-stopping or end-capping co-reactant is one of (a) C₁₂ to C₄₀₀ hydrocarbyl substituted succinic acid or anhydride, (b) long chain monocarboxylic acid of the formula RCOOH where R is C₁₂ to C₄₀₀ hydrocarbyl, (c) amines containing only a single reactive amino group per molecule, (d) alcohols containing only a single
25 reactive hydroxy group per molecule, and (e) mixtures of (a) - (d).

11. An oil composition comprising a major proportion of oil selected from lubricating oil and fuel oil and 0.01 to 49 wt. % of the oil soluble composition according to any of claims 1 to 10.

30

12. A process for producing gel-free composition of claim 5, comprising:

(a) functionalizing an oil soluble, unsaturated α -olefin
35 polymer, having a Mn of 700 to 10,000 and a polydispersity of 1 to 5 selectively at unsaturated sites thereof;

(b) grafting the polymer with an ethylenically unsaturated carboxylic acid-producing material, either before, after, or simultaneously with functionalizing the polymer in step (a), the grafting being in the presence of free radical initiator, such that, after said polymer has been grafted and functionalized, 5 said polymer is substituted with an average of 0.5 to 5 carboxylic acid producing moieties per polymer chain; then

(c) contacting the reaction product from step (b) with at least one nucleophilic post-treating reactant being (i) amines containing only a single 10 reactive amino group per molecule, (ii) alcohols containing only a single hydroxy group per molecule, (iii) polyamines containing at least two reactive amino groups per molecule, (iv) polyols containing at least two reactive hydroxy groups per molecule, (v) aminoalcohols containing at least one reactive amino group and at least one reactive hydroxy group per molecule, and (vi) mixtures of (i) to (v); provided that when 15 the nucleophilic post-treating reactant contains more than one reactive group per molecule, the post-treating reactant is used in combination with a monofunctional chain-stopping or end-capping co-reactant to form the gel-free composition.