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ASHLESS DISPERSANTS, THEIR PREPARATION, AND THEIR USE

Technical Field

This invention relates to ashless dispersants for use in oleaginous media, notably oils of lubricating viscosity, and hydrocarbonaceous fuels such as middle distillate fuels and heavier burner fuels.

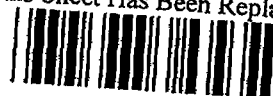
Background

Chemical additives for lubricating oils are used to control the physical and chemical properties of lubricating oils. These additives are used to modify oil viscosity and viscosity index, to make the oils more resistant to oxidation, and to keep engines and other mechanical equipment clean and protected against corrosion and wear. Water-soluble additives are also commonly used in applications ranging from aqueous hydraulic fluids to household cleaners and cosmetics.

Hydrocarbon-based chemical additives are designed for specific functions by choosing a hydrocarbon type and molecular weight range or molecular weight distribution to allow the additives to function in the fluid type of interest. For instance, high molecular weight polymers can be used to increase viscosity and viscosity index of mineral oils or synthetic oils. Water soluble polymers of polar compounds can be used to thicken water, or even allow water to be pumped more easily. Polar head groups can be designed to be attached to low or high molecular weight hydrocarbon tails to achieve detergency, dispersancy, antiwear or anticorrosion performance.

The hydrocarbon tail can be derived from natural fats or oils, or from petroleum fractions. Synthetic tails can be assembled by the polymerization of olefins or functionalized olefins or by polycondensation of difunctionalized olefins or saturated compounds.

The patent literature frequently describes the use of polymers of olefins having 2 to 6 carbon atoms for use as oil-soluble tails suitable for use in making oil additives. Indeed, some patents refer to use of polymers of even longer



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chain olefin monomers for this purpose. Extensive use is made of ethylene and butene or isobutylene oligomers in forming oil additives. High molecular ethylene-propylene olefin copolymers are commonly used to increase the viscosity index of lubricating oils. Propylene trimer and tetramer have been used as low molecular weight tails, and technology to make branched C_{20} to C_{100} polypropylene has been developed.

Despite the vast amount of work conducted heretofore, a need exists for novel ashless dispersants that have enhanced thermal stability and/or that can enable use of smaller amounts of viscosity index improvers in formulating finished lubricants, giving a cost reduction. Because of the relatively high temperatures to which finished lubricating oils are exposed during actual service conditions, improved thermal stability is a desirable property in ashless dispersants. The advantages of having an ashless dispersant which contributes viscosity increase to the lubricant and thus reduces the amount of viscosity index improver needed in the finished oil is referred to, for example, in U.S. Pat. No. 4,234,435.

The Invention

This invention is deemed to fulfill the foregoing need by providing and utilizing an ashless dispersant having in its chemical structure at least one aliphatic substituent derived from a special type of polymer. The special polymers used in forming the dispersants are copolymers of propylene characterized in that (a) they are liquid, substantially linear polymers, (b) they have stereo-irregularity in the polymer chain, (c) at least 60 mol percent, preferably at least 75 mol percent and more preferably at least 85 mol percent of the polymer has a terminal divalent methylene group ($=CH_2$), and (d) they contain up to 25 mol percent of a C_4 to C_{18} monoolefin, and preferably a C_4 to C_{10} monoolefin, polymerized into the polymer chains.

Pursuant to preferred embodiments, the above special propylene copolymer used in forming the dispersants has a viscosity ratio (VR) value of less than 4.0, and preferably less than 3.7. As used herein, the term "VR value" means the



quotient determined by the expression:

$$VR = \frac{Vis(b)}{Vis(a)}$$

- 5 wherein Vis(a) is the kinematic viscosity (KV) of the propylene copolymer at 100°C in units of centistokes (as determined by ASTM Method No. D 445) and Vis(b) is the cold cranking simulator (CCS) viscosity of the propylene copolymer at -20°C in units of poise (as determined by ASTM Method No. D 2602),
10 wherein the measurements are made upon a 2 wt % solution of the propylene copolymer in an oil (herein termed the "reference oil") comprising S150N (solvent 150 neutral) mineral lubricating oil (Exxon Company U.S.A.), wherein the such reference oil is characterized by an ASTM D 445 kinematic
15 viscosity of 5.2 cSt (100°C) and an ASTM D 2602 CCS viscosity of 19.2 poise (± 0.4 poise) (at -20°C). The "VR" value of the reference oil is thus about 3.7 ± 0.1 .

- As to type, the ashless dispersants of this invention can be succinic ester-amide dispersants, succinimide dispersants,
20 succinic triazole dispersants, succinic amide-triazole dispersants, or Mannich base dispersants. Process technology that can be adapted for producing these various types of dispersants can be found in the literature. For example, an ene reaction (sometimes referred to as a thermal reaction)
25 between the special copolymer of propylene and maleic anhydride yields an alkenyl-substituted succinic anhydride. This then can be converted into an alkenyl succinic ester-amide using conditions such as are described in U.S. Pat. Nos. 3,219,666; 3,282,959; 3,640,904; 4,426,305 or 4,873,009; or into an
30 alkenyl succinimide using conditions such as are described in U.S. Pat. Nos. 3,172,892; 3,219,666; 3,272,746; or 4,234,435; or into an alkenyl succinic triazole or alkenyl succinic amide-triazole dispersant (depending upon reaction proportions employed) using conditions such as are described in U.S. Pat.
35 Nos. 4,908,145 or 5,080,815. By alkylating a phenolic compound with a special propylene copolymer as described above using a Lewis acid catalyst such as BF_3 or $AlCl_3$, and using reaction conditions such as are described in U.S. Pat. No. 3,736,353,

an alkyl-substituted phenol is formed. Then by employing known reaction conditions such as are described in U.S. Pat. No. 3,736,357, the alkylated phenol is reacted with an aldehyde such as acetaldehyde, propionaldehyde, butyraldehyde, 5 valeraldehyde, furfuryl aldehyde, etc., but preferably formaldehyde or a formaldehyde-producing reagent such as paraformaldehyde, formalin, etc., and a polyamine or a polyhydroxy-substituted amine, a Mannich base dispersant of this invention is formed.

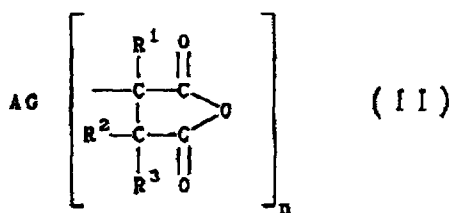
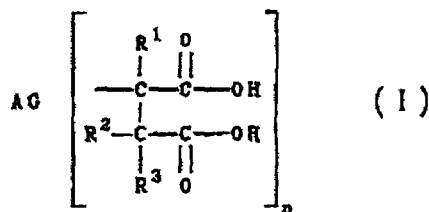
10 Polyamines (including polyether polyamines) and polyhydroxy amines that can be used in forming the dispersants of this invention have at least one primary or secondary amino group in the molecule. Amines of this type and also polyols that can be used in forming ester-amide dispersants of this 15 invention are extensively described in the patent literature, such as, for example U.S. Pat. Nos. 4,234,435, 4,873,009 and 5,137,980.

The ashless dispersants of this invention can be post-treated (i.e., reacted) with various post-treating agents such 20 as are referred to in U.S. Pat. Nos. 4,234,435 or 5,137,980. Preferred post-treated ashless dispersants of this invention are those which have been borated by reaction with a suitable boron-containing material, such as boric acid or other boron acids, boron oxide, boron trihalides, ammonium borate, super- 25 borated ashless dispersants, etc. Generally speaking, the borated ashless dispersants will contain from about 0.01 to about 1% by weight of boron and preferably from about 0.05 to about 0.5 weight % of boron based on the weight of the active dispersant (i.e., omitting from consideration the weight of any 30 diluent or unreacted components that may be present in the dispersant).

Another embodiment of this invention is a succinic acid or anhydride having in its chemical structure a hydrocarbyl substituent derived from a special propylene copolymer as 35 described above. These succinic derivative compositions can be depicted by the general formulas:

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where AG is an aliphatic group derived from the special propylene copolymer described above; R¹, R² and R³ are, independently, hydrogen atoms or hydrocarbyl groups containing up to 7 carbon atoms each; and n represents the average number of the depicted succinic moieties that are bonded by a carbon-to-carbon bond to the aliphatic group derived from the special propylene copolymer; and R¹, R² and R³ are hydrogen atoms or hydrocarbyl groups. When one or more of R¹, R² and R³ is/are hydrocarbyl, each such hydrocarbyl group is preferably and independently, a C₁₋₄ alkyl group. Most preferably R¹, R² and R³ are all hydrogen atoms. In most cases n is in the range of 1 to 2, typically from 1 to 1.6, and preferably from 1 to 1.3. These dicarboxylic acid or anhydride substituted propylene copolymers of this invention are useful per se as additives to fuels and lubricants, and in addition are useful as intermediates in the synthesis of the dispersants of this invention. In this latter utility, a composition of formula (i) or (ii) (or a mixture thereof) is reacted with a nucleophilic reactant, such as one or more amines, alcohols, aminoalcohols or other compound containing at least one (and preferably more than one) acylatable amino group and/or at least one (and preferably more than one) acylatable hydroxyl group.



The special propylene copolymers usually will have number average molecular weights in the range of about 300 to about 5000, typically in the range of about 500 to about 3000, and preferably in the range of about 600 to about 2100, all as
5 determined, for example, by gel permeation chromatography using poly(propylene glycol) standards. The copolymers contain in the range of about 1 to about 25 mol percent, preferably about 3 to about 25 mol percent, and more preferably about 5 to about
10 25 mol percent of one or more monoolefin comonomers which preferably have the formula $H_2C=CHR$ where R is an alkyl group of 2 to 16 carbon atoms, and preferably having 2 to 8 carbon atoms. The propylene copolymers are liquid, i.e., they are in the liquid or at least gel-like state of aggregation at 25°C.

Typically the copolymers of this invention contain an
15 average in the range of about 15 to about 250 propylene moieties in the polymer chains.

Methods for producing the special propylene copolymers involve polymerization of a suitably-proportioned mixture of propylene and at least one C_{4-18} α -olefin comonomer in the
20 presence of a catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl transition metal compound) and an aluminoxane compound. The metallocene catalyst component is one or more organometallic coordination compounds such as the cyclopentadienyl derivatives of a Group
25 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 metallocenes of a Group 4b metal such as titanium, zirconium,
30 and hafnium. The aluminoxanes employed in forming the reaction product with the metallocenes are themselves the reaction products of an aluminum trialkyl with water. Details concerning such catalyst systems and their use can be found in the literature, e.g., in U.S. Pat. No. 5,229,022.

35 In general, the ashless dispersants producible pursuant to this invention are characterized by having enhanced thermal stability, by having relatively high useful viscosities when



employed in lubricating oil, and by possessing good dispersancy effectiveness. In addition, ashless dispersants of this invention can be produced having good shear stability. Moreover, it is possible to produce ashless dispersants of this
5 invention having better handleability (e.g., lower viscosities at low temperatures) than comparable dispersants made from polyisobutylene.

Accordingly, as compared to the same ashless dispersant made with a polypropylene homopolymer of the same number
10 average molecular weight but not meeting the combined requirements of (a), (b), and (c) above, the dispersants of this invention tend to have higher thermal stabilities, higher useful viscosities, at least equivalent dispersancy, and equal or better shear stability. And as compared to the same ashless
15 dispersant but made with a polyisobutene of the same number average molecular weight, the dispersants of this invention tend to have lower viscosities at low temperatures, and thus better handleability at low temperatures.

In contrast to stereo-regular polypropylene such as
20 obtained with Ziegler-Natta catalysts, the copolymers of propylene used pursuant to this invention are formed by a route that gives a substantially linear product having a controlled amount of branching. While useful in forming dispersants, the homopolymers of this type do not possess or contribute to the
25 dispersant the superior low temperature properties of the propylene copolymers of this invention.

Accordingly, among the embodiments of this invention is an ashless dispersant having in its chemical structure at least one aliphatic hydrocarbyl substituent derived from a liquid,
30 substantially linear copolymer of propylene, said copolymer having stereo-irregularity and containing up to 25 mol percent of C_4 to C_{18} and more preferably C_6 to C_{10} monoolefin polymerized into the polymer chain, at least 60 mol percent of said polymer having a terminal vinylidene group, said dispersant being a
35 Mannich base formed from (i) a phenol having said aliphatic substituent thereon, (ii) an aldehyde, and (iii) an amine selected from polyamines and polyhydroxy amines. In these



dispersants the preferred aldehyde is formaldehyde or a formaldehyde-forming reagent and the preferred amine is a polyamine, most preferably an ethylene polyamine such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, or pentaethylene hexamine. As is well known in the art, commercially available mixtures of polyethylene polyamines are often composed of mixtures of linear, branched and cyclic species. Thus commercially available mixtures of this type having an average in the range of about 2 to about 8 nitrogen atoms per molecule can be used.

Another embodiment is an ashless dispersant having in its chemical structure at least one aliphatic hydrocarbyl substituent derived from a liquid, substantially linear copolymer of propylene, said copolymer having stereo-irregularity and containing up to 25 mol percent of C_4 to C_{18} and more preferably C_4 to C_{10} monoolefin polymerized into the polymer chain, at least 60 mol percent of said polymer having a terminal vinylidene group, said dispersant being a succinic ester-amide formed from (i) an alkenyl succinic acylating agent having said substituent thereon and (ii) an N-substituted poly(hydroxyalkyl) amine or a combination of a polyamine and a polyol, which polyamine and polyol are reacted with said acylating agent concurrently or sequentially in any order. Of these dispersants, it is preferable to react the acylating agent with an alkylene diamine having 4 to 12 carbon atoms in the molecule and at least about 2.5 hydroxyalkyl groups per molecule in accordance with the teachings of U.S. Pat. No. 4,873,009. Most preferred dispersants of this type are formed by reacting the acylating agent with hexamethylene diamine having about 3 hydroxyalkyl groups per molecule.

Still another embodiment of this invention is an ashless dispersant having in its chemical structure at least one aliphatic hydrocarbyl substituent derived from a liquid, substantially linear copolymer of propylene, said copolymer having stereo-irregularity and containing up to 25 mol percent of C_4 to C_{18} and more preferably C_4 to C_{10} monoolefin polymerized into the polymer chain, at least 60 mol percent of said polymer



having a terminal vinylidene group, said dispersant being a succinimide formed from (i) an alkenyl succinic acylating agent having said substituent thereon and (ii) a polyamine having at least one primary amino group in the molecule. Preferably the
5 polyamine used is at least one cyclic or acyclic ethylene polyamine having an average of from 2 to 8 and preferably from 3 to 6 nitrogen atoms per molecule. It is even more preferably to employ pure or technical grade ethylene polyamines selected from diethylene triamine, triethylene tetramine, tetraethylene
10 pentamine, and pentaethylene hexamine.

A further embodiment of this invention is an ashless dispersant having in its chemical structure at least one aliphatic hydrocarbyl substituent derived from a liquid, substantially linear copolymer of propylene, said copolymer
15 having stereo-irregularity and containing up to 25 mol percent of C_4 to C_{18} and more preferably C_4 to C_{10} monoolefin polymerized into the polymer chain, at least 60 mol percent of said polymer having a terminal vinylidene group, said dispersant being a product formed by reacting (i) an alkenyl succinic acylating
20 agent having said substituent thereon and (ii) a basic salt of aminoguanidine wherein the molar ratio of said aminoguanidine to said acylating agent is in the range of about 1.4:1 to about 2.2:1 such that the product obtained upon reaction thereof exhibits a dominant infrared peak at 1640 cm^{-1} . Preferably,
25 the basic salt of aminoguanidine used is aminoguanidine bicarbonate.

A still further embodiment of this invention is an ashless dispersant having in its chemical structure at least one aliphatic hydrocarbyl substituent derived from a liquid, substantially linear copolymer of propylene, said copolymer
30 having stereo-irregularity and containing up to 25 mol percent of C_4 to C_{18} and more preferably C_4 to C_{10} monoolefin polymerized into the polymer chain, at least 60 mol percent of said polymer having a terminal vinylidene group, said dispersant being a
35 product formed by reacting (i) an alkenyl succinic acylating agent having said substituent thereon and (ii) a basic salt of aminoguanidine wherein the molar ratio of said aminoguanidine



to said acylating agent is in the range of about 0.4:1 to about 1.3:1. Preferably, these products exhibit an infrared spectrum having peaks in the region of about 1580 and about 1690 cm^{-1} . Another preferred product of this type yields an infrared spectrum having a peak in the region of about 1720 cm^{-1} .

Yet another embodiment of this invention is an ashless dispersant having in its chemical structure at least one aliphatic hydrocarbyl substituent derived from a liquid, substantially linear copolymer of propylene, said copolymer having stereo-irregularity and containing up to 25 mol percent of C_4 to C_{18} and more preferably C_4 to C_{10} monoolefin polymerized into the polymer chain, at least 60 mol percent of said polymer having a terminal vinylidene group.

Another embodiment of this invention comprises the use of from 0.5 to 20% by weight, and preferably from 3 to 15% by weight, of an ashless dispersant of this invention in an oil of lubricating viscosity in order to provide a viscosity increase to said oil, and thereby to enable a reduction in the amount of viscosity index improver required to achieve a target viscosity.

The use of from 0.5 to 20% by weight, and preferably from 3 to 15% by weight, of an ashless dispersant of this invention in an oil of lubricating viscosity subjected to an elevated temperature (e.g., at least 200°C and preferably at least 250°C) during use to provide dispersancy without substantial thermal degradation of the dispersant, is another embodiment of this invention.

A still further embodiment of this invention is the use in forming an ashless dispersant of a liquid, substantially linear copolymer of propylene to create a substituent of said ashless dispersant that renders the dispersant capable of providing a beneficial viscosity increase in an oil of lubricating viscosity when the dispersant is dissolved therein at a concentration within the range of 0.5 to 20% by weight, said copolymer having stereo-irregularity and containing up to 25 mol percent of C_4 to C_{18} and more preferably C_4 to C_{10} monoolefin polymerized into the polymer chain, at least 60 mol



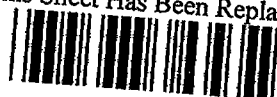
percent of said polymer having a terminal vinylidene group.

Preferred dispersants of this invention are those that have the ability to increase the 100°C kinematic viscosity of an additive-free base mineral oil that has a 100°C kinematic
5 viscosity in the range of 5.0 to 5.5 cSt by at least 50%, more preferably by at least 60%, and most preferably by at least 70%, when dissolved therein at a concentration of 3.5 wt% based on the total weight of the resulting solution.

This invention in another of its embodiments provides a
10 functionalized "ene" reacted propylene copolymer substituted with at least one C_4 to C_{10} monounsaturated dicarboxylic moiety, the starting polymer from which the functionalized copolymer is derived comprising an unsubstituted copolymer with monomer units derived from propylene and from at least one alpha-olefin
15 of the formula $H_2C=CHR$ where R is an alkyl group of from 2 to about 18 and preferably 2 to about 10 carbon atoms, wherein the molar content of propylene in said starting polymer is about 75 to about 95 percent, wherein at least 60 mol percent of said starting polymer has a terminal $=CH_2$ group, and wherein said
20 starting copolymer has a viscosity ratio (VR) value of less than 4.0 (preferably less than 3.7); said functionalized polymer having a functionality in the range of from 0.5 to 2.

The ene reaction product mixture comprising the desired propylene-alpha-olefin-substituted dicarboxylic acid material
25 (e.g., propylene-1-butene copolymer-substituted succinic anhydride) formed by the process of this invention will generally contain unreacted copolymer, (that is, copolymer which is unsubstituted by the mono- or dicarboxylic acid moiety), in a concentration of less than about 40 wt. % (e.g.,
30 less than 35 wt. %), more preferably less than about 30 wt. % (e.g. from zero to 25 wt. %).

The ene reaction product mixture composed of (i) a propylene-alpha-olefin copolymer-substituted dicarboxylic derivative (e.g., a propylene-1-hexene copolymer-substituted
35 succinic acid or anhydride) and (ii) unreacted copolymer can be used as an additive in the same manner as the substituted succinic acids or anhydrides described in U.S. Pat. No.



4,234,435. However, these ene reaction products have the distinct advantage of being substantially halogen-free while at the same time possessing highly advantageous viscometric properties. Thus, an oil of lubricating viscosity containing
5 a minor amount of an acid or anhydride ene reaction product of this invention constitutes another embodiment of this invention.

Another highly important and advantageous utility for the foregoing ene reaction product mixtures of components (i) and
10 (ii) is their use in forming succinic derivative dispersants such as succinimide, succinic ester, succinic ester-amide, succinic amide-triazole, and succinic triazole dispersants. Such dispersants are characterized by a combination of beneficial properties including lack of halogen content,
15 desirable viscometric properties, good thermal stability, desirable dispersancy properties, and good shear stabilities. Suitable reaction conditions and reactants for converting the foregoing ene reaction product mixtures of (i) and (ii) into these succinic derivative dispersants appear in the patent
20 literature cited above, and in U.S. Pat. No. 5,229,022.

This invention in another of its embodiments provides a functionalized Mannich base reacted propylene copolymer directly substituted via a carbon-to-carbon bond onto a hydroxybenzylamino moiety, preferably a hydroxybenzylpolyamine
25 moiety, the starting copolymer from which the functionalized copolymer is derived comprising an unsubstituted copolymer with monomer units derived from propylene and from at least one alpha-olefin of the formula $H_2C=CHR$ where R is an alkyl group of from 2 to about 18 and preferably 2 to about 10 carbon
30 atoms, wherein the molar content of propylene in said starting polymer is about 75 to about 95 percent, wherein at least 60 mol percent of said starting polymer has a terminal $=CH_2$ group, and wherein said starting copolymer has a viscosity ratio (VR) value of less than 4.0 (preferably less than 3.7); said
35 functionalized polymer having a functionality in the range of from 0.5 to 2.

As used herein the term "functionality" refers to the



average number of functional groups that are chemically bonded onto the functionally-substituted copolymer molecules in the product mixture. Thus unreacted copolymer molecules are excluded from consideration when ascertaining the functionality of the functionalized product. Methods for determining functionality on this basis are known to those skilled in the art.

These and other embodiments will be apparent from a consideration of this specification and the appended claims.

10 The following examples illustrate the practice and advantages achievable by the practice of this invention. These examples are not intended to limit the generic scope of this invention.

In a first series of experiments various copolymers used in forming the dispersants of this invention were prepared and their viscometrics at low and high temperatures were compared to other polyolefin polymers. These experiments serve to illustrate that the propylene-1-olefin copolymer-based dispersants of this invention have even better low temperature properties than dispersants made from a corresponding propylene homopolymer made under the same general polymerization conditions. For example, while the propylene homopolymer-based dispersants can be effectively used in many types of lubricating oils, their low temperature performance thus far has not been sufficient to enable their use in certain oils such as 5W-30 multi-grade oils, which are designed for use at low temperatures. Moreover, it has been found, that copolymerizing a mixture of propylene with C_4 , C_6 or C_{10} linear alpha-olefins gives low temperature properties better than the base oil itself, and better than products described in U.S. Pat. Nos. 5,225,091, 5,225,092, and 5,229,022.

Examples 1-6 illustrate the syntheses of copolymers used in these experiments.

Example 1

35 A 600 mL autoclave was charged with 0.52g (10 μ mole) of 1 β zirconocene in toluene, 2.0 g (10 mmole) of methylaluminoxane (MAO, and 35 mL of toluene. The autoclave was removed from the



nitrogen atmosphere in the dry box, cooled to 5 to 13°C, and charged with 168g of polymer grade propylene. The reactor was warmed slowly to 33°C and stirring was continued for 3 hours. Work-up as described below gave 120.7g (65% conversion) of polypropylene.

The infrared spectrum of the product showed it to be amorphous, and the proton NMR showed the product to contain only ethylidene protons in the 4.6 to 4.8 ppm region of the NMR spectrum, where protons bonded to carbon-carbon double bonds are known to absorb.

General Work-up: The reactor was cooled, and the catalyst quenched by the addition of 3 g of methanol from a small bomb that was pressurized to 100 psi with oxygen. The reactor was vented, first at atmospheric pressure, and then under vacuum, while warming at 40°C. The reactor contents were then diluted with 10 ml of heptane, and washed with 34g of 6.5% hydrogen chloride solution. The organic layer was separated, washed with 50g of saturated sodium carbonate, and filtered. The solvents were stripped by heating to 180°C under vacuum.

20 Example 2

The 600 ml autoclave was charged with 0.78 g of 1% zirconocene in toluene, 2.0g (10 mmole) MAO, and 35 mL toluene in a dry box. The reactor was removed from the dry box, cooled to 10°C, and charged with 11.1g (0.0792 mole) 1-decene, and then 220 g (5024 mole) propylene. The reactor was warmed to 40°C and stirring was continued for 3 hours. Work-up as described in Example 1 gave 12.0g (5.2%) of propylene/1-decene copolymer.

Example 3

The autoclave was charged with 0.78g of 1% zirconocene dichloride in toluene, 3.0g of MAO, 14.8g (0.11 mole 1-decene), and 50 mL toluene. The reactor was cooled and charged with 75g (1.8 mole) propylene. The reaction was stirred for 3 hours at 40°C, and then worked-up as described in Example 1 to give 43.3g of copolymer (48% conversion).

Example 4

The autoclave was charged with 0.78g of 1% zirconocene

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dichloride, 3g of MAO, and 50 mL of toluene. After cooling in an ice bath, 13.3g (0.095 mole) 1-decene and 225g for 3 hours at 40°C. Work-up as in Example 1, but without methanol quenching, gave 26 g of copolymer (10.9% conversion).

5 Example 5

The autoclave was charged with 1.14 g of 1% zirconocene dichloride, 3.0g of MAO, and 35 mL of toluene. The reactor was cooled and charged with 20g (0.357 mole) 1-butene, 180g (4.28 mole) propylene, and stirred for 2 hours at 47°C.

10 Work-up as in Example 1 gave 112g copolymer (65% conversion).

Example 6

The autoclave was charged with 1.14g of 1% zirconocene dichloride, 3.0g MAO, 50 mL toluene, and then 23g (0.27 mole) 15 1-hexene. The reactor was then cooled and charged with 278g (6.6 mole) propylene, and the reaction was stirred for one hour at 47°C. Stirring was discontinued, the temperature was maintained at 47°C for an additional 2 hours, and the reaction was worked-up as in Example 1 to give 61.8 g of copolymer 20 (20.5% conversion).

U.S. Patent Nos. 5,225,091, 5,225,092 and 5,229,022 describe ethylene copolymers that have good low temperature properties. The data in these patents that illustrate this point was developed by dissolving 2% by weight of polymer in 25 Exxon 150N base oil, and measuring the 100°C and -20°C viscosities. The ratio of the -20°C viscosity in poise, divided by the 100°C viscosity in centistokes (cSt) is VR. VR for Exxon 150N is 3.7, and when VR is less than 3.7, the low temperature properties of the polymer are improved.

30 The VR values in the patents ranged from 3.3 for an 1100 number average molecular weight (Mn) polymer, to 3.5 and 3.6 for 2710 and 1750 Mn polymer, and included on sample of 1390 Mn with a VR of 3.8.

35 Commercially available polybutene and polypropylene samples from Amoco Corporation gave VR values that ranged from 3.4 to 4.0 when tested in the same Exxon 150N base oil.

In contrast, the 1-butene/propylene and 1-hexane/propylene

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copolymers of this invention gave VR values ranging from 2.59 to 3.44. One 1-decene/propylene copolymer gave a VR value of 3.69. These values show that propylene copolymers can be made that have comparable or better low temperature properties than the ethylene copolymers described in the foregoing patents.

Results of these experiments are summarized in Table 1.

Table 1

	Description	% Conversion	Viscosity of 2% Polymer in Exxon 150N		
			100°C	-20°C	VR
	Amoco polybutene	--	5.72	2226	3.89
10	Amoco polybutene	--	5.61	2144	3.82
	Amoco polypropylene	--	5.56	1888	3.40
	Amoco polypropylene	--	6.43	2589	4.03
15	Amoco polypropylene	--	5.78	2043	3.53
	Propylene/decene copolymer	5.2	7/04	1907	2.71
20	Propylene/decene copolymer	48.2	7.22	2665	3.69
	Propylene/decene copolymer	10.9	8.21	2606	3.17
	Propylene/hexane copolymer	65.0	6.02	2073	3.44
25	Propylene/butene copolymer	20.5	5.00	1294	2.59
	Exxon 150N Base Oil	--	5.45	1920	3.70

Examples 7-11 illustrate preparation pursuant to this invention of alkenyl succinic anhydrides from propylene-1-butene and propylene-1-hexene copolymers and the preparation pursuant to this invention of bis-copolymer succinimides by reaction of the resultant alkenyl succinic anhydrides with a commercially available technical grade of tetraethylene

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pentamine (Dow S-1107 polyamine).

Example 7

To a mixture of 112.4g of the C3/C4 copolymer from Example 5 and 0.028g of dimethyldibromohydantoin (DBH) at 235°C under nitrogen was added 6.2g (0.063 mole) of molten maleic anhydride over a two hour period. After four hours, an additional 0.028g of DBH and 6.2g of maleic anhydride were added, and stirring was continued for 14 hours. The temperature was then raised to 241°C and the excess maleic anhydride was removed under vacuum. The product was 71% active as determined by column chromatography on silica gel, and had an acid number of 0.378.

Example 8

To 33.6g (0.0127 mol) of the copolymer succinic anhydride (COSA) prepared in Example 7 was added 1.2g (0.00635 mol) of S-1107 polyamine, and the mixture was stirred under nitrogen for one hour at 175°C and one hour at 185°C.

Example 9

C3/C6 copolymer was prepared as described in Example 3, but with a Al to Zr ratio of 1000 to 1, and reaction carried out at 60°C for 1.3 hours, and a C3 to C6 ratio of 10. The copolymer was reacted with maleic anhydride by the general procedure of Example 7 to give 76% active COSA having an acid number of 1.26. The COSA 41.1g (0.0518 moles) was reacted with 4.89g (0.0259 mol) of S-1107 by the general procedure of Example 7 to give 43.5g of bis-succinimide.

Example 10

C3/C4 copolymer was prepared as described in Example 9, with a 10 to 1 C3 to C4 mole ratio, at 45°C, for 3.0 hours. COSA was prepared by reaction with maleic anhydride as described in Example 7 to give 34% active COSA having an acid number of 0.647. Reaction with S-1107 as in Example 7 gave the bis-succinimide.

Example 11

C3/C6 copolymer was prepared as described in Example 9, with a 5 to 1 mole ratio of C3 to 1-hexene, at 45°C for 3.0 hours. COSA was prepared by reaction with maleic anhydride as described in Example 7 to give 79% active COSA having an acid



number of 1.475. A solution of 11.8g of 100 neutral process oil and 39.7g (0.0586 mol) of COSA was reacted with 6.15g of S-1107 as in Example 7 to give 55.4g of 65% active bis-succinimide.

- 5 Examples 12 and 13 illustrate the formation of propylene copolymer-substituted phenols and the production of Mannich base dispersants from such substituted phenols, all pursuant to this invention.

Example 12

- 10 A solution of 30g (0.03 mole) of copolymer (10 to 1 propylene to 1-butene, as in Example 9), and 9.7g (0.10 mol) of phenol complexed with 5 weight percent boron trifluoride, in 30 mL of heptane, was stirred for 2.5 hours at 50°C. The solution was then neutralized with ammonia gas and filtered.
15 the solution was then stripped to 180°C under vacuum to give 27.8g of 86% active (as determined by column chromatography on silica gel) para alkylated phenol, as determined by infrared spectroscopy.

- At 88°C, 3.0g (0.037 mol) of 37% aqueous formaldehyde was
20 added to a mixture of 18.4g of the alkylphenol, 3.4g of tetraethylenepentamine, 3.4g of oleic acid, and 3g of 100 neutral process oil. After one hour at 116°C, the temperature was raised to 155°C and an additional 4.54g (0.056 mol) of formalin was added. The reaction was stirred for 3 hours and
25 then filtered.

Example 13

- A 10 to one mole ratio of propylene to 1-hexene was used to prepare copolymer at 60°C for 1.5 hours as in Example 9. Alkylation of phenol was carried out as in Example 12 to give
30 90% active alkylphenol.

- A mixture of 28.4g (0.0334 mol) of alkylphenol, 5.8g (0.0307 mol) TEPA, 5.65g oleic acid was reacted with 4.87g (0.060 mol) of formalin at 116°C, and then 7.58g (0.0935 mol) of formalin at 155°C, as described in Example 12, followed by
35 the addition of 7.3g of 100 neutral process oil.

Viscometrics made possible by use of succinimide and Mannich base dispersants of this invention are illustrated in



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Table 2. In these runs, the dispersants were blended at a concentration of 6.5 wt % into a 5W-30 mineral lubricating oil formulated with a commercially-available viscosity index improver (Shellvis 90 VII). The viscosities of the oil blends at 100°C in cSt and at -25°C in poise were measured, and the VR' values were calculated in accordance with the expression:

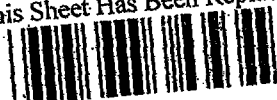
$$VR' = \frac{\text{Vis(B)}}{\text{Vis(A)}}$$

10 wherein Vis(A) is the kinematic viscosity (KV) of the dispersant product at 100°C in units of centistokes (as determined by ASTM Method No. D445) and Vis(B) is the cold cranking simulator (CCS) viscosity of the dispersant product at -25°C in units of poise (as determined by ASTM Method No. D 2602).

Table 2

	Copolymer Dispersant Used	Viscosities of Dispersants in 5W-30 lubricating oil		VR' Value
		100°C	-25°C	
20	Example 7	12.6	4664	3.70
	Example 8	10.1	3501	3.48
	Example 9	9.70	3359	3.46
	Example 10	9.67	3619	3.74
	Example 11	9.59	2955	3.08
25	Example 12	9.95	3344	3.36
	Example 13	9.02	2557	2.83

In addition to the foregoing advantages achievable by the practice of this invention is the fact that propylene has been historically less expensive than isobutylene or even a mixed stream of butenes. This cost differential may increase in the future as the use of isobutylene and other butenes is increased to make oxygenated blending agents, such as methyl tert-butyl ether for use in gasoline and other fuels.



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In formulating finished lubricating oils containing one or more of the ashless dispersants of this invention, various other additive components can be utilized. These include low-base and overbased alkali and/or alkaline earth metal
5 detergents, such as the sulfonates, sulfurized phenates and salicylates of lithium, sodium, potassium, calcium and/or magnesium, and the alkaline earth metal calixerates (note U.S. Pat. Nos. 5,114,601 and 5,205,946); antiwear and/or extreme pressure agents such as metal salts of dihydrocarbyl
10 dithiophosphoric acids (e.g., zinc, copper or molybdenum dialkyldithiophosphates); oxidation inhibitors such as hindered phenolic antioxidants, aromatic amine antioxidants, sulfur-containing antioxidants, and copper-containing antioxidants; supplementary dispersants such as succinimide dispersants,
15 succinic ester-amide dispersants, and Mannich base dispersants; friction reducing and/or fuel economy improving additives such as glycerol monooleate, pentaerythritol monooleate, long chain acid esters of glycols, sulfurized olefins, sulfurized unsaturated fatty acids and sulfurized unsaturated fatty acid
20 esters; rust and corrosion inhibitors; foam inhibitors; viscosity index improvers; polymeric dispersant-viscosity index improvers; demulsifying agents; and the like. Such additives can be employed in the base oil at their customary use concentrations, which are known to those skilled in the art and
25 reported in numerous patent disclosures. For further details concerning such additives, one may refer for example to U.S. Pat. Nos. 4,664,822; 4,908,145; 5,080,815 and 5,137,980.

The base oils used in formulating finished lubricants containing the ashless dispersants of this invention can be
30 derived from petroleum (or tar sands, coal, shale, etc.). Likewise, the base oils can be or include natural oils of suitable viscosities such as rapeseed oil, etc., and synthetic oils such as hydrogenated polyolefin oils; poly- α -olefins (e.g., hydrogenated or unhydrogenated α -olefin oligomers such
35 as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; poly-



silicones; fluorohydrocarbon oils; and the like. Mixtures of mineral, natural and/or synthetic oils in any suitable proportions are also useable. The term "base oil" for this disclosure includes all the foregoing. In most cases the base oil is preferably a petroleum-derived mineral oil of the types conventionally used in forming passenger car or heavy duty diesel engine oils. The fact that the base oils used in the compositions of this invention may be composed of (i) one or more mineral oils, (ii) one or more synthetic oils, (iii) one or more natural oils, or (iv) a blend of (i) and (ii), or (i) and (iii), or (ii) and (iii), or (i), (ii) and (iii) does not mean that these various types of oils are necessarily equivalents of each other. Certain types of base oils may be used for the specific properties they possess such as biodegradability, high temperature stability, or non-flammability. In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the various types of base oils discussed above may be used in the compositions of this invention, they are not necessarily equivalents of each other in every instance.

The ashless dispersants of this invention can be blended into oils of lubricating viscosity separately and apart from other additive components. Preferably however, the dispersants are formulated into an additive concentrate or "package" which is then used in formulating the finished lubrication compositions. The package will usually contain up to 50 wt% of diluent with the balance being the active additive components, namely, at least one dispersant of this invention and optionally, but preferably, one or more other additive components, such as those referred to above and/or in various patents cited herein. From 5 to 60 wt% of the concentrate can be one or more dispersants of this invention. This invention also provides a composition which consists of 1 to 99 wt % of an active dispersant of this invention and from 99 to 1 wt% of diluent oil. Other additives, including diluents that may be associated therewith, can be blended into such compositions to



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form additive packages of this invention.

The dispersants of this invention can also be used as additives in hydrocarbonaceous fuels such as gasoline, diesel fuel, gas oils, jet fuels, cycle oils, burner fuels, bunker fuels, and the like. Amounts within the range of 0.5 to 10% by weight will usually be employed, although departures from this range can be made.

Lower molecular weight versions of the polymers of propylene referred to hereinabove can be used in alkylation of aromatic hydrocarbons. These alkylated materials (e.g., alkylated benzene, alkylated toluene, alkylated xylenes, etc.) can then be sulfonated and overbased to form highly useful alkali or alkaline earth metal-containing detergents and rust inhibitors. Alternatively, the polymers of propylene can be used to alkylate hydroxy-substituted aromatic hydrocarbons, which can be sulfurized and neutralized or overbased to form metal-containing phenate detergents.

Except as referred to in the examples, all percentages of the dispersants of this invention are in terms of the weight of active dispersant in relation to the total weight of the overall composition under discussion.

The complete disclosure of each U.S. Patent cited anywhere hereinabove is incorporated herein by reference as if fully set forth in this specification.

This invention is susceptible to considerable variation in its practice. Accordingly, this invention is not intended to be limited by this specific exemplifications set forth hereinabove. Rather, this invention is intended to embrace the subject matter within the spirit and scope of the appended claims and the permissible equivalents thereof.

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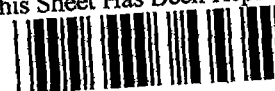


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Claims

1. A dispersant having in its chemical structure at least one aliphatic hydrocarbyl substituent derived from a liquid, substantially linear copolymer of propylene, said copolymer
5 having stereo-irregularity and containing up to 25 mol percent of C_4 to C_{18} monoolefin polymerized into the polymer chain, at least 60 mol percent of said polymer having a terminal vinylidene group.
2. A dispersant according to Claim 1 wherein said copolymer
10 has a viscosity ratio (VR) value of less than 4.0.
3. A dispersant according to Claim 1 wherein the monoolefin polymerized into the polymer chain in an amount of up to 25 mol percent is a C_4 to C_{10} monoolefin and wherein said copolymer has a viscosity ratio (VR) value of less than 3.7.
- 15 4. A dispersant according to Claim 1 wherein said dispersant is a Mannich base formed from (i) a phenol having said aliphatic substituent thereon, (ii) an aldehyde, and (iii) an amine selected from polyamines and polyhydroxy amines.
5. A dispersant according to Claim 3 wherein said dispersant
20 is a Mannich base formed from (i) a phenol having said aliphatic substituent thereon, (ii) formaldehyde or a formaldehyde-forming reagent, and (iii) at least one polyamine.
6. A dispersant according to Claim 1 wherein said dispersant is selected from the group consisting of succinimide
25 dispersants, succinic ester-amide dispersants, succinic triazole dispersants, and succinic amide-triazole dispersants.
7. A dispersant according to Claim 4 wherein said dispersant is a succinic ester-amide formed from (i) a succinic acylating agent having said substituent thereon and (ii) an N-substituted
30 poly(hydroxyalkyl) amine or a combination of a polyamine and a polyol, which polyamine and polyol are reacted with said acylating agent concurrently or sequentially in any order.
8. A dispersant according to Claim 7 wherein said dispersant is formed by reacting said acylating agent with an alkylene
35 diamine having 4 to 12 carbon atoms in the molecule and at least about 2.5 hydroxyalkyl groups per molecule.

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9. A dispersant additive according to Claim 8 wherein said alkylene diamine is hexamethylene diamine having about 3 hydrox-yalkyl groups per molecule.
10. A dispersant according to Claim 1 wherein said dispersant
5 is a succinimide formed from (i) a succinic acylating agent having said substituent thereon and (ii) a polyamine having at least one primary amino group in the molecule.
11. A dispersant according to Claim 3 wherein said dispersant
10 is a succinimide formed from (i) a succinic acylating agent having said substituent thereon and (ii) a polyamine having at least one cyclic or acyclic ethylene polyamine having an average of from 3 to 6 nitrogen atoms per molecule.
12. A dispersant according to Claim 1 wherein said dispersant
15 is a product formed by reacting (i) a succinic acylating agent having said substituent thereon and (ii) a basic salt of aminoguanidine wherein the molar ratio of said aminoguanidine to said acylating agent is in the range of about 1.4:1 to about 2.2:1 such that the product obtained upon reaction thereof exhibits a dominant infrared peak at 1640 cm^{-1} .
- 20 13. A dispersant according to Claim 12 wherein said basic salt of aminoguanidine is aminoguanidine bicarbonate.
14. A dispersant according to Claim 1 wherein said dispersant is a product formed by reacting (i) a succinic acylating agent having said substituent thereon and (ii) a basic salt of
25 aminoguanidine wherein the molar ratio of said aminoguanidine to said acylating agent is in the range of about 0.4:1 to about 1.3:1.
15. A dispersant according to Claim 14 wherein said product exhibits an infrared spectrum having peaks in the
30 region of about 1580 and about 1690 cm^{-1} .
16. A dispersant according to Claim 14 wherein said product exhibits an infrared spectrum having a peak in the region of about 1720 cm^{-1} .
17. A dispersant according to Claim 14 wherein said basic salt
35 of aminoguanidine is aminoguanidine bicarbonate.
18. A lubricating oil composition comprising oil of lubricating viscosity containing from 0.5 to 60% by weight of



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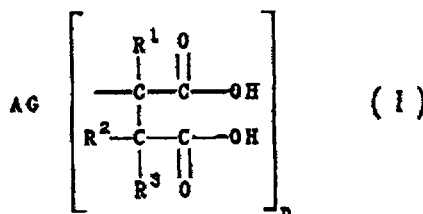


a dispersant of Claim 1.

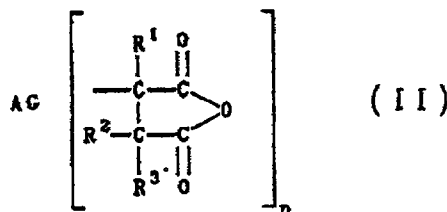
19. A lubricating oil composition comprising oil of lubricating viscosity containing from 0.5 to 60% by weight of a dispersant of Claim 5.

5 20. A lubricating oil composition comprising oil of lubricating viscosity containing from 0.5 to 60% by weight of a dispersant of Claim 11.

21. A succinic derivative composition of the formula:



or



- 10 or a mixture thereof, wherein AG is an aliphatic group derived from a liquid, substantially linear copolymer of propylene, said copolymer having stereo-irregularity and containing up to 25 mol percent of C₄ to C₁₈ monoolefin polymerized into the polymer chain, at least 60 mol percent of said polymer having
- 15 a terminal vinylidene group; R¹, R² and R³ are, independently, hydrogen atoms or hydrocarbyl groups containing up to 7 carbon atoms each; and n represents the average number of the depicted succinic moieties that are each bonded by a carbon-to-carbon bond to the aliphatic group derived from said copolymer, and
- 20 is in the range of from 1 to 2.

